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FINAL REPORT

**ASSESSMENT OF RESEARCH NEEDS
FOR ADVANCED HETEROGENEOUS CATALYSTS
FOR ENERGY APPLICATIONS**

Prepared for:

**U.S. Department of Energy
Office of Energy Research
Office of Program Analysis**

By:

**Consultec Scientific, Inc.
725 Pellissippi Parkway, Suite 110
Knoxville, TN 37932-3300**

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ABSTRACT

This report assesses the direction, technical content, and priority of research needs judged to provide the best chance of yielding new and improved heterogeneous catalysts for energy related applications over a period of 5-20 years. It addresses issues of energy conservation, alternate fuels and feedstocks, and the economics and applications that could alleviate pollution from energy processes.

Recommended goals are defined in three major, closely-linked research thrusts:

- I. **CATALYTIC SCIENCE** — Establish a scientific knowledge of essential catalyst structure/performance relationships and work toward developing the ability to predict the catalytic capabilities of novel materials.
- II. **ENVIRONMENTAL PROTECTION BY CATALYSIS** — Prevent pollution by developing economical processes that are free of pollutant formation. Diminish pollution by achieving higher selectivity in fuels and chemicals manufacture and by new and improved catalytic processes for the removal of pollutants.
- III. **INDUSTRIAL CATALYTIC APPLICATIONS** — Develop energy-saving, environmentally benign processes for manufacture of liquid fuels and commodity chemicals based on domestic natural gas, biomass, and coal. Emphasize research on synthesis gas ($\text{CO} + \text{H}_2$) production and conversion, oxidation catalysis, new methods of hydrogen production, and the synthesis of novel materials for catalytic applications.

This study was conducted by an eleven-member panel of experts from industry and academia, including one each from Japan and Europe. Discussions were held with a wide variety of authorities, supplementing an intensive review of technical literature. Panel conclusions were assisted by critical peer reviews.

There is a high level of confidence that the research proposed can provide catalytic technology which will achieve major economic and environmental improvements in energy applications.

Volume I provides a comprehensive Executive Summary, including Research Recommendations. Volume II first presents an in-depth overview of the role of catalysis in future energy technology in chapter 1. Then current catalytic research is critically reviewed and research recommended in eight topic chapters: 2. Catalyst Preparation: Design and Synthesis; 3. Catalyst Characterization: Structure/Function; 4. Catalyst Performance Testing; 5. Reaction Kinetics/Reactor Design; 6. Catalysis for Industrial Chemicals; 7. Catalysis for Electrical Applications; 8. Catalysis for Control of Exhaust Emissions; and, 9. Catalysts for Liquid Transportation Fuels from Petroleum, Coal, Residual Oil, and Biomass.

EXPERT PANEL

This report has been prepared by a panel of experts who have evaluated the research needs for advanced heterogeneous catalysts for energy applications. The project has been conducted under a grant to Consultec Scientific, Inc., Knoxville, TN from the U.S. Department of Energy, Office of Energy Research. Dr. G. Alexander Mills served as the Principal Investigator. The following distinguished scientists served as members of the panel:

Dr. G. Alexander Mills
Principal Investigator
Department of Chemical Engineering
University of Delaware

Dr. George W. Parshall
Central R&D Department
Science and Engineering Laboratory
E.I. Dupont de Nemours & Co.

Dr. Russell R. Chianelli
Corporate Research Science Laboratory
Exxon Research & Engineering Co.

Dr. Jule A. Rabó
U.O.P., Inc.

Professor Henry C. Foley
Center for Catalytic Science & Technology
Chemical Engineering Department
University of Delaware

Dr. Jens Rostrup-Nielsen
Haldor Topsøe A/S
Lyngby, Denmark

Professor Gary L. Haller
Dept. of Chemical Engineering
Mason Laboratory
Yale University

Professor Wolfgang M.H. Sachtler
Center for Catalysis & Surface Science
Department of Chemistry
Northwestern University

Dr. Heinz Heinemann
Lawrence Berkeley Laboratory
University of California

Professor Kenzi Tamaru
Department of Chemistry
Science University of Tokyo

Dr. James E. Lyons
Applied R&D Department
Sun Company

Dr. Harvel A. Wright
Program Manager
Consultec Scientific, Inc.

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PEER REVIEWERS

Dr. John Armor
Corporate Science and Technology Center
Air Products and Chemicals, Inc.

Dr. David Gray
Energy, Resources, Environmental Systems
The Mitre Corp/Civil Systems

Professor Alexis T. Bell
Department of Chemical Engineering
University of California, Berkeley

Dr. Leo E. Manzer
Experimental Station
E.I. duPont de Nemours Co., Inc.

Dr. Ralph J. Bertolacini
Amoco Oil Company

Dr. Kathleen Taylor
Physical Chemistry Department
General Motors Corporation

Dr. Frank P. Burke
Research and Development
CONSOL, Inc.

Professor Irving Wender
Chemical/Petroleum Engineering Department
University of Pittsburgh

Dr. Flynt Kennedy
Research and Development
CONSOL, Inc.

Mr. Ronald Wolk
Electric Power Research Institute

Professor Bruce Gates
Department of Chemical Engineering
University of California, Davis

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Chapter 1

CATALYSIS OVERVIEW

Jule A. Rabó

1.1 INTRODUCTION

This overview chapter gives a broad-stroke account of the role of heterogenous catalysis in future energy technology. The sections in this chapter address the societal impact of catalysis, its current evolution as a science and technology, and the role of heterogeneous catalysis in the energy industry, a role aimed at achieving energy savings either in production or in ultimate utility as fuel. New challenges and directions for advanced catalysis are also discussed. The final section lists recommendations for short- and long-range priorities with a focus on catalysis fundamentals and science.

1.2 HISTORY AND SOCIETAL IMPACT

Industrial catalysis received its largest initial impetus from the discovery of ammonia synthesis at the beginning of our century. From the 1930s, petroleum refining technology has been mainly developed in the U.S., driven by a chain of major discoveries in hydrocarbon catalysis made in industrial laboratories, aided by pioneering scientific fundamentals emerging from our leading universities. Successful industrial technology emerged in almost every case by combining catalyst chemistry and reactor process engineering in a creative way. Heterogeneous catalysis, more than other areas of chemical synthesis, requires creative engineering solutions to cope with catalyst-reactant interaction (fixed bed, fluid bed, slurry bed, moving bed), reaction heat transfer, and catalyst regeneration related problems. Successful engineering solutions of these problems are critical for competitive process economic performance in all areas of advanced catalytic processing. Present petroleum technology, with its key catalytic process steps used worldwide, became mainly a product of U.S. industry, with enormous economic benefit to our economy. The sales of proprietary catalytic technologies under license and proprietary catalysts became one of the largest and most profitable worldwide businesses in U.S. industry, providing high quality employment for skilled workers.

We will briefly review the societal impact of catalysis with data provided for the fuels and combined fuel and chemical industrial segments.

How important is catalysis to industry and, more broadly, to humanity? A recent report (Creek, 1989) sets the value of the worldwide catalyst market at \$5 billion, with \$1.9 billion alone in the United States; by the year 2000 it will grow to \$6.5 billion worldwide and to \$2.4 billion in the U.S. The cost of catalysts is estimated to be about 0.1 percent of the value of the fuels produced and about 0.22 percent of the petrochemicals produced *via* catalysis (*Chem Week*, 1979). This cost translates to worldwide catalysis product values for fuels and chemicals of \$2.4

trillion. This amount is more than the gross national product (GNP) of some major industrial nations and is about half of the U.S. GNP. In the U.S. the value of fuels and chemicals derived from catalysis in 1990 was \$891 billion or 17% of GNP. Since in process economics the value-added contributions by catalysts far outweigh the cost of the catalysts, the impact of catalysis must be measured by the impact of its products, not only by the cost of the catalyst itself (Roth, 1991). In the last decade, catalysis has also become the key technology for the protection of our environment, in addition to its role in the fuel and petrochemical industries. Here, part of the challenge is to reduce pollutants emitted in the processing of fuels and chemicals; another challenge is to help produce new, environmentally friendlier fuels and chemicals. An additional and ever-growing role is to reduce undesirable emissions from power plants and automobiles. In the latter field alone, the yearly catalyst market in the United States was about \$650 million in 1989. In Europe, the total catalyst market was \$900 million in the same period, and growth was projected to \$1.8 billion by 1993, with auto-emission catalysts being the fastest growing component.

The societal impact of the fuel and petrochemical industries, in which catalysis is a critical component, also needs to be considered. According to a recent study of U.S. industry, the chemicals and fuels industry was the largest of all U.S. industry segments, with yearly sales of \$210 billion, compared for example with \$127 billion for automobiles (M.I.T., 1990). In 1990, employment in the petroleum industry in the United States was 750,000 compared to 1.04 million in the automobile industry. The pivotal role of catalysis is best displayed in a study reporting that of the 63 major product and 34 process innovations made between 1930 and 1980 in the chemicals and fuels industries, more than 60% of the products and 90% of the processes were based on catalysis (Bennett *et al.*, 1988, 1990). This information clearly points to the critical role of catalysis not only in the chemical and fuel industries but also to economic progress in our whole society (Cusumano, 1992).

Beyond the many contributions of catalysis measurable in numbers, our human society has been immeasurably enriched by the improved quality of life and comfort provided by the products of catalytic processes.

Catalysis has also been absolutely critical to the economic success of the U.S. chemical industry. As discussed in Chapter 6, most major products of this industry are manufactured by catalytic processes. Continued innovation in catalysis and process engineering has made the U.S. chemical industry one of the strongest in the world. In contrast to many other domestic industries, the chemical industry is a very successful exporter of its products. It has consistently maintained a large positive balance of trade with other nations (\$18.8 billion in 1991), which illustrates the importance of technology for the competitiveness of the U.S. manufacturing economy.

1.3 ROLE OF HETEROGENEOUS CATALYSIS IN THE ENERGY INDUSTRY

Heterogeneous catalysis plays a profound role in the energy industry. The ability of catalysts to facilitate difficult hydrocarbon transformations, and to guide chemical reactions toward desired reaction paths at high selectivity, permits the energy industry to produce the full range of quality

motor fuels from the changing feedstocks available worldwide. The amazing flexibility of catalytic chemistry also allows the refiners to respond not only to differences in feedstock but also to changes in market needs, without penalty in quality. These characteristics of catalysis technologies are essential for the production of high quality fuels at a cost affordable to the public.

All liquid feedstocks used in the energy industry contain sulfur and often additional heteroatoms which are considered undesirable if released to the environment. Therefore, there is a need to remove these undesirable components either from the feed, from the product, or from the combustion effluent. These environmentally important operations involve fuel manufacturing processes, powerplants, automobile engines, exhausts, *etc.* Heterogeneous catalysis is the only feasible technology that can be applied in this wide ranging field with the desired high degree of efficiency and relatively low cost. The ability of heterogeneous catalysts to function in an extremely wide range of temperatures permits their application both at low temperatures required in certain fuel synthesis steps (isoparaffin alkylation) and at higher temperatures required in catalytic cracking, and even at very high temperatures existing in automobile exhaust manifolds. The techno-economic significance of catalysis rests on the following factors: a) ability to produce quality fuels from varying feedstocks, b) flexibility to produce a changing slate of fuels to respond to changes in demand, and c) high catalytic selectivity to desired products resulting in large value-added gain in most catalytic process steps. In some cases even the replacement of existing catalysts with new, more efficient catalysts also causes large economic benefits. For example, the replacement of the amorphous silica-alumina catalyst with zeolites in the catalytic cracking process gave rise to a value-added gain amounting to several billion dollars yearly in the U.S. alone. For these reasons, development of superior catalysts remains a valid technological objective as long as the limits of technology leave room for either environmentally or economically significant improvements.

The role and full impact of catalysis in energy related technology is best displayed by the scope of the chemical transformations it facilitates. Today, the principal source of motor fuels is petroleum. Its conversion to gasoline, turbine, and diesel fuels critically depends on catalytic action. Catalysts must convert the extremely broad range of hydrocarbons (decorated with both sulfur and nitrogen heteroatoms) found in various petroleum feedstocks into sulfur and nitrogen free hydrocarbons of well defined boiling range, hydrocarbon type and structure. Catalysis technology available at present has the capability to convert distillate petroleum feedstocks or gaseous hydrocarbons ($\geq C_3$) to hydrocarbon motor fuels of almost any specification. Production costs, the nature of available feedstocks, and changing market needs give rise to preferred processing schemes in the overall petroleum refining operation.

These amazingly wide-ranging chemical transformations in petroleum refining are based mainly on two types of catalytic transformations: hydro-dehydrogenation and acidic hydrocarbon catalysis. The first controls the distribution of hydrogen among hydrocarbon products while the acid catalysis controls the carbon number and boiling range, the skeletal structure, as well as the types of hydrocarbons produced. Advanced catalysts available today combine these two catalytic functions with highly specific catalyst structure features, called shape selectivity, to control the size of molecules produced and other chemical features. Using an appropriate choice and

mixture of catalyst functions for catalytic processing, the carbon and hydrogen content of a petroleum feedstock can be redistributed to a fuel of almost any desired specification. Of course, raw material availability and production costs limit industrial applications to the most cost-effective technology schemes.

Catalytic efficiency, in terms of activity, selectivity, and operating costs, including that of a catalyst, are the key to superior technology in this field. It should be noted that in petroleum refining, the value-added advantage provided by advanced catalysts usually far outweighs the cost of the catalyst itself. The economic benefits justify, for example, the broad use of noble metals in refining catalysts. Since current hydrocarbon transformations in motor fuel production mainly rest on hydrogenation/dehydrogenation and on acid catalysis, the most important catalyst components are transition metals, often noble metals, and solid acids. In the latter category zeolites achieved particular prominence because of their outstanding acid type activity coupled with "molecular sieve" selectivity.

As a result of recent advances in petroleum refining catalysis, the transformation of hydrocarbon feedstocks, substantially free of solid inorganic components, can be converted to any desired motor fuel chosen within thermodynamic limitations, using chemically inert, solid catalysts, with few exceptions. The most notable exceptions are reactions requiring super acid catalysts, for example, the alkylation of isobutane with butene to produce the alkylate gasoline component. Here, the efforts to replace the corrosive and environmentally undesirable hydrogen fluoride or sulfuric acid catalysts with environmentally friendly solid catalysts has not succeeded as yet.

It should also be noted that the outstanding flexibility and selectivity achieved in catalytic hydrocarbon transformations is limited to the conversion of hydrocarbon feeds to hydrocarbon fuels of other specifications. The conversion of hydrocarbon feeds to products containing heteroatoms has been successfully developed only for unsaturated hydrocarbons, but not for paraffins and naphthenes which are most abundant both in petroleum and in natural gas. This limitation in catalysis technology poses great challenges to future energy technology, as will be discussed later.

1.4 HETEROGENEOUS CATALYSTS AND CATALYSIS PHENOMENA

Catalysts facilitate chemical reactions to proceed at greatly enhanced rates. While catalysts always benefit reactivity and reaction rates, they also control, or at least influence, selectivity. Catalytic effects are usually based on chemical phenomena; however, physical characteristics of the catalyst are also important, and in most cases they are critical to optimum performance, because the physical features control the distribution of catalytic sites and the diffusion of both reactants and products.

Catalysts, while participating in the catalytic process, do not undergo change following typical catalytic reaction cycles. Thus, a catalytic site can carry out the catalyzed reaction cycle thousands or millions of times without losing activity. Ultimately, depending on reaction conditions, particularly the temperature and the chemical environment, catalysts lose activity or selectivity as a result of slow chemical change or deposition of coke or other debris, causing

interference either with the chemistry or with diffusion related transport phenomena. Following deactivation, catalysts are often regenerated by oxidative burn-off of carbonaceous deposits. In other cases, the spent catalyst must undergo chemical treatment called rejuvenation, usually aimed to reconstitute the original active sites such as fine metal dispersions. Ultimately, spent catalysts have to be replaced with fresh catalysts. Noble metals and other valuable components are usually recycled from the spent catalyst onto the fresh catalyst, depending on the economic incentive, while other components are discarded or may have to be managed, depending on their environmental effect and value.

Heterogeneous catalysts are solids, usually consisting of one or several catalytically active materials and one or more catalyst supports or solid additives aimed to provide fine and stable dispersions for the catalytically active materials (metals, oxides, *etc.*) and supporting particles. Supports provide a porous framework to permit access to the active sites for the reactants and free exit for the products from the catalyst particles. Specific control of access to and from catalytic sites on the basis of the molecular sieve effect is used sometimes to serve as a basis for catalytic selectivity. For these reasons, both chemical and physical characteristics play important and inseparable roles in the catalytic process. Therefore, beginning with the initial concept of a practical solid catalyst through the research and developmental steps of catalyst evolution, both chemical and physical features have to be optimized together to find the best interplay between these characteristics with the overall catalytic process in mind. Catalyst life and deactivation are additional important characteristics affecting process design and economics.

In catalyst synthesis, and in the ultimate catalyst manufacturing process, the catalytic active sites usually develop step by step. Catalyst supports may be utilized first in order to support precursors of the catalytic sites with desired concentrations and distributions. The active form of catalysts is usually achieved following optimized thermal and chemical treatments. Often, catalysts attain their active form only in the reaction environment in the catalytic process. In order to prepare catalysts with maximum efficiency, the synthesis process must follow synthetic steps carefully optimized in research programs.

As a result of the importance of the specific details of catalyst synthesis steps, it is necessary to establish specifications for the catalyst following each successive synthesis step. Therefore, the characterization of catalysts covers the whole range of intermediates as well as the finished, and even the spent catalysts.

In addition to the characterization of the catalytic solid, an additional important role of characterization is the elucidation of the chemistry of the catalytic reaction. This includes the catalytic active sites and the reaction intermediates formed between active sites and reactants, leading to product formation. This information is important to recognize the sequence of catalytic reaction steps with sufficient chemical and structural information, to enable the catalysis chemist to apply our existing science base, for example, organic or inorganic chemistry, material science or surface chemistry, to correct the observed catalyst deficiencies, and ultimately to develop advanced catalysts efficiently. In-depth information on catalytic sites and on the reaction mechanism at atomic/molecular level provides the most effective, thus the most valuable,

predictive scientific tools for the efficient development of advanced catalysts. This consideration places high value on *in situ* investigation of catalysts in the reaction environment.

Heterogeneous catalysis is an interface phenomenon. The catalytic sites formed on the surface of the catalyst interact both with the matrix of the solid catalyst and with the reactants. The interaction with the solid mainly involves atoms adjacent to catalytic sites. However, in some important cases the interaction between active sites and large segments of the catalytic phase, particularly crystals, results in long range effects which dominate catalytic performance (acidic zeolites).

Our knowledge of the structure of solids, particularly crystals, is highly developed by the use of X-ray crystallography and other quantitative tools which can be also applied, to a more limited extent, even to microcrystalline materials found in solid catalysts. By comparison, our knowledge of the surface of solids, including crystals, is much more limited. The available information here mainly rests on progress in surface science which has been developed to a great extent through the study of large single crystals, and results have been obtained with ligated and unligated metal clusters. In spite of great recent progress in surface science, the atomic structure of the surface of microcrystalline materials, often representing the anchor of the catalytic active sites in practical catalysts, is less understood. This deficiency in our knowledge places large emphasis on a future need to focus fundamental research on a direct characterization of catalytic active sites and reaction intermediates at the atomic/molecular scale. This information is crucial in order to achieve a higher predictive power for the science used in the conduct of research in the evolution of advanced catalysts.

Catalysis is an interdisciplinary science and technology. The catalytic reactions take place in the solid-gas interface. Therefore, the study of catalysis phenomena involves the solid matrix, the surface of solids, gas diffusion, reaction kinetics, and process engineering. The topic of the catalyst solid itself is a wide-ranging, complex science which embraces substantial portions of solid state chemistry as well as new, growing areas of synthetic inorganic chemistry, such as zeolites, clays, metals, and alloys. As a result, catalysis is an interdisciplinary field with large areas common with other fields of science and technology, and with others specifically related only to catalysis.

At present, heterogeneous catalysis is rapidly moving from a mainly experimentally driven endeavor in energy and chemical technology to a scientifically deeper rooted discipline of enormous industrial and economic potential. In the past decades progress depended mainly on intuition and on broad experimental scoping of the envisioned chemistry. The rate of progress was limited by the absence of precise models of active sites and of the path of catalytic reaction chemistry. In the absence of this fundamental knowledge, the feedback information guiding the next experiment for improvements was often absent, incomplete, or inaccurate. As a result, the time and cost required for the development of new, successful industrial catalytic processes has been very large, effectively limiting new catalysis technology to a few world leaders in the chemical and energy industries.

It is envisioned that progress in catalyst characterization and theoretical modeling will grow rapidly in the next 10-15 years. The anticipated future progress in computer technology will greatly facilitate theoretical modeling and data analysis in all experimental work. *Such events should, in the not too distant future, facilitate an operative linkage between the catalyst conception → synthesis → characterization and theoretical modeling → practical catalytic test → catalyst improvement steps.* This should bring about information feedback to improve development of advanced catalysis processes efficiently. To be on the leading edge of this development, to improve the predictive power of the knowledge base in heterogeneous catalysis would be an important advantage.

1.5 CURRENT STATE OF EVOLUTION IN CATALYSIS SCIENCE

The amazing concept of catalysis, that a foreign material can greatly accelerate chemical reactions without itself changing in the process, has inspired many theoreticians and experimentally inclined chemists and chemical engineers. This field offers opportunities of great scientific and enormous economic significance. As a result, catalysis, which began as a mainly experimental endeavor in chemistry, substantially broadened in the last 40 years to include, among its researchers representatives of a wide array of disciplines, such as chemistry, engineering, material science, and surface science. The totality of these disciplines reflects the multidisciplinary character of the field of catalysis. The amazing chemical concept of catalysis inspired the birth of numerous early "theories" many of which required modifications or did not survive a careful check of their general applicability. Problems usually centered on a lack of adequate limitations given for the applicability of the proposed hypotheses.

To conceive the best future strategy for heterogeneous catalysis in energy technology, first it is necessary to recognize the state of evolution in catalysis science. The important questions are whether the whole scientific basis of catalytic phenomena has been uncovered and whether catalysis phenomena have been adequately described to render catalyst development tractable using present day science. To answer these questions we shall briefly examine the two areas most important in energy related catalysis: metal catalysis and acid catalysis with zeolites.

1.5.1 Metal Catalysis

Science in *metal catalysis* has been greatly aided by several factors. Studies on metal alloys and on metal complexes provided basic information on the implication of atomic geometry and electronic structure on chemisorption and catalysis. Fundamental concepts such as the *ensemble effect* and the *ligand effect* in heterogeneous catalysis are based on these results. Studies of metal single crystals were of great help to further substantiate such concepts; this includes results on *microcrystals* exhibiting a variety of crystal faces studied by means of the field electron and the field ion microscope, and *macrocrystals* exhibiting only one single crystal face and studied, *e.g.*, by LEED, AES, or XPS. The evolution of an amazing array of surface science techniques provided both *ex situ* and *in situ* investigative tools, such as surface crystallography using low-energy electron diffraction (LEED), for the study of metal surfaces. In addition, the structure of ligands, such as carbon monoxide and olefins, has been defined together with the metal atom or cluster with which they are associated. In this field, ^{13}C nuclear magnetic

resonance (NMR) spectroscopy, electron energy loss spectroscopy (EELS), and other spectroscopic techniques have been particularly effective.

Since industrial metal catalysts usually contain one or two metals and an oxide in addition to a variety of additives, much attention has been given to alloy chemistry, particularly on the metal surface, on metal-oxide interaction, and on adsorbate-adsorbent interaction. The complexity raised by these phenomena induced attempts to generalize the chemistry by taking into account concepts from both organometallic chemistry and solid-state chemistry. The significance of electronic versus structure effects has been debated at length.

In spite of the enormous growth of information on the surface chemistry of noble metals, some important aspects of metal catalysis remain unexplained, and the apparent complexity of catalysis phenomena seems to have grown. This suggests a balancing act between the organometallic complex formed between surface metal atoms and the reactant molecule and the whole metal crystal, based on the thermodynamic preference of each species. Quantitative evaluation of the energy balance between the short-range effects in the organometallic "molecule" and the long-range effects in the metal crystal is difficult, and such calculations can be handled only by using approximations, particularly regarding the long-range effect. For example, the phenomena of "corrosive chemisorption" and "chemisorption induced surface reconstruction" that were first reported in the 1960s illustrate the dynamic nature of the chemisorption process which usually involves multiple relocations of the atoms of the chemisorbing surface. The activation energy for these reconstructions is lower for the small particles in supported metal catalysts that are typical for industrial applications, than in macroscopic single crystals exhibiting close-packed crystal faces. There are also several new, unexplained phenomena. In hydrocarbon catalysis on noble metals, a carbonaceous overlayer covers a significant amount of the metal, affecting or even templating the surface metal layer with important involvement in surface chemistry and in catalytic mechanism. The specific role of this carbon overlayer is unknown. In another recent case, it was found that under certain conditions carbon monoxide and oxygen on platinum produce a dynamic cycle, forming a carbon-monoxide-rich overlayer followed by an oxygen-rich overlayer, in a cyclic manner. Both the carbon-monoxide-rich overlayer and the oxygen-rich overlayer display a long-range order, which suggests a long-range directing effect of unknown source. Again, the problem of reconciliation between short-range and long-range effects emerges.

Clearly, even when using the whole array of surface science techniques available today, the study of noble metal single crystals still reveals new, unexplained phenomena. Recently interest has grown in the modeling of catalytic phenomena on noble metals using both *ab initio* methods and a variety of approximations in the computations for the long-range effects that cannot be handled today by rigorous, *ab initio* methods even with the use of supercomputers. However, recent work in theoretical modeling shows promise to explain and possibly to predict the changes in specific surface ligand formation, for example, the formation of ethylidene vs. ethylene pi complex on platinum, affected by changes in valence of the metal.

Compared with single crystals, industrial metal catalysts are vastly more complex. Instead of having well-grown crystals, they usually contain a variety of supported metal clusters or alloy

particles. Industrial catalysts are usually multifunctional, that is, they serve more than one role in chemistry and technology. The result is a complex catalyst composition and chemistry with chemical interactions between various ingredients. Research on zeolite supported metal clusters has revealed an important interaction between metal atoms and zeolite protons. The metal-proton adducts not only stabilize small clusters against agglomeration and concomitant loss of active sites, they also appear to combine the catalytic functions of separate metal sites and Brønsted acid sites as visualized in the classical model of bifunctional catalysis. The apparent "electron-deficiency" of these hybrid sites has been claimed to be a major cause for their enhanced catalytic performance. More research will be needed to substantiate these novel concepts. For these reasons, in the past, chemical intuition and experience has played as large a role as science in developing new and better industrial catalysts. Thus, in spite of a great enlargement of knowledge, researchers are still searching for the "light at the end of the metal-catalysis tunnel".

1.5.2 Acid Catalysis with Zeolites

In catalysis with metal oxides, the elucidation of catalytic phenomena has been aggravated by a lack of techniques available to define the structure of the surface with the precision required to construct useful theoretical models for reaction intermediates. This troublesome uncertainty about surface structure was to be absent in *acid catalysis with zeolites*. At the time of the discovery of zeolite catalysis, researchers hoped that X-ray crystallography would provide precise information on all atoms in the zeolite crystal, and thus catalytic sites would be well defined. Now, 35 years after the discovery of crystalline H-Y zeolite and after three decades of great success in industrial applications, researchers may finally be close to explaining, with some precision, the structure and chemistry of protonic catalytic sites in zeolites.

In this case, the problem of characterizing protonic sites rests on the fact that these sites are usually introduced by a proton attack on an oxide ion *via* thermolysis of the NH_4^+ cation. The proton, with its large electron affinity and minuscule size, affects not only the lone electron pair of the adjacent oxide ion, but also the bonds surrounding the newly formed acidic hydroxyl group. The result is a dislocation in the Si-OH-Al linkage that evaded precise characterization until recently.

The experiments with H-X and H-Y zeolites over 35 years ago showed that with aluminosilicates, crystallinity is critical for strong acid catalytic action. Early hopes to define the protonic catalytic sites were hampered by the chemical instability of the primary protonic sites in zeolite crystals. This instability caused various degrees of framework aluminum hydrolysis. Whether the partially hydrolyzed aluminum, or possibly its combination with the nonhydrolyzed protonic site, is the strong acid catalytic site has been a recurring question all through the years. Numerous IR spectroscopic investigations involving protonic zeolites provided little more than fingerprint-type characterization (Creek, 1989). H MAS NMR spectroscopy also offered hope for fundamental information on protonic acidity; however, the small range of the proton chemical shift limits the observation of differences between acidic hydrogens in solid acids to a small range. Furthermore, the acid catalytic action in catalysis should correspond to the deprotonation energy of the solid, that is, the energy needed to transfer

the proton from the catalyst to the reactant, more than to the mere polarity of the O-H linkage which is traced by static spectroscopic observations. The actual transfer of the proton to the reactant molecule involves substantial changes in the bond structure all around the protonic site. These changes depend on many material factors, including the polarity of the O-H linkage and the polarizability of the surrounding bonds, as well as on some long-range effects.

Theoretical modeling has been applied to elucidate the case of zeolite acidity by using $R_3Al-OH-SiR_3$ type molecules and, more recently, by using larger model segments of the zeolite crystal. The most important result of the theoretical modeling work is the conclusion that the bond structure of the Al-OH-Si group controls the ionic character and the acidity of the O-H linkage. According to this model, the deprotonation energy of zeolites decreases; consequently, the acid strength increases with increasing Si-OH-Al bond angle. Thus, the intrinsic strength of acid sites must also increase with increasing Si-OH-Al bond angles. This conclusion, drawn from theory, finds good corroboration with the relationship between Al-O-Si bond angles of zeolites, such as Y, mordenite, and ZSM-5 and their acid catalytic activity.

The precision of theoretical modeling becomes questionable when it has to reconcile the results between short- and long-range effects in zeolite structures. The problem is centered on a recently proposed interpretation regarding the cause of the great difference in acid catalytic activity and acid strength between H-zeolite crystals and amorphous silica-alumina gels of comparable chemical composition. The interpretation rests on the idea that, without the influence of outside factors, the protonated Al-OH-Si groups prefer to form strongly covalent O-H bonds by forming relatively low (sp^3 -type) Al-O-Si bond angles. In zeolites, and particularly in silicon-rich zeolites, the Al-O-Si bond angles range between 135° and 170° ; thus, they are higher than sp^3 -type bond angles. It was suggested that lowering these high angles for the Al-OH-Si units, without affecting the nonprotonated Si-O-Si linkages also present in the zeolite crystal, is prevented or at least minimized by the zeolite crystal in order to maintain long-range order in the lattice. Thus, if long-range order in the crystal prevails over the short-range bonding preference of the Al-OH-Si group, then the original, large bond angles will be retained. In this case, the zeolite retains its crystallinity and displays strong acidity. On the other hand, in cases where the local bonding preference prevails (adjacent to OH group), the crystal may collapse, and the OH groups will be of much weaker acidity. Indeed, H-zeolites with high aluminum and consequently high H-content ($Si/Al \leq 2$) all lose crystallinity, and crystalline H-zeolites all require the presence of stable Si-O-Si linkages in the zeolite crystal. The observed structural loss is probably the result of the reduction of the bond angle in the Al-OH-Si groups. This new theory suggests that the maintenance of crystallinity and the consequent strong acidity found in silicon-rich zeolites ($Si/Al > 2$) depend on an energy balance between the favored bond formation of a single Al-OH-Si group and the bond formation favored by the crystal. The latter favors retention of long-range order and symmetry. Here again, the issue is the balance and reconciliation between the short- and long-range effects.

The arguments outlined above attribute the lower acidity of amorphous silica-alumina gel to lower Al-OH-Si bond angles relative to those found in crystalline H-zeolites. However, most recent experimental evidence suggests a new and unanticipated chemical step. 1H MAS NMR evidence taken following dehydration of amorphous silica-alumina gel and H-Y zeolite indicates

that upon removal of the last H_2O molecule, the amorphous material responds by actually breaking the Si-O linkage in the Al-OH-Si unit while the dehydrated H-Y zeolite maintains its original Al-OH-Si linkages. These distinctly different chemical steps presumably occur because when the stabilizing H_2O ligand is removed, the Al-OH-Si unit prefers to form a strong O-H bond in the silica-alumina gel by cleaving the Si-O bond and forming a strongly covalent Al-OH linkage. In silicon-rich zeolite crystals this step is prevented, probably because of the stabilizing effect of the long-range atomic order and related lattice energy of the crystal.

1.5.3 Conclusions

These two short and sketchy excursions into metal and acid catalysis certainly do not portray the depth of science in these fields. They were only intended to exemplify the point that catalysis researchers are still "digging deep in the tunnel". Although some light is filtering through, the basic problem remains the same as before: to search for the precise characterization of the catalytic site and for the chemistry of the catalytic reaction mechanism.

Past research in catalysis fundamentals, however, was not in vain. Our enhanced knowledge in metal and acid catalysis resulted in better planning and higher efficiency in all stages of R&D. The highest predictive value of information is related to precise definition of the catalytic site and reaction mechanism. In metal catalysis, such information is still limited to metal single crystals and does not extend to practical, multicomponent catalysts containing microcrystalline metal particles. In the case of acidic zeolites, however, our knowledge base is rapidly approaching that of homogeneous catalysis. While many details will be reinterpreted and debated for many years to come, the present concept of the catalytic site together with a more or less firm knowledge of the crystal structure surrounding the active sites provide powerful predictive value to researchers experienced in the field. This knowledge base has been utilized to direct research to the synthesis of new zeolite-type materials. It has been also used recently to develop several new, fuel technology related processes for the processing of hydrocarbon feedstocks. With these highly structured crystalline catalysts, the catalytic capabilities display unique effects and product selectivities previously only known for enzyme catalysts.

Beyond the important, intrinsic characteristics of zeolites, such as strong acidity and molecular sieve character, the growing predictive power of our knowledge base with these crystalline catalysts has been also responsible for their commercial success: today between 30-50% of all catalysts sold worldwide are zeolite-based materials. The conceived higher probability of success in a chemical manipulation using a crystalline material such as a zeolite, resulting from higher predictive power of knowledge, renders zeolites attractive as research topics both in catalysis and in other fields of material science.

This brief assessment suggests that the best long-range strategy in energy related catalysis, just like in other fields of catalysis, is twofold: to carry out research for the discovery of new, advanced catalysts and catalytic materials and to focus fundamental research on the elucidation of catalytic sites and catalytic reaction mechanisms at the atomic/molecular level.

1.6 FUTURE CHALLENGES FOR CATALYSIS IN ENERGY TECHNOLOGY

The major challenges for new and more flexible catalysis technology come from new and changing feedstocks, markets, and from environmental considerations.

1.6.1 Changes in Petroleum Feedstocks

At present the principal feedstock for motor fuels is petroleum. This feedstock varies considerably, depending on its source. The principal variations are differences in distillate content, asphaltene and inorganic content in the distillation residue, and the heteroatom concentration (S,N) throughout the whole boiling range. Since the preferred feedstock is one with high distillate and low S, N content, these feeds have been used at a high rate, leaving feedstocks with higher residue and heteroatom contents for future use. The expected result is a gradual increase in the use of heavier feeds in future years. Since the principal products of petroleum refining are distillate motor fuels, a trend to heavier feedstocks will increase the conversion of both heavy distillates and residual feeds to motor fuels. There are, at present, several commercial processes for the conversion of heavy/residual feedstocks to motor fuels.

The conversion of heavy distillates and residual feeds to motor fuels is mainly carried out by the catalytic cracking and hydrocracking processes. The catalytic cracking process, FCC, has been converting residual feeds to gasoline either by using its conventional vacuum distillate feedstock with 10-20 percent admixed residue content or by using pure residual feeds. The processing of residual feeds requires more complex catalyst technology because of the high inorganic (V, Ni) and heteroatom (S,N) content. Because of the relatively lower hydrogen content of the residue, the yield of gasoline is low and the coke formation on the catalyst is much higher. For this reason, the catalyst usage and its cost is substantially higher. New catalysts and new process technologies have been developed in recent years to protect the cracking catalysts from rapid deactivation caused by the vanadium and nickel present in residual feeds.

An increasing future trend toward heavier feedstocks, particularly the use of the residue itself, poses great challenges to future catalyst technology in the catalytic cracking process. At present, the deleterious vanadium and nickel content of residual feeds is either removed in a preprocessing step on sacrificial sorbents or cheap catalysts, or it is deposited directly on the cracking catalyst. The latter application increases catalyst usage threefold, with substantial added cost and added technological complexity. For these reasons, there is a need to discover selective and cheap methods for the removal of vanadium and nickel from residues. In addition, future catalysts used for the efficient treatment of residual feedstocks need higher durability and fuel product selectivity. Higher durability is needed, first, to cope with the more demanding regenerator conditions (high temperature and steam) caused by the increased coke formation and, second, for the tolerance of vanadium and nickel in the feed. Major improvements in any one of these areas would have major economic significance. Desire for higher fuel product flexibility in the catalytic cracking of residual fuels stems from the fact that the hydrogen content increases in the following order: residue < diesel oil < turbine oil < gasoline. Therefore, most effective hydrogen economy and highest fuel yield would conceptually favor the production of the relatively hydrogen-poor diesel oil.

To maximize the production of the valuable, hydrogen-rich motor fuels (gasoline, turbine, and diesel oil) from heavy distillates and residual feedstocks, the industry developed hydroprocessing to combine conversion to lower boiling range with hydrogen enrichment. Several proven commercial processes have been developed and are used worldwide for the hydroconversion of heavy distillates and residues. The addition of hydrogen allows a great increase in motor fuel yields ranging around 110-120 volume percent for heavy distillate feeds. The economic benefits of such greatly enhanced motor fuel product yields are partially compensated for by higher capital and operating costs and by the use of high pressures and the consumed hydrogen. In addition to higher motor fuel yields, the hydrocracking technology has broad flexibility to produce either gasoline, turbine, or diesel oil as markets and economics demand. In contrast, in the catalytic cracking process the principal product is gasoline.

A trend toward heavier petroleum feeds in the future projects a need to remove larger amounts of the sulfur and nitrogen heteroatoms *via* hydrotreatment process. The removal of sulfur is necessary from both motor fuels and heating fuels because of environmental considerations, while the removal of nitrogen is needed because it is a poison for cracking catalysts. Future improvements in this field will be directed to development of superior catalysts to permit higher selectivity and milder process conditions (lower pressure) in the hydrodesulfurization and hydrodenitrification processes. Future trends toward heavier petroleum feedstocks will result in increased demand for hydrogen in petroleum refining. Processes with the ability to cogenerate hydrogen, instead of consuming it, will be welcome in future refinery schemes (cyclical process).

1.6.2 Natural Gas, Syngas

Natural gas plays a pivotal role as an energy source in the generation of electricity, heat, and as a raw material for hydrogen and syngas in fuels and chemicals production. The availability of large natural gas resources in the U.S. and abroad, together with the declining supply of petroleum in the U.S., raises interest in the role of methane as feedstock for motor fuels. The main interest is to convert methane at its production location to useable motor fuels or at least to a liquid product that can be easily converted to motor fuels. The primary conversion to liquid is essential to enable cheap transportation *via* pipeline or ship from remote natural gas locations to the use areas.

At present, there is no industrial technology available for the direct conversion of methane in a single step to high quality motor fuels. The process schemes available at present either require several steps, show low thermal efficiency, or produce motor fuels of inadequate quality. Research for the conversion of methane is conducted using the following chemical paths:

methane → syngas → methanol → gasoline
methane → C₂-C₄ olefins → gasoline
methane → syngas → alcohol mixtures
methane → methanol.

Potentially, every one of these process schemes has a chance of success if catalysts are discovered to operate at high selectivity at economically attractive conditions. Ultimately, one should grade these new processes both by process economics and by their thermal efficiency. The latter consideration should favor the chemically most efficient, direct catalytic conversion to motor fuels. The assessment of the favored route of methane to motor fuels also requires careful consideration regarding the integrated use of methane and petroleum in the overall refining operation and the wide scale application of methanol alone or in mixture with gasoline as motor fuel.

It should be noted here that in contrast to the great flexibility available for the catalytic conversion of hydrocarbon feeds to hydrocarbon products of different specification, using hydrodehydrogenation and acid type catalysis, *vide infra*, the conversion of hydrocarbons to products containing oxygen is limited. Efficient and selective conversion of hydrocarbons to oxygenates is well developed for unsaturated hydrocarbons, but not for the paraffins abundant in both petroleum and natural gas. In the latter case, commercial success is limited to chemically stable molecules (butane to maleic anhydride). Therefore, direct oxidation of paraffins to the corresponding oxygenates such as alcohols and ethers from paraffins is one of the principal challenges for catalyst chemists in future energy technology. The reaction of paraffins with oxygen is thermodynamically favorable, therefore it offers the possibility to carry out the conversion at low temperatures and pressures in a single step. The direct conversion of methane to methanol and of light paraffins to corresponding alcohols or ethers are key objectives for future fuel technology.

So far, the results of research on direct oxidation of paraffins to alcohols and ethers show high selectivity only at low conversions and limited catalyst life. However, some of the recent results in paraffin oxidation using enzyme-like catalysts show that new advanced catalysts here will probably require a departure from traditional petroleum refining catalysts to new catalytic materials with uniform and highly structured catalytic sites, such as enzyme-like molecules. These catalytic molecules may be fixed or encapsulated in zeolites or other solids. Uniformity of catalytic sites and very high catalytic specificity, such as displayed by encapsulated catalytic molecules, will require new approaches to catalyst synthesis, in order to attain and to maintain the chemical and thermal stability required for these chemically fragile catalysts in practical use. Beyond discoveries in catalyst synthesis there is also a need for effective, innovative heat removal from the catalyst bed in the oxidation process to permit high conversions without unacceptable temperature rise in the catalyst.

One of the roles of growing importance in the use of syngas and natural gas is the production of hydrogen both for the energy industry and for chemicals manufacturing.

1.6.3 Liquid Transportation Fuels from Coal and Biomass

Declining petroleum resources and the availability of large coal resources in the U.S. render coal a strategically desirable feedstock for both solid and liquid fuels. The diverse and complex composition of coal, containing substantial amounts of noncombustible solids and a host of environmentally undesirable components (S, N), renders the conversion of coal a complex and

expensive technological problem. In spite of major sustained efforts and considerable discoveries in coal liquefaction catalysis in the last seventy years, to date no economically and environmentally satisfactory solutions exist which would render coal competitive with petroleum or with natural gas. So far, the indirect liquefaction of coal *via* syngas intermediate deserves higher attention because of the flexibility it provides for choice of fuel and because it limits the handling of inorganic solids and the nitrogen and sulfur bearing compounds to the syngas producing step. These benefits simplify the fuel producing steps; however, they render the syngas production expensive, particularly because of the large cost of plant equipment needed in syngas generation and purification. Clearly, in this technology catalyst chemistry and process engineering must be applied synergistically with an eye on both technology and on process economics. The conversion of syngas to fuels (methanol, mixed oxygenates, diesel oil) is highly exothermic, requiring creative reactor design to remove reaction heat efficiently and at acceptable equipment cost (slurry-bed reactor).

While the catalytic conversion of syngas to liquid fuels offers certain flexibility to produce hydrocarbons or alcohol type fuels, both approaches need further improvements before practical applications can be implemented. Among other problems, the primary hydrocarbon fuel produced from syngas needs further processing steps to meet needs for use in combustion engines. In the conversion of syngas to alcohol fuels, substantial progress has been made both in catalyst selectivity and in reactor technology to achieve efficient heat removal at low equipment cost. Regarding the production and catalytic conversion of syngas, there are several opportunities for the integration of syngas into process schemes involving the production of electricity, motorfuels, or chemicals. In the conversion of syngas it is preferable to produce oxygenated fuels/chemicals with a value exceeding that of the corresponding hydrocarbon products, in order to increase thermal efficiency, to lower the exothermic heat of reaction, and to provide products with properties specifically responsive to future needs in high product selectivity and environmental concern.

Keeping in mind that sound energy-technology strategy must lead to the highest possible utilization of the energy sources, it is necessary to rate the calorific efficiency of various reaction routes from feed to fuel, and even beyond, to the efficiency of the final combustion step (engine efficiency). Based on this consideration, all promising reaction schemes for the conversion of coal to gaseous or liquid fuels need to be examined. Among these alternative reactions the low-temperature conversion of carbon (carbonized coal) with steam deserves special attention

because of its high thermal and raw material efficiency to produce methane. A successful catalytic process here would require a movement of the active catalyst from the processed coal backward to the fresh carbon feed, a difficult chemical and engineering problem.

In the conversion of coal and biomass to motor fuels, one may encounter both catalytic and engineering problems of such magnitude that they may affect feasibility at any given level of available technology. Because of this, it is necessary to carry out reviews periodically to

establish priorities based on overall strategy, promoting superior approaches in priority when their feasibility has been demonstrated.

1.6.4 Changes Resulting From Environmental Considerations

Interest in protecting the environment has increased and expanded greatly. The challenge is to preserve the benefits of modern technology without seriously contaminating the natural world.

Three strategies are available for reducing the impact of chemicals on the environment: waste minimization, emission abatement, and remediation. Waste minimization calls for the design and development of products and processes that are inherently low-polluting or non-polluting. The abatement of emissions can often be achieved by trapping harmful effluents or converting them to harmless substances, for example, conversion of nitric oxide to nitrogen. Where an environmental lapse has occurred, effective means of remediation are needed. As shown by the examples in the following sections, catalysis can contribute to these three approaches.

Changes resulting from environmental considerations involve new specifications for gasoline resulting in the reformulation of this fuel, deeper desulfurization of distillate motor fuels, control of undesirable emissions in fuel production, powerplant and automobile exhaust control, and the replacement of corrosive catalysts with chemically inert catalysts.

1.6.4.1 Gasoline Reformulation

While the current understanding of how the individual components of gasoline affect various environmental issues is limited, several components in gasoline are now considered harmful to the environment if released into the atmosphere at high concentrations as either spills, vaporization losses, or the result of incomplete combustion. They include aromatics, notably benzene, which is a carcinogenic reagent; high-vapor-pressure hydrocarbons such as butane; and chemically reactive hydrocarbons such as olefins and sulfur compounds, which could promote the formation of smog and acids. The industry is responding to the environmental concern and the resultant environmental law by making changes in existing processes and by developing new catalytic processes needed to satisfy new gasoline specifications.

Among the petroleum conversion processes (cracking, hydrocracking), the hydrocracking will retain a vital role in producing motor fuels with environmentally desirable hydrocarbon compositions (low sulfur, low unsaturates) at high yields.

Innovations in catalytic cracking catalysts over the last 30 years, particularly the introduction of zeolite catalysts, have improved the conversion of the heavier components of crude oil to gasoline and diesel oil, allowing a reduction in crude imports to the United States of more than 400 million barrels a year. In the future, new types of cracking catalysts and additional process steps will be required to produce motor fuels that are environmentally more acceptable. To reduce the aromatics content of gasoline and at the same time provide higher octane, fluid catalytic cracking (FCC) catalysts must produce more olefins. The highly reactive olefins then can be isomerized, oligomerized, or alkylated with paraffins to produce high quality gasoline

components. Olefins can also be reacted with methanol to produce a variety of high-octane ethers. New generation, zeolite-type catalysts have also been proved active in isomerizing and oligomerizing olefins to a variety of liquid fuels.

Cracking catalysts will also have to become more rugged to endure the higher temperatures required to produce more olefins for subsequent processing into oxygenates for gasoline. The catalytic cracking process has been the workhorse of modern refineries for 30 years and, with improved catalysts, will continue to be an important process for converting the heavier end of crude oil into gasoline and to a lesser extent to diesel fuel.

The need to reduce the amount of aromatics and to introduce the mandated oxygenates in gasoline has created a need for oxygenated hydrocarbons as replacement octane enhancers. Today the two predominant oxygenates used as octane enhancers are methyl tertiary butyl ether (MTBE) and ethanol (EtOH). However, other oxygenates, such as methanol and higher alcohols, ethers, acetates, and carbonates are known octane boosters. Some of these compounds have been evaluated only partially for their performance characteristics and may represent major growth opportunities for oxygenated fuels. Currently, approximately 150,000 barrels per day of oxygenated compounds (MTBE and EtOH) are added to gasoline in the United States. By the year 2000, projections indicate that 750,000 barrels per day (the equivalent of roughly 10% of current U.S. production of petroleum) of oxygenates will be required in the United States for the gasoline pool. In the United States, the 1990 MTBE production capacity was 117,200 barrels per day. By 1993, it is targeted at 256,400 barrels per day. Iso-olefins (*e.g.*, isobutylene) are now produced as a by-product of fluidized catalytic crackers in petroleum refineries. These quantities will support the production of ether at a rate of only 200,000 to 300,000 barrels per day.

The isomerization of nC_4 to C_6 olefins produced in the catalytic cracking process could greatly boost the production potential of gasoline oxygenates without substantial added cost to the refiner. The catalyst challenge here is to achieve high skeletal isomerization selectivity and particularly to attain adequate catalyst life, durability, and still to carry out the isomerization reaction. The production of olefins is expected to gain new flexibility in the choice of feedstock by the development of efficient and selective catalysts and processes for the oxidative dehydrogenation of both long and short chain paraffins, including methane.

The process technology leading to the majority of oxygenates now in use has been made efficient through catalyst modifications and engineering design. However, new processes leading to the same oxygenates may have cost advantages if cheaper feedstock sources (crude oil versus coal versus natural gas) are found.

If the reformation of gasoline proceeds, in order to provide oxygenated gasoline of sharply reduced olefin and aromatics content, there will be a need to find additional methods to maintain and to increase gasoline octane, and also to find new hydrogen production sources. While the current automobile engine design prevails, higher gasoline octane may translate into higher calorific efficiency, as long as the balance of efficiencies between combustion and "octane production" is positive. This consideration points to a need to carry out the skeletal

isomerization of all gasoline paraffins to the maximum permitted by thermodynamics. Such conversion requires environmentally friendly solid, strong-acid catalysts with the ability to carry out isomerization of long paraffins and naphthenes without undesirable cracking. At present, the catalytic reforming process provides the high octane gasoline aromatics and a large part of the hydrogen needed in petroleum processing. If gasoline's aromatics content is reduced, then less hydrogen will be generated, thus the need for new hydrogen sources. Such new sources may be found in the catalytic conversion of $C_1 - C_4$ paraffins directly to aromatics, producing chemical feedstocks.

The environmental trend to reduce the S and N heteroatoms in fuels to lower levels and reduce the amounts of unsaturated hydrocarbons in all fuel categories places a growing burden on fuel production technology to find additional sources of hydrogen at an acceptable cost.

1.6.4.2 Replacement of Corrosive Refinery Catalysts with Chemically Inert Materials

The alkylation of paraffins with olefins is an important refinery operation. The process reacts isobutane with olefins, generally propylene and butenes, to produce highly branched C_7 and C_8 paraffins, respectively. They constitute a premium high-octane gasoline component (95 to 98 research octane number for C_4 alkylate). The alkylation process is assuming increasing importance with increased olefin production from modern FCC units and with the recent emphasis on lower olefin and aromatics content in the gasoline product.

Both of the currently used liquid acid catalysts, sulfuric acid and hydrogen fluoride, are corrosive. Acid waste disposal of sulfuric acid, and particularly of liquid hydrogen fluoride, is a potential health hazard. As a result of increasing concerns and possible legislative action addressing environmental and safety issues, current alkylation processes are facing increasing scrutiny.

The formidable challenge to the industry is the development of a new, solid catalyst for isobutane alkylation. The new process must have high yield of alkylate, selectivity to produce high-octane gasoline, long life cycle, regenerability, and greatly reduced environmental and safety risks. This challenge would benefit from broad-based fundamental studies of acid catalysis and from increased exploratory research for solid superacids. At the present time, no satisfactory solid motor fuel alkylation catalyst exists. An alternate, if temporary, solution in this field may be a combination of modifications such as the application of additives used in the chemistry of the currently used halide catalyst, resulting in substantial reduction of undesirable emissions and even the hazard of accidental emissions in the alkylation process.

1.6.4.3 Plant and Automobile Emission Control

Catalytic technology is playing an ever-increasing role in environmental protection. In 1989, for the first time in the United States, the market for emission control catalysts (largely for automotive emissions) exceeded the market for petroleum refining catalysts. In addition, the area of stationary emission control (e.g., from power plants) will also experience large (20% per year) growth in the years ahead. Many chemical production plants also need to reduce

emissions. Thus, novel catalysis will in many cases be the critical technology that enables most of the benefits created by the chemical and petroleum industries to be maintained, but with improved preservation of the environment.

Catalysts for automotive emission control are now well developed in the United States and, in general, meet mandated standards for removal of hydrocarbons, CO, and NO_x. Recent Clean Air Act revisions will require significantly greater reductions in 1993 in the emissions of hydrocarbons, CO, and NO_x than those that are now mandated. In addition, stringent local automobile emission standards, as in California and Vermont, will require up to a tenfold reduction in emissions by the late 1990s. These reductions will require more active and more stable catalysts and new reactor designs that enhance low-temperature performance. Because of the rapidly escalating price of rhodium, which promotes NO_x reduction, the industry needs to develop lower-cost NO_x reduction catalysts or practical catalysts for NO_x decomposition. Cleaner gasolines may provide opportunities to develop lower-cost catalysts that contain a smaller amount of the expensive noble metals. Finally, substantially improved technology needs to be developed for the recovery and the recycling of noble metals, including rhodium because of its high cost and low natural abundance.

Power plant emission control is another major area of opportunity for catalysis. In particular, NO_x emissions need to be removed either *via* selective catalytic reduction (SCR) or, if achievable, *via* the preferable NO_x dissociation to produce nitrogen and oxygen, eliminating the need for reducing agents. The abatement of NO_x from power plants is important in efforts to control acid rain and photochemical smog, the latter being linked with harmful ozone production. Selective catalytic reduction removes NO_x in flue gas by reacting oxides of nitrogen with ammonia to form nitrogen and water. The catalyst is the heart of SCR technology, and it must provide both high activity and high selectivity (toward nitrogen formation). Major improvements in performance are desirable toward the conversion of nitrogen oxides directly to nitrogen and oxygen.

An important gas emission believed to affect the environment is CO₂. There is a need to develop a long range industrial/environmental strategy aimed at containment if not reduction of the air's CO₂ level. The primary goal is to develop competitive processes for the production of hydrogen, chemicals, and energy sources not involving CO₂ production or providing reduced CO₂ production.

1.6.4.4 Replacements for Chlorofluorocarbons

Chlorofluorocarbons play an important role at present as energy transfer agents (refrigerants) in industry and everyday life. Therefore, their environmental impact is of concern to the energy industry.

Chlorofluorocarbons (CFCs) are now believed to contribute to the seasonal ozone depletion over the Antarctic continent. However, because they are crucial to many aspects of modern society and have no available replacements, ceasing their production immediately is not practical. By 1988, the total CFC consumption worldwide had grown to 2.5 billion pounds per year for use

as refrigerants, foam-blowing agents for polystyrene and polyurethane, and industrial solvents and cleaning agents.

Ironically, the high stability and inertness of CFCs, which make them so valuable, have led to their downfall. Once released at ground level into the atmosphere, they rise slowly into the stratosphere, where they are degraded by high-energy radiation from the sun and release chlorine-containing free radicals that trigger a catalytic ozone depletion cycle. Following detailed, though not definitive studies, agreement was reached on a major global environmental treaty, the Montreal Protocol, to phase out CFC production by January 1, 1996. A race by all CFC producers then began to find suitable and environmentally acceptable substitutes. The strategy is to reduce its atmospheric lifetime by introducing hydrogen into the molecule so that it is removed from the atmosphere by reaction with hydroxyl radicals in the stratosphere. The commercially viable synthesis of these new compounds is a major challenge for catalysis because catalysts used for the production of CFCs lack the required selectivity and activity to be acceptable for the production of hydrogen-containing substitutes.

New catalytic processes have been developed to begin large-scale commercial production of hydrogen-containing chlorofluorocarbon replacements, both hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs). The HFCs are satisfactory alternatives to the CFCs in many applications, but they are more expensive than the materials that they replace. Replacements must also be found for the HCFCs because they contain chlorine and can damage the ozone layer, although to a much lesser extent than the CFCs. Major advances in catalytic science and technology will be required to develop production processes for fully acceptable substitutes in applications such as refrigeration, air conditioning, insulating foams, and fire extinguishing fluids.

1.6.4.5 Recycle and Recovery of Catalytic Material

Catalysts, if released into the environment, often represent substantial health hazards. Therefore, the containment and/or recycle of relevant components of spent catalysts provide both environmental and economic incentives. In the case of noble metals there is a further incentive, namely the irreplaceability of these heavy elements which are critical for future energy and chemical technologies.

1.7 FEEDSTOCKS FOR THE CHEMICAL AND PETROCHEMICAL INDUSTRIES

The chemical and petrochemical industries draw their raw materials from petroleum and natural gas. The main chemical intermediates are hydrogen, olefins, and aromatics. Hydrogen is used widely in chemical syntheses, from the production of ammonia to the many products requiring hydrogen addition. Olefins are used both as short carbon chain (C_2 - C_4) for polymerization and for the synthesis of a great variety of heteroorganic compounds, while long chain olefins (C_{12} - C_{18}) are used for both plastics and chemicals production. At present, there are several processes available in the pet. oleum/petrochemicals industry to produce desired chemical feedstocks from various raw materials. Feedstock for the production of C_2 - C_4 olefins is provided from natural gas liquids, straight-run petroleum distillates, and distillates produced in the hydrocracking process.

Both short and long chain olefins are produced from the corresponding paraffins *via* selective oxidative dehydrogenation. Aromatics are produced by extracting the desired fraction from gasoline reformates or from the aromatic residue formed in light olefin production. New emerging technology is also available for the direct conversion of C₃-C₄ paraffins to mixed aromatics, producing hydrogen as a valuable by-product.

The most important future objective in the production of petroleum feedstocks is to increase the chemical efficiency of the catalytic processes used to produce chemical feedstocks in order to maintain the competitiveness of our petrochemical and chemical industries. These industries with their successful worldwide business provides an outstanding, positive trade balance for the U.S. Maintenance of our leadership position here is of highest strategic interest for the U.S. economy.

1.8 NEW APPROACHES TO ADVANCED CATALYSIS

1.8.1 Introduction

Great technological advances have been realized since the thirties in all areas of the energy industry. In this evolution, heterogeneous catalysis played the pivotal role to convert available feedstocks to quality fuel products. Most of the technological advances rest on the flexibility, efficiency, and durability of catalysts developed for the conversion of one hydrocarbon type to hydrocarbons of different specifications. Similarly, good progress has been achieved in the conversion of olefins to oxygenates, useful as motorfuels. Progress is evident in other areas of the energy industry as well. As a result of long sustained research, improvements have been realized in the catalytic conversion of syngas to methanol, mixed alcohols, or to mixed hydrocarbon fuel. A practical, industrial catalyst has also been developed for the direct conversion of retorted shale oil to quality turbine and diesel oil. The most important omission in this chain of success is the direct conversion of saturated hydrocarbons to oxygenates (and to other heteroorganic compounds). This reaction, if carried out efficiently, would allow the production of all oxygenates needed beyond those obtainable economically from FCC produced olefins. It would also allow the production of methanol from methane directly, leaving out the costly and energy inefficient syngas intermediate product. There are some encouraging recent research results on selective paraffin oxidation catalysis. The new catalysts applied here operate at near room temperature using enzyme-like catalytic molecules (porphyrin, phthalocyanine, *etc.*) either in solution, encapsulated in zeolites, or in other structured supports.

It is important to review critically what has been accomplished in the past, with a view to future challenges. Recognition of some of the general characteristics of our traditional heterogeneous catalysts, as well all those we envision today, could lead to advanced catalysts of the future. For sure, no conceptual generalization will lead to success in every application. Nevertheless, such analysis may be useful to guide in the selection of alternate approaches.

It seems useful here to compare the main chemical and performance characteristics of current industrial heterogeneous catalysts with enzyme catalysts. Enzymes, as we know, are intermediate to large size molecules with multifunctional catalytic roles played by different

segments of the molecule. Enzyme catalysts have identical active sites. These usually highly structured catalyst molecules are much more efficient (in turn-over number) than current industrial catalysts; however, they are much more fragile. They are readily destroyed by high temperatures or in a reactive chemical environment. The latter limits the practical applications of these materials, even though much has been recently accomplished to "fix" enzymes to improve their stability and technological applicability. In contrast to enzymes, traditional heterogeneous catalysts have a range of active sites. Lack of uniformity of active sites results in compromise in selectivity and in chosen process conditions. The ability of our traditional catalysts to operate in an extremely broad range of temperatures renders them practical, particularly in cases where limiting thermodynamics require high temperatures not suitable for large and sensitive feed molecules. However, in cases where thermodynamics or other process constraints are absent, it is worthwhile to consider the development of new types of catalysts with uniform catalytic sites for advanced catalysis in future energy technology.

Priority for choices in future energy technologies need to follow basic guidelines in future energy strategy and in competitive economics. Such consideration points to a need to analyze the economics and the calorific efficiency of alternative paths from fuel feedstocks through fuel production to ultimate combustion. Calorific efficiencies with attendant economics must be considered in the context of the whole life cycle of fuels. Comparative analysis of this type, as well as environmental considerations, should help to rank the value of new technology steps. This consideration makes it attractive to try to introduce advanced catalysts into the combustion step. Catalytic or nanometric treatment of combustion surfaces may lead to superior engine design, higher thermal efficiency (see discussion below on new materials), or superior environmental effect. In order to create the invention of such complex, novel approaches it is desirable to carry out feasibility studies by multidisciplinary teams of experts with proven track records in creative approaches to map out opportunities in this field.

1.8.2 New Catalytic Materials

In the last four decades the largest impact on heterogeneous catalysis was the introduction of new catalytic materials. Since the great success of zeolite catalysts in industry, catalyst synthesis adopted several synthesis topics and characterization methods from materials science. Catalyst synthesis, a critical subdiscipline of catalysis, has developed a methodology of its own. Today the objectives of catalyst synthesis are far-reaching. They include the whole variety of industrial oxide catalysts, supported metals, biocatalysts, and zeolites and other microporous or layered materials such as clays, with wide ranges of chemical compositions, pore sizes, and crystal structures. With zeolites, large pore size seems to be of premium value. Large-pore zeolites with pore sizes of about 8 Å are yearly bested by new microporous crystals with pore sizes of 12 Å and most recently with about 20 Å pores. The main incentive for catalysis in this field is that these large pores, acting as molecular sieves, may benefit catalytic selectivity in the treatment of heavy petroleum products. They may also act as receptors for immobilized, enzyme-like molecules. At present, this area of synthesis research is achieving a high rate of productivity worldwide.

As scientists look for guiding principles for strategy in future catalysis, they must contemplate the differences between biocatalysts and man-made catalysts. Biocatalysts have uniform catalytic sites, and they have high catalytic selectivity. Man-made heterogeneous catalysts, such as oxides, supported metals, and even acidic zeolite crystals, contain a range of active sites. With non-uniform active sites, the catalytic specificity to the desired product is lower. This simplistic comparison between biocatalysts and traditional heterogeneous catalysts points to catalytic-site uniformity as a desirable feature for future heterogeneous catalysts.

Several approaches have recently been used to develop solid catalysts with uniform catalytic sites. The "fixing" of enzymes on supports and, more recently, the immobilization of enzyme-like molecules in zeolites are good examples. In the latter case, catalytic molecules, such as porphyrin, phthalocyanine, or salen, each containing a variety of transition metals, have been immobilized in zeolite crystal cavities using ship-in-bottle synthesis. Recent data indicate synergistic phenomena between the zeolite structure and the occluded complex. These phenomena give rise to substantial stabilization of the complex. The result is higher catalytic turnover numbers achievable relative to the solution of the same complex. In addition, catalytic specificity is strongly influenced not only by the active complex itself, but also by the uniform spatial constraint around active sites. Such spatial constraint is provided by the intracrystalline environment (*regio* selectivity) of the zeolite support.

Microporous crystals may also offer several new strategies to provide uniform catalytic sites. Recent developments in the synthesis of microporous crystals, particularly in aluminophosphates, permit the synthesis of compositions containing a variety of transition metal ions in the crystal framework. These tetrahedral ions are on the intracrystalline surface. They can occupy identical crystallographic sites by the proper choice of crystal type, transition metal, and its concentration. Some tetrahedral cations have been observed to be capable of reversible change in coordination, from tetrahedral to octahedral, upon hydration-dehydration cycles. Therefore, these transition metal cations are probably accessible to varying degrees to catalytic reactants. They may also be suitable sites for the synthesis of larger, enzyme-like catalytic centers.

Uniform catalytic sites combined with shape selectivity offer new opportunities in catalysis. The substitution of aluminum or other small framework cations of microporous crystals such as zeolites with larger, transition metal cations must result in a distortion of the substituted crystal site that causes stretching and bending of adjacent bonds. This crystal-site distortion may result in a distortion of the local site symmetry, leading to stereospecificity or even chirality. Such changes may even form the basis for stereospecific catalysis.

In addition to three-dimensional crystalline microporous materials, near uniform porosity with variable micropores has been prepared with crystalline layer structures (pillared clays) and even with amorphous inorganic oxides. These materials, if provided with adequate thermal/hydrothermal stability and flexibility in choice of pore size, may find use in heavy oil processing as well as other energy related applications.

Beyond the advanced, highly structured catalytic materials there is a need to improve the synthesis of traditional catalytic material such as oxide type supports and catalysts, sulfides and supported metals, particularly noble metals.

In the past, acid catalysis has been the key catalytic reaction in all motor fuel production technologies. Acid catalysis, using environmentally friendly catalysts, is also essential to achieve future goals in energy technologies. The environmental constraints and the need to treat heavy oils and new feedstocks place high priority on the discovery of superior solid acid catalysts. Improvements are needed to achieve all ranges of acid strength from moderate to super acid strength, to display uniform or near uniform acid strengths of active sites, and adequate thermal and chemical stability for practical applications. These materials may be crystalline or amorphous. They may also be surface decorated with suitable activating groups ($\text{ZrO}_2 - \text{SO}_4$). High acid strength is needed to carry out reactions at ambient temperature in cases where high temperatures produce undesirable thermodynamic or other chemical limitations.

In other fields of catalyst synthesis, a particularly important breakthrough in catalysis would be the synthesis of thin, continuous layers of microporous crystals that are usable as *catalytic membranes*. This development, when combined with inventive reactor/process design aimed to overcome mass transfer limitations of membranes, would probably revolutionize not only catalyst synthesis but also catalytic reactor design because of its large potential applications in combining molecular-sieve type separations with catalysis. In spite of its large potential impact, no new, inspiring approaches that are comparable in novelty and creativity to those used in the synthesis of new molecular sieves are apparent.

Aiming at the formation of uniform surfaces and uniform catalytic sites, it is conceivable that the atomic force microscope or a mechanical system of similar design may be used not only to monitor the surface layer of crystals, but also to modify them. Ultimately, scientists may devise a mechanism to imprint or replicate uniform surface structures on metals or oxides so that they become uniform catalytic sites.

Combustion engines designed today have limited thermal efficiency, based on the spherical propagation of the pressure wave generated by the fuel combustion. An examination should be made to see if combustion engine efficiency could be improved by the application of nanometrically engineered combustion surfaces, possibly zeolite-type membranes, to create oblong pressure waves with attendant enhancement in thermal efficiency.

1.8.3 Catalyst Characterization

Beyond the routine physical and chemical analyses used in catalyst synthesis, catalyst characterization is needed to define a catalyst beyond its chemical composition and crystalline components, so that its catalytic properties can be reproduced. Furthermore, in the development of new catalysts, chemical concepts regarding composition or structure are conceived. Following synthesis, the match between the envisioned chemical concept and the actual catalyst product must be confirmed. Catalysts also undergo changes in use. Industrial catalysts are usually used for several months or years before they are replaced, regenerated, or rejuvenated.

In this period, the catalyst degrades in performance to a certain extent, and characterization is needed to indicate the change in the property most relevant to catalytic performance. Successful industrial catalysts are often multifunctional, that is, they contain several catalyst components. Their manufacture requires meticulous characterization following each significant catalyst synthesis step. Regeneration or rejuvenation of used catalysts also requires a proof of restoration of catalytic properties, as well as both physical and chemical characteristics. Therefore, characterization involves a long list of physical and chemical methods and usually also includes an actual catalysis test. Clearly, catalyst characterization serves many needs, from research to manufacture. The characterization may relate to the catalyst support, to the precursor phases of the catalyst, to the catalytic site, or to the catalytic reaction itself.

Any experimental plan developed for the creation of a better catalyst requires a description of the catalytic site and its catalytic function that is as accurate as possible. Superior knowledge of the active site obviously translates to a better plan for catalyst improvements. This consideration leads to the most important future objective in catalysis characterization: the *characterization of catalytic sites at the atomic level*, with sufficient detail in chemistry and structure to allow the planning of modifications, leading to desired changes in chemical and catalytic characteristics. This objective requires a depth of knowledge similar to that existing today in homogeneous catalysis. Since the catalyst surface and particularly the catalytic active sites are usually sensitive to the chemical environment, the characterization should be carried out in an environment consistent with the reaction environment, and preferably it should be carried out *via in situ* experiments.

Beyond the atomic and molecular description of the catalytic site itself, scientists must also seek to understand the relationship between the chemistry of the active site and long-range effects exerted by the crystalline base or other long-range phenomena, such as ordered overlayers. Long-range effects can be important, and in some cases they are the key to catalytic phenomena. The formation of a catalytic site or reaction intermediates tends to distort the crystal, causing disorder. The direction of the long-range effect is generally the maintenance or restoration of lattice order to increase thermodynamic stability of the whole crystal. The quantitative assessment of the preferred bond structure at the catalytic site (short-range effect) of the whole crystal (long-range effect) is difficult because of the large size of the computational terms related to the long-range effect. Therefore, scientists need to search for some traceable spectroscopic evidence to monitor long-range stress in catalyst crystals.

Since catalysis is a surface phenomenon and since the active ingredients in supported metal catalysts are small metal clusters, relevant information on sites and adsorbed molecules on metal particles is provided by FTIR, NMR, EXAFS, and Mössbauer spectroscopy. For macroscopic surfaces, *e.g.* of single crystals, information can be obtained by LEED, elemental analysis (ISS), and XPS. Opportunity to monitor valence and atomic surface structure may be provided by advanced ESCA equipment furnished with a high intensity, monochromatized X-ray source. This may become an effective method to characterize the chemistry and the atomic structure of the surface of both metal and oxide-type catalysts in the near term.

Characterization of catalytic active sites at the atomic scale received a great boost from the development of the electron tunneling, ETM, and atomic force, AFM, microscopes. These methods have the potential to reveal the surface structure of both metals and oxides and to show atomic dislocations. They can even map the atoms and molecules of the chemisorbed overlayer. In addition, these techniques may also have the potential for indicating the bonding characteristics of surface atoms by applying perturbations. Such measurements may be developed in the future to characterize the chemistry of surface atoms. Today, however, the electron tunneling and atomic force microscopes are only designed to monitor the surfaces of single crystals. To render these revolutionary, atomic-level characterization techniques useful to catalysis, there is a need to redesign the delicate mechanical control system to allow monitoring of microcrystalline material. Such redesign would involve the development of improved mechanics and computer software to allow the mapping of small crystal surfaces and the automatic reorientation of the sample to find the next crystal surface. The development of electron tunneling and atomic force microscopic techniques for microcrystalline catalysts would be an important step in achieving catalytic site characterization of practical catalysts at the atomic level.

Future progress in catalysis science also needs expanded knowledge of the reaction chemistry so that scientists can contemplate modifications for catalyst improvement. With this long-range objective in mind, the determination of the catalytic reaction steps and reaction intermediates is essential to future progress. Recent years have seen excellent progress in this field from a variety of sophisticated techniques, including ^{13}C NMR, EELS, and FTIR, for the identification of chemisorbed molecules and catalytic reaction intermediates on noble metals. The next step in this field is to extend the application of these techniques to industrial catalysts, including supported metal catalysts, oxides, and acidic zeolites, under practical reaction conditions. In this field, methods with adequate response time are also needed to identify relatively unstable reaction intermediates as well.

The ultimate purpose of gaining detailed knowledge about catalytic sites and catalytic reaction intermediates is to bring catalysis, as a branch of chemistry, to the level where the predictive scientific quality of the experimental plan compares to that used today in inorganic or organic synthesis.

In order to improve the effectiveness of catalysis R&D in future years, to grade the quality of available choices, and to rank the experimental options based on relevant scientific considerations, appropriate theory is needed in the modeling of catalytic sites and catalytic reaction intermediates. Quantum-mechanical modeling should be applied with a critical attitude in the application of assumptions used to abbreviate the computation of the short-range and, especially, the long-range effects. The development of scientifically reliable theoretical modeling is a challenging and difficult task. Today, *ab initio* calculations are still limited to small atom clusters or they require the use of generalized or simplified expressions for long-range effects. The future direction in theoretical modeling is almost obvious. If current trends in computer and software development continue, scientists cannot escape the conclusion that in the future computational modeling will probably be one of the fastest growing areas in catalysis science. For this reason, theoretical modeling will no doubt have an important place in future catalysis.

The ultimate objective is to develop an operative linkage between catalyst conception → synthesis → characterization → theoretical modeling → catalytic test and catalyst improvement. Such linkage between these steps provides the most effective feedback for the evolution of the advanced catalysts needed in future energy technology.

1.8.4 Industrial Catalytic Process Development

The objective of industrial catalysis is to develop economically superior processes based on innovations that lead to the use of cheaper feedstocks, to higher product yield, or to other process efficiencies that translate to superior process economics. Industrial research organizations depend on their experience, which is based on both successful and unsuccessful experiments in catalyst synthesis or on the process side, to develop their favored research strategy.

Recent success in the use of bio-derived catalysts in a variety of pharmaceutical syntheses and specialty chemicals syntheses substantially broadened the spectrum of the knowledge base from which the research strategy for advanced catalytic processes should be conceived. Because of the differences in applicable catalyst types, such as enzymes, zeolites, superacids, and supported metal systems, the catalysts and the processes of competing approaches may be profoundly different. They may even require researchers of different disciplines for efficient, creative pursuit. Future industrial success for new catalysis technology will probably favor those scientists who can consider all potential options from the point of view of catalyst types and process approaches to develop the best conceptual research strategy. Developing new competitive catalytic process technology is indeed a complex job that requires a broad-minded research organization and people of excellence in a whole spectrum of disciplines, including chemical synthesis, chemical engineering, and materials science.

These considerations and the challenges discussed above lead to the following recommendations in the pursuit of industrial catalytic process work:

- ▶ Learn from biocatalysis and homogeneous catalysis and seek catalyst synthesis approaches that develop catalysts with uniform catalytic sites. Look for approaches for uniform catalytic sites not only in the use of enzyme-like species but also in seeking novel approaches of "surface synthesis", using both metals and oxides. Industrial catalysts are often multifunctional. Sometimes the functions relate to two interacting catalytic steps (bifunctional catalysts). However, in many cases only one or more catalyst additives are present to help correct a certain catalyst deficiency, such as rapid metal aggregation, or to aid catalyst burn-off. Based on past experience, if a new catalyst does not have sufficiently high catalytic selectivity or activity, fixing these initial problems requires using additives, dopants, or expensive catalyst regenerative or rejuvenation methods, often requiring large costs and long time periods. For these reasons, a strategy aiming from the start at uniform catalytic sites may be a rewarding principle.

- ▶ Acid catalysis is the most common and important catalytic function in industrial hydrocarbon catalysis. All ranges of acidity, including mild, strong, and "super" acidity, are important for distinct areas of industrial applications. Environmental considerations place high priority on the development of chemically inert, solid superacids for a variety of manufacturing processes. This need focuses attention on the theory of solid acids. Theory is needed to elucidate the specific role and contributions of structural and chemical factors affecting strong and super acidity as well as of the interaction between protonic and Lewis-acid sites. The goal is to gain maximum acid strength and to control the reaction mechanism. A basic understanding here would provide a rich basis for new, superior synthesis approaches to solid acid catalysts in the whole range of acidity.
- ▶ Implementation of new environmental technology needs both improved and new catalysts. Among these, high priority should be given to the catalytic decomposition of nitric oxide to nitrogen and oxygen in order to eliminate the use of ammonia as reducing agent.
- ▶ Successful industrial catalysis technology requires the creative combination of catalyst chemistry and reactor/process engineering in order to solve problems in catalyst-reactant interaction (fixed bed, fluid bed, slurry bed, moving bed), heat transfer, and catalyst regeneration. Successful engineering solutions of these problems are critical for competitive process economic performance in every energy related application. Imaginative catalyst flow control, such as fluid, or moving bed applications, has revolutionized catalytic cracking, gasoline reforming, and ethylene polymerization, greatly increasing product quality and the feasibility of achieving these processes. Such process innovation can release the processes from reactor-size constraints and provide superior operational control and stability with added benefits in the optimization of operating conditions. In several areas, new creative engineering may benefit future catalysis technology. New imaginative process solutions may be similar to those successfully applied recently in sorption-separation processes with respect to countercurrent reactant-flow control, use of desorbents, *etc.* These ideas may find applicability in cases of multistep catalytic reactions conducted in a single catalyst bed, particularly in cases using multiple feeds. Catalytic sensors also have an important role in future technological advances.

1.9 THE DISCIPLINE OF CATALYSIS

The makeup of the catalysis discipline is continuously evolving. In the last forty years, researchers in surface science, material science, inorganic synthesis, and theory have given catalysis great scientific strength. The most important aspect of this change is the broadening of scientific topics and the focus toward more quantitative scientific methods. This trend will, no doubt, stay with catalysis in the future as well. The field will broaden to include biocatalysis and new areas of inorganic synthesis for new catalytic materials. Surface science will blossom, together with theory, particularly when theory can play a role as a predictive tool in an operational linkage between conceptual planning and catalyst synthesis.

Changes in the future makeup of the discipline of catalysis must be reflected also in the institutional training of future scientists. Therefore, efforts should be made to develop broad as well as scientifically sound curriculums at selected universities where catalysis programs are on the teaching agenda.

1.10 RECENT RESEARCH TRENDS

The direction and management of catalytic research for future applications have been examined critically in recent years. The 1985 National Research Council report 'Opportunities in Chemistry' selected chemical catalysis as one of only five topics to be given national priority. This report also recommended "New mechanisms and incentives should be sought for strengthening the links between industrial and academic research". Recent in-depth studies have provided further insight and recommendations for research for energy applications (DOE 1985, 1989). Research to provide for alternative fuels and environmental protection has been of particular concern.

However, in sharp contrast, industrial catalytic research has greatly decreased in the past decade, particularly research for synthetic fuels. The drastic reduction in oil prices led to the conclusion that synthetic fuels research is too long-term for industry. Other factors deemed to restrict manufacturing opportunities in the U.S. are the increasingly costly and uncertain environmental restrictions, restrictions that do not apply to manufacture overseas.

A different concern perceived to limit research progress is the recognition that there is insufficient collaboration between the science base and the engineering community on the practical application to process and reactor development.

Recognizing the opportunities and problems in conducting longer range catalytic research, many countries in Europe (Belgium, France, Germany, and the United Kingdom) and Japan have in the past five years created organizational structures to implement increased catalysis research and particularly to encourage effective industry/academia/government cooperative programs. It is no longer believed feasible to leave to chance the very intimate relationships that exist between scientific progress and industrial developments. There is only a limited amount of technical research available and choices of paramount importance must be made. This approach is being increasingly discussed internationally (Haggin, 1993).

1.11 RECOMMENDATIONS

This chapter lists recommendations focused on fundamentals and on new approaches in catalysis. Recommendations are given for short-term (up to 5 years) and for long-term (up to 20 years). All supported approaches must take into account future trends in environmental policy.

1.11.1 Short-Term Goals

1. Develop instrumental methods for the characterization of the chemistry and structure of catalytic active sites and catalytic reaction intermediates, applicable to commercial catalysts.
2. Develop durable catalyzed combustion system for turbines (and engines) aimed at substantial NO_x emission reduction.
3. Develop the theoretical basis of acid strength, from weak to superacid, for environmentally friendly solid acid catalysts.
4. Carry out preliminary study to evaluate the potential advantage and preferred applications for heterogeneous catalysts of uniform active sites.
5. Carry out a preliminary study to evaluate new approaches to advanced, high efficiency engines applying catalytic combustion surface. Among various options nanometrically engineered combustor surface creating oblong (rather than spherical) pressure waves should also be considered.

1.11.2 Long-Term Goals

1. Develop practical techniques for the characterization of the chemistry and atomic structure of catalytic active sites and catalytic reaction mechanism, preferably under reaction conditions.
2. Support fundamental research in catalysis aimed to develop functional linkage between catalyst synthesis, characterization, theoretical modeling, testing, and catalyst improvement.
3. Develop catalyzed combustion systems (turbines, engines) aimed at higher thermal efficiency and reduced emissions.
4. Develop techniques for selective, direct oxidation of paraffins, including methane, to corresponding oxygenates.
5. Develop advanced catalyst/reactor concepts aimed at complete conversion, minimized by-product formation and efficient heat removal.
6. Develop low temperature catalytic conversion of coal with H₂O.

7. Develop techniques for catalytic desulfurization/denitrification of fossil fuel feedstocks below 1 ppm level at mild reaction conditions.
8. Develop solid catalyst compositions with uniform active sites aimed at energy saving technologies.

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Chapter 2

CATALYST PREPARATION - DESIGN AND SYNTHESIS

Henry C. Foley

2.1 INTRODUCTION

The purpose of this chapter is to examine the basic notions and premises of catalysis preparation as a science, to delineate the likely driving forces for new catalyst development, and to specify important topical research thrusts for catalyst design and synthesis over the next ten years.

2.2 GLOBAL OVERVIEW OF CATALYST DESIGN AND SYNTHESIS RESEARCH

"Nevertheless, the importance to both theory and the practice of catalysis warrants a sustained experimental attack on the specification of active centers in heterogeneous catalysts. This requires a theoretical framework ... its construction calls for imagination and a willingness not to be confined by current concepts. Not until we can say for many catalyzed reactions that the mechanisms are known will heterogeneous catalysis finally pass from an art to a science."—G.C. Bond (1974)

Under ideal conditions catalysis science is the science of the "steady state". Heterogeneous catalysts by their very nature are non-equilibrium structures, or at best they are metastable states of a material. In most cases the solid surface of the catalyst and, often the product and reactant matrix above it, may be quite far from equilibrium. Examples of metastable and non-equilibrium structures of catalysts include dispersed metal particles on a high surface area support, a metal oxide in contact with a hydrocarbon reactant, or a highly hydrated zeolite located *in vacuo*. For each case the identifiable structure is dependent upon the pathway that led to its creation. In actuality the full structural development of the catalytically active material may not be complete even after pretreatment, but the interfacial structure will continue to evolve until the reactant and product matrix reach a steady state with the solid surface.

This aspect of catalytic materials preparation has been recognized, but only implicitly, in terms of the dependence of catalytic activity and selectivity upon pretreatment method. Conditions for calcination and reduction of supported metals control their activity and to some extent their selectivity. Now, however, a deeper recognition of the time-factored nature and path dependence of the development of a catalyst's interfacial, and in some cases bulk, structure must be included as a part of ongoing research aimed at the synthesis of new catalytic materials. A portion of this research should be focussed on developing an understanding of the transient phenomena associated with differences in structural attributes that lead to the catalytically active phase.

New research in catalyst design and synthesis should seek to reduce total complexity by increasing structural uniformity and specificity of working catalysts. Highly structured materials with uniform sites are inherently more easily "defined" than those that have a distribution of

active sites. With higher structural definition comes a higher degree of predictability and hence better opportunity for *ab initio* design. The long-range goal of *ab initio* catalyst design, to start at the molecular level of the active site and to extend through to the long-range structure of the solid, can be reached eventually, but only by embracing even more science in heterogeneous catalysis. Success will require an ongoing integration of the key-enabling sciences of inorganic, organometallic, and computational chemistry, with chemical reaction engineering and materials science. It can be argued that catalysis design and synthesis defines the intersection of chemistry, chemical reaction engineering, and materials science (Burton and Garten, 1977) (Figure 1).

Figure 1. Catalysis Design and Synthesis Defines the Intersection of Chemistry, Chemical Reaction Engineering, and Materials Science.

The research thrusts in the design and synthesis of new catalytic materials must strike a balance between an emphasis on the short-range structure of the active site and the longer-range structure of the solid that constitutes the environment surrounding the active site. Advances in zeolite catalysis teach us that design and synthesis of new catalyst materials must include consideration of the full range of molecular phenomena that make up the process of heterogeneous catalysis, and not just those steps associated with bond-making and bond-breaking at the active site. Diffusion of molecules or ions to and from the vicinity of the active site, as well as energy transfer processes, must be provided for in the design and synthesis. The active site and the bulk structure surrounding it are physically and functionally inseparable. Creative new approaches that force coupling between physical processes and chemical reactions in well-defined ways through control of catalyst structure offer excellent prospects for entirely new processes with lower energy requirements and low to zero waste production.

Equally important will be research aimed at developing a molecular-level understanding of catalytic materials that are inherently non-uniform, that is complex, but well-suited for applications. For example, in petroleum refining, complex mixtures of reactants must be processed efficiently. These complex mixtures can be represented as distributions of different structural attributes. For these systems catalytic materials must present complementary distributions in their physical and chemical properties in order for efficient reaction to proceed. At the global level these materials appear amorphous or disordered, but at the local level these same materials have microstructures that provide the necessary "active sites" for specific reactions. Then, in a very real sense, these materials may be considered to be comprised of distributions of different active sites. This nonuniformity is advantageous for technology, but it complicates the science by frustrating attempts to fully elucidate structure and function, especially under real process conditions. However, progress has been made. A good case in point, perhaps the best, is that of ammonia synthesis, for which fundamental research has built a depth of understanding that is probably unrivaled by any other subfield of heterogeneous catalysis (Jennings, 1991), even though the industrial catalysts are complex solids.

Building on past efforts, the elucidation of complex, industrial catalyst structures must be pursued with renewed vigor. This will require an integration of experimentation and computation. Computation, or simulation, provides a means for expressing the extent of understanding that has been developed at any given point in time. Computation also provides a necessary guide for further experimentation and interpretation of new results. It seems possible, and even probable, that by focusing new research that couples the real surges in the power of computing with breakthroughs in instrumental methods, such as atomic force microscopy, more rapid progress will be made on the problem of structural and functional elucidation of complex catalysts.

At the other end of the spectrum, the synthesis and fabrication of interesting new materials that are either mimics of technical catalysts, or prototypes of new catalysts, can be conducted in ultrahigh vacuum using the methods that have been developed for electronic materials processing. More specifically, by using methods like molecular beam epitaxy (MBE), atomic layer epitaxy (ALE), or low pressure chemical vapor deposition (LPCVD), surface and materials scientists can begin to prepare more complex and more relevant materials that are still quite well-suited to their analysis methods. Some research has begun along these lines and the results appear to be quite interesting in prospect (Zuburtikudis, 1992).

As mentioned earlier in this section it will be necessary also to develop new and better probes of industrial catalysts, especially in their working state, a regime that is as yet largely inaccessible to analysis by spectroscopy. This problem is one that is at least as old as the field of catalysis research, and yet remains unsolved. So, it seems reasonable to focus some research on the development of new methods that address this problem. In the next chapter of the report, this topic is taken up in more detail, however, it is worth considering at this point as a trend in catalyst preparation science that is likely to advance a partial solution to this problem.

As catalyst preparative methods become increasingly more sophisticated, in other words as catalyst preparation becomes catalyst synthesis, industrial catalyst structures will become more

uniform, less difficult to rigorously analyze, and hence more well-defined. Next, with this drive toward more uniformity in catalysts and the advantages it confers, will come the deeper involvement of synthesis specialists trained in inorganic and organometallic chemistries in heterogeneous catalysis. Their involvement will come as a response to the challenges in new "supramolecular syntheses" of materials mandated by specific needs in heterogeneous catalysis technology. In particular, increased interest in materials that can provide both catalysis and separation, shape selectivity, and even molecular recognition will drive research in supramolecular syntheses. By necessity in pursuit of these goals one will carry out characterization as a natural part of synthesis. With time, as this group comes to dominate heterogeneous catalysis as it already dominates homogeneous catalysis, the artificiality of divorcing analysis and characterization from preparation and synthesis will tend to disappear. Innovations in developing structural information on the active site during catalysis will be driven by the same group. The continuing development of new and increasingly powerful spectroscopic methods, such as nuclear magnetic resonance, for the analysis of solids that parallel those available for the analysis of solutions, will make it easier to develop molecular level insights into catalyst systems in their working state. It is anticipated that in the next ten years advances in mechanistic understanding of heterogeneous catalysts rivaling those in homogeneous catalysis can and will be made.

2.3 HETEROGENEOUS CATALYST: DESIGN AND SYNTHESIS

2.3.1 Computation and Catalyst Design

Computation will be required in order to shorten the time and to lower the expense traditionally required to move from process conceptualization to implementation (Cusumano, 1992). To carry out process design that simultaneously starts at both the level of the catalyst and the macroscopic level of the reactor will require unprecedented levels of coordination between experimental research and engineering development, that can only be achieved through implementation of emerging computational methods (van Santen, 1987; 1989; 1990). At the current level of computational sophistication in process simulation and chemical kinetics, it is possible to explore the impact of a prospective new catalyst on an optimal process flow sheet given experimental data on rates and selectivities. In this way, preliminary results from experimental research can be extended, computationally, to answer questions of technical feasibility. With this, the best and worst case evaluations of economic and environmental efficiency for new, would-be processes can be done early. In the future, with more powerful computational methods, it may be possible to specify the requirements of the catalyst in terms of the process constraints and then to connect these directly to an optimal set of catalyst structural attributes (Boudart, 1987; 1992). These attributes will form the specific targets of catalyst synthesis. In this way experimentation will not be replaced, but rather it will be assisted and enhanced by computation with a reduction in the time and expense required for development, and in so doing risk will be reduced and profitability enhanced. In the meantime, catalysis research and development must seek to deepen and integrate the functional relationships between conceptualization, theory, synthesis, characterization, and experimental testing of new materials.

2.3.2 Molecular Design and Synthesis of Heterogeneous Catalysts

If computing capability at the molecular level continues to accelerate during the next ten years at the pace at which it has over the last ten years, then it is possible to envision teams of industrial chemists and chemical engineers working together in parallel, rather than in series, to do new process design and development from the level of the catalyst up to the level of the units. Currently, this scenario is still not possible, largely because of the severe limitations on computing the kinetics of catalytic reactions based solely on the structures of solids and the molecules that they are interacting with in the reaction/product matrix. Yet, it is not implausible to expect that the kind of technical progress that must be made in order to do this in catalysis science and technology will be made. For this to become a realization, catalysts must be structurally uniform, highly characterizable and hence "well-defined," so that clear connections can be established between the local structure of the active site and its reactivity.

For enzymatic and homogeneous catalysts, uniformity of active sites is nearly axiomatic. Manifestations of this in the case of homogeneous catalysts are evident (Collman *et al.*, 1987; Parshall and Ittell, 1992). Changes in the identity of the metal center in an octahedral or square planar ligand array produce gross changes in catalytic chemistry required to span the plethora of different process needs, and for any given process chemistry subtle changes in activity and selectivity can be brought about through adjustments in the structure of the ligands. Phosphine ligands in particular can be used to control the steric as well as electronic factors at a low valent metal center. Alkyl groups attached to a phosphorous nucleus distribute in space in a way that diminishes nonbonded repulsive interactions. As the alkyl groups grow in size, they spread further apart, increasing their "cone angle" and thereby shielding the metal center to which the phosphine ligand is attached, like an open umbrella, from attack. At the same time, inductive effects of the alkyl or alkoxy groups on phosphorus can amplify its basicity and in turn increase electron density at the transition metal center. Nature has gone even further in that the macromolecular environment around the active site confers a high degree of substrate specificity and even molecular recognition. Currently, chemists can do a good job of building mimetics for the active sites in some enzymes, for example of the Blue Copper Proteins (Karlin and Zubieta, 1986), but the full effect of the active site combined with its macromolecular environment is difficult to fully analyze, let alone imitate. Yet, it is just this coupling between the uniform active sites and their highly specific molecular environments that we seek to emulate with heterogeneous catalysts, the synthetic analogues to enzymes. Shilov (1992) has championed this approach and refers to it as "catalysis with organized molecular systems". These organized molecular systems are multicomponent systems designed along the lines of enzymes.

To achieve the goal of producing catalysts with high active site uniformity and well-defined structures, catalyst preparation must be raised to the level of synthesis. The problem is one that is more germane to a synthetic specialist, such as an organometallic or inorganic chemist, than it probably is to any other chemical professional. Synthetic chemists routinely design and assemble molecules with uniform and "well-defined" structures. This already is done for zeolitic catalysts. Despite this it is not appropriate to expect classical synthetic chemists to produce the next revolution in heterogeneous catalysis design and synthesis. Instead, this must be done by catalysis chemists and engineers, the applied scientists who know the field, what the major

questions are, and what are significant new problems worthy of pursuit. It is expected that professionally trained inorganic and organometallic chemists, in addition to chemical reaction engineers and materials scientists, will cross over from their traditional fields of expertise into the arena of heterogeneous catalysis to pursue interdisciplinary research themes. Hence the real challenge for the next twenty years is to bring the most powerful methods and approaches of supramolecular synthesis and characterization into heterogeneous catalysis, and this must be done by those chemists and engineers who identify themselves with catalysis and seek to define it as a true discipline.

Since heterogeneous catalysis is a discipline that necessarily resides at and defines the intersection of chemistry, chemical reaction engineering, and materials science, the interdisciplinary nature of the field will become even more evident in the future. Catalysis is concerted molecular phenomena that goes beyond bond-making and bond-breaking processes and into the transport of heat and mass between the gas liquid and solid phases. The solid catalysts are not simply two-dimensional solid surfaces, as some would represent them, but are richly structured, highly textured, complex phases that lie between two and three dimensions. Because of this the catalyst scientist cannot work effectively within the normal confines of local molecular structure that form the core of interest for the traditional chemist; nor can the catalyst scientist be a traditional reaction engineer, since a full appreciation of catalytic reaction networks and elementary steps must include the structure of the catalyst and some conceptualization of its active site or sites. Neither can the materials scientist examine only the static structure of the solid, since a catalyst is not a catalyst until it is dynamically interacting with a reactant and product matrix. So catalysis pushes at the envelopes associated with each of these fields as disciplines in their own right and forces the practitioner to expand his or her field of interest and expertise.

As such, catalysis scientists are applied scientists working very close to technology, but they must seek to integrate even more fully the enabling aspects of the pure sciences of inorganic and organometallic chemistry with chemical reaction engineering, surface, and materials science. With the future goal of *ab initio* design of catalysts from the microscopic level of the site up to the macroscopic level of reactors as a driving force, a new discipline and science can emerge. If *ab initio* design of uniform active sites in supramolecular architectures is the *raison d'être* of catalysis research, then the integration of the pure and applied sciences must proceed expeditiously, but in an earnest, scholarly as well as applied fashion.

2.3.3 Application of Solid State Electronics Technology for Catalysis Design and Fabrication

Nanoscale devices and machines are an emerging frontier of engineering science (Drexler, 1992). Catalysts are truly nanoscale devices that deserve to be mentioned in the same "high-technology" context as electronic devices. In contrast to solid state electronics, the role they play in technology is more hidden and removed from everyday experience and so they are less apt to be considered in the context of recognizable high technologies. Despite this difference, there are parallels and similarities between heterogeneous catalysts and solid state electronic devices that are worth considering.

Transistors, the microscopic components of integrated circuits, epitomize solid state technology. The degree to which microstructure and composition can be controlled, especially with silicon VLSI microfabrication methodologies, is impressive (Ghandi, 1983). Features that are on the order of 0.1 microns are routinely fabricated, and emerging methods allow for the feature size to be reduced to a few tens of nanometers or less. Silicon substrates are prepared with bulk purities meeting or exceeding 99.999%, and doping can be done at the level of a few parts per million with high reproducibility. Furthermore, during the last decade silicon microfabrication methods have transformed the micromachining of other three-dimensional structures including sensors, accelerometers, and capacitors. Even a gas chromatograph column has been fabricated on a chip of silicon! (Angell *et al.*, 1983).

Catalytic phenomena and catalysts are even more challenging to treat than electronic phenomena and solid state electronic devices. In contrast to electronic devices that rely upon the phenomenon of solid state electron transport, catalysts rely upon phenomena that consist of several simultaneous molecular-level processes. Until recently electronic devices with micron to tenth-micron feature sizes could be treated and designed on the basis of sound theoretical models for the electronic structures of solids. In contrast, the treatment of catalysts demands that more specific molecular level considerations be taken into account, on length scales that are below the limits of continuum level models. As a result, there is no one overarching theory to guide catalytic materials design.

In the broadest general terms, catalytic phenomena consist of processes of energy and mass transport, and bond making and breaking. At the level of transport phenomena good advances have been made in theory, particularly in the treatment of molecular diffusion through porous solids. If the global rate of a catalytic process is controlled by Fickian or Knudsen diffusive transport to an active site where reaction occurs, then it can be described adequately by a continuum level analysis and *ab initio* design can be accomplished. However, even for some transport-limited problems, accurate, continuum level descriptions break down as the operative physics approach the molecular level. An example is the problem of simulating molecular transport in ultramicropores that have dimensions similar in size to the transporting molecules. With zeolites theoretical advances have been made in simulation of transport, especially for materials with high silicon to aluminum ratios for which good potential functions are available, and at low adsorbate loadings (Cook *et al.*, 1992; van Santen *et al.*, 1992).

It is suggested that there is an analogy between the physics of solid state electronic devices and heterogeneous catalysts. It is further suggested that advanced techniques used for solid state electronic devices, coupled with modern theoretical transport calculations can be a fruitful area to be investigated for design and fabrication of new and improved heterogeneous catalysts.

2.4 RESEARCH THRUSTS FOR CATALYST DESIGN AND SYNTHESIS

In this section are described new thrusts for heterogeneous catalysis research over the next twenty years. These new thrusts are described first in terms of new "effects" or "concepts" that have been identified as important to the advancement of the field, but which are not fully explored scientifically, and the degree to which they can be exploited for new catalyst

technology, as yet, has not been fully defined. This section motivates the next section in which new thrusts in heterogeneous catalysis are given in terms of the traditional disciplines or enabling sciences of inorganic and organometallic chemistry, chemical reaction engineering and computation, and materials and surface science. The two sections are coupled in that the exploration of new catalysis "effects" will demand advances that can only be brought to fruition through new research using the methods and techniques of these disciplines.

2.4.1 New Catalysis Effects and Concepts

"It is proposed that major progress in catalysis occurs in a stepwise manner. Breakthroughs which revolutionize technology occur every five to ten years. After such a breakthrough, there are extended periods during which fundamental research investigating the underlying phenomena leads to better understanding and gradual improvement of the new technology. During such periods, it may appear that a field or even the whole of catalytic technology is relatively mature. This is, however, a misconception because history teaches us that fields which appear mature are suddenly revitalized by a major discovery." (Heinemann, 1988).

Over the last two decades tremendous strides have been taken in catalysis as science and catalysis as technology. In the past, especially in the first half of this century, catalysis science naturally and necessarily followed technology. Discovery guided by intuition ran well ahead of logical analysis and synthesis. This can be documented for many cases, including ammonia synthesis, reforming, hydrotreating, cracking, and Fischer-Tropsch syntheses. With these technologies in the lead, catalytic science was advanced in specific areas such as promoted bulk metals, catalysis by supported metals and alloys, non-metal catalysts, solid acids, zeolites, and other molecular sieves. From these research thrusts came deeper understanding, which in turn led to new concepts and the identification of effects in catalysis, such as electronic versus textural promotion, metal-support interactions, surface organometallic chemistry, structure sensitivity and insensitivity, and kinetic coupling, to name a few. Over time, these concepts and effects have been raised to the highest levels of scientific rigor and now constitute the foundation of catalysis as science. At this point in time the science of catalysis, it can be argued, does not lag behind the technology. With the science, embodied in synthesis and analysis, in the lead, new catalyst technologies can be developed more rapidly than through the slower processes of empiricism. This is not to suggest that unexpected, fundamentally new catalytic phenomena will not be discovered or invented; they will be, but even for these cases the process of discovery and the implementation of such discoveries should be accelerated by the science.

Over the past ten years a few new concepts and effects have emerged from catalysis technology and science, that define the frontier for the next ten years. An exploration of these concepts and effects is motivated by the promise that they offer for major advancement of the field, both as science and as technology. In particular these new concepts include the following:

- ▶ Combined catalysis and separation
- ▶ Shape selectivity and molecular recognition

- ▶ Site isolation
- ▶ Multifunctionality
- ▶ New solid acids and bases
- ▶ Numeric and heuristic computing for design.

2.4.1.1 Catalysis and Separation

Combining *catalysis and separation* into one unit operation (Figure 2) has many appealing, potential advantages for selected problems in catalytic technology. At the macroscopic level one example of this integration of two unit operations into one is catalytic distillation in which the plates of a distillation tower are loaded with catalyst, reactants are fed to the column, products are formed at the catalyst, and the components of the reactant and product matrix are distilled away from each other to be taken off the column in pure form at different points along its height. The potential advantage of this particular approach is that capital costs may be lower, but more importantly, closed system equilibrium-limited conversions may be overcome with substantial savings in energy.

Simultaneous Processing

- Combine two unit operations into one
- Overcome thermodynamic constraints
- Energy integration

Figure 2. Classical Sequential Processing Versus Simultaneous Processing with Integrated Reaction and Separation.

As interesting as the integration of distillation and reactor technology is, the integration of membranes and catalytic reactors is even more interesting (Armor, 1989; 1992) (Figure 3). As in the case of the reactive distillation, the same incentives exist for integrated reactor and membrane technology: potentially lower capital costs and release of the closed system, equilibrium constraints. However, with the integrated membrane-reactor approach an additional, very important incentive is the potential to substantially lower the total energy requirements for the conversion of reactant to pure, unmixed products. In conventional catalytic process technology, which includes an upstream reactor and downstream distillation train, major costs are tied up in the capital and energy expenditures that are necessarily associated with distillative separation. In principle, the energy costs for a well-defined and efficient membrane reactor unit should be substantially lower than those for conventional technology.

Having recognized the potential advantages of membrane reactor technology, it must also be recognized that it will probably have application in selected niches of process chemistry that can most benefit from the advantages it offers (Cicero and Jarr, 1990; Shu *et al.*, 1991; David *et al.*, 1992). Lower energy costs and the release of equilibrium constraints, offered by membrane-

Figure 3. Approaches to Catalysis and Separation by Three Distinct Methods.

reactor technology, are particularly important considerations for developing new approaches to endothermic reactions. Currently, the commercial use of saturated hydrocarbons, especially components of natural gas, as feedstocks for fuels, fuel additives, and chemicals is limited by the thermodynamics of dehydrogenation. A good example is ethane to ethylene (Tsotsis *et al.*, 1992), another is isobutane to isobutene. The latter is particularly interesting since isobutene is used to produce MTBE and the demand for it outstrips current capacity. Despite the fact that there are industrially practiced technologies for producing isobutene from isobutane, such as the Catofin^R process, the increase in demand and the need for ever improving processes with higher efficiencies drives new research. New approaches to this and other hydrocarbon dehydrogenation motivate the fuller exploration of catalytic membrane-reactor technology in all its possible forms.

Enough early research into catalytic membrane-reactor technology has been done to be able to lay out the most important areas of topical research. First, at the level of the materials used as high temperature membranes, the options are metal alloys with exclusive permselectivity for hydrogen, ceramic membranes with Knudsen-like diffusional mechanisms, hybrid structures of the two, and new molecular sieving membranes based on zeolites, ultramicroporous carbons and other monolithic forms of molecular sieves (Burggsaaff *et al.*, 1991). New research needs to be done on the materials issues associated with each of these, especially with respect to synthesis of new structures and the mechanisms for deactivation and failure for both new and existing membrane systems (Wang *et al.*, 1992; Foley *et al.*, 1993). At another level the analyses of the dynamics of membrane reactors are not generally well described or understood, particularly for the systems that operate on the basis of the Knudsen mechanism, despite exceptions for a few specific cases that are more well-described. These two problems — materials and dynamical modeling—frustrate design and implementation. Finally, for the case of low to moderate temperature dehydrogenation, driven to high conversion by hydrogen transport through the membrane, catalysts must be able to withstand coking and other forms of deactivation which are expected to be somewhat accelerated at lower hydrogen fugacities in the reaction zone.

2.4.1.2 Shape Selectivity and Molecular Recognition

Zeolites have revolutionized catalysis and have provided a degree of control over reaction dynamics that was previously unattainable (Csicsery, 1976). Initially used as solid acid catalysts for hydrocarbon cracking, presently zeolites have demonstrated utility in a wide array of reaction chemistries including acid-catalyzed fine chemicals synthesis, Fischer-Tropsch synthesis, oxidations, and even base-catalyzed reactions. Not only are zeolites useful catalysts for a wide array of reaction chemistries, they also lead to markedly different selectivities when compared to non-zeolitic catalysts. As patterns of selectivity emerged and were analyzed, an effect termed *shape selectivity* was recognized to be caused by mediation of transport and reaction by the zeolite framework. Upon further analysis shape selectivity was conceptualized to arise through one of three mechanisms in the zeolite pore structure — reactant transport, product transport, or transition state constriction. In essence, reactant and product shape selectivity, which constitute the bulk of examples of shape selectivity, are the ultimate forms of separation and catalysis. The zeolite catalyst is a nanoreactor device that combines the two unit operations into one on a microscopic level.

An example of this coupling of reaction and separation at the microscopic level is given by the synthesis of para-xylene from methanol and toluene over a pore-mouth narrowed ZSM-5 catalyst (Haag and Chen, 1987) (Figure 4). Methanol and toluene transport into the core of the zeolite through the layer of narrowed pores and react to give an equilibrium distribution of products. At equilibrium the selectivity to para-xylene under standard process conditions is approximately 20%. For the treated zeolite catalyst the selectivity can rise to over 80%. The reason is that the equilibrium at the core of the catalyst is continuously and selectively bled in favor of the para-xylene. Para-xylene has a substantially higher diffusivity than that of either ortho- or meta-xylene, presumably because of its more streamlined shape. Taken from another point of view, this example of zeolite product shape selectivity and preferential transport is one of the few cases in which a heterogeneous solid catalyst can begin to approach the level of selectivity and "molecular recognition" embodied in cellular enzymatic catalysis. Other microporous molecular

Figure 4. Product Shape Selectivity in the Synthesis of Para-Xylene from Methanol and Toluene Over a Modified H-ZSMS Catalyst.

sieves with medium pore sizes, such as SAPO-11, also display this behavior. In fact, the AlPO₄ family of molecular sieves and their isomorphically substituted analogues are under intense scrutiny for application in both petroleum-related and chemicals-related catalysis (John *et al.*, 1992). Hence the phenomenon may be far more generally exploitable than was once recognized.

The ultimate in "molecular recognition" will come about when chiral catalysis can be done with a zeolite or molecular sieve. David (1993) suggests that it should be achievable through a detailed consideration of molecular topography.

What is now accepted as shape selectivity has broadened the original view of zeolites as unusual solid acids to one of "nanoscale reactors" that control transport to and away from the active sites where bond-making and breaking occur. In the limit of zeolite framework effects, it can be shown that the pore structure actually constrains the transition state of certain reactions, thus altering selectivity. The restricted transition state phenomenon can prevent transalkylation during bimolecular alkylation of aromatics. It was not a long jump to realize that zeolites also could be used to confine and limit the growth of metal particles within their pores. This has been demonstrated in a number of cases and appears to have relevance not only for catalysis, but also for the synthesis of electronic devices based on quantum-dot principles. At the same time it has been realized that the basis for shape selectivity in zeolites is their molecular-sized pores and this is a feature that is not exclusive to zeolites but rather is a general property of any solid material with connected free-volume and molecular-sized pores.

With this realization has come an explosion of new materials with unexpected molecular sieving properties. Examples include silico-aluminophosphates, carbogenic molecular sieves, transition metal-silicates, some transition metal oxides and new silica-aluminates with tunnel structures that can be synthesized with virtually a singular pore size but over a wide range of single values (Kresge *et al.*, 1993).

In many ways these materials offer the ultimate in separation and catalysis since they can be depended upon to integrate the two at the molecular level. The frontiers for synthesis in this area of catalytic materials seem limitless and advances can be expected to accelerate. Modeling, particularly of reaction and molecular transport, in these structures has only just begun to be seriously attacked. Two primary problem areas need much deeper consideration: computation methods and potential functions. Even with the tremendous advances that have been made in computing power and efficiency, these computations are massive and even in simplified form they rapidly outstrip reasonable CPU times with the best available hardware and software. Today practical *ab initio* calculations are limited to about ten moderately heavy atoms. Excellent opportunities exist for attacking the problem with more effective computing strategies, for example parallel processing, or with more effective theoretical approaches to simplify the computation while maintaining the essential features of the problem — density functional analysis is one such approach. At another level even if the computing problem could be resolved instantly, the simulations of transport in molecular sieving media would still be frustrated, except for only the simplest cases, by the lack of adequate potential functions to account for realistically complex interactions that account for the coupled electrostatic as well as van der Waal forces exerted by zeolite structures on adsorbates.

Eventually, research in shape selective materials will lead to shape selective membranes providing the ultimate in membrane reactor technology, and hence catalysis and separation. MCM-40 from Mobil (Kresge *et al.*, 1993) is a good example of the kind of new, highly structured microporous material that can be expected to emerge in catalysis over the next decade.

2.4.1.3 Site Isolation

With the synthesis of uniform active sites also goes the notion of *site isolation*. If parallel pathways leading to different products are catalyzed by different sites for the same reactants on a nonuniform catalyst, then in principle a particular pathway could be favored and selectivity increased by the extent to which one site can be synthesized over another. Hence, the motivation to explore the synthesis of uniform active sites. If active sites are in close proximity, then there is also the possibility that intermediates can diffuse between these sites opening up the potential for sequential and possibly deleterious reactions to occur. Isolation of these sites to prevent diffusive or reactive communication between them can provide increased selectivity, especially in favor of the early products in a series of reactions. This provides the driving force for exploring the synthesis of kinetically isolated uniform sites.

An example of site isolation and its effect on selectivity is provided by the case of allylic oxidation over uranium and antimony oxides (Grasselli and Burrington, 1981) (Figure 5). As in any selective oxidation, the objective is to develop a catalyst that will produce the highest yield possible of desired product, in this case acrolein. Over UO_3 and USbO_5 , propene is converted at equivalent conditions primarily to carbon dioxide and water, the undesired deep oxidation products. However, over $\text{USb}_3\text{O}_{10}$ propene is converted to acrolein with high selectivity. The different and substantially better behavior of $\text{USb}_3\text{O}_{10}$ is attributed to site isolation (Grasselli and Suresh, 1972; Oyama, *et al.*, 1993) (Figure 6). Inspection of the crystal structures of UO_3 and USbO_5 shows that in the former, uranium oxide sites are surrounded by other uranium oxide sites, whereas in the latter, the lattice planes are comprised of rows of uranium oxide sites separated by rows of antimony oxide sites, so that in one dimension uranium sites are adjacent to antimony sites but in the other dimension they are still adjacent to each other. But with the $\text{USb}_3\text{O}_{10}$ structure, uranium sites are islands surrounded by a band of antimony oxide sites, so that uranium oxide centers are only adjacent to antimony oxide centers and are never found adjacent to other uranium sites. This island-like structure led to the concept of site isolation and it is to this structural feature that the selectivity is ascribed.

This concept of site isolation may be useful in the design of new oxidation and oxidative dehydrogenation catalysts for other more demanding reactions. After all, the most selective oxidation catalysts are natural enzymes and these systems are completely site isolated. In fact, good progress has been made by mimicking the site isolation of enzymatic active sites with fluorinated metalloporphyrins (Eflis and Lyons, 1992). Site isolation in solids comparable to that achieved in the metalloporphyrins may be obtained through the use and occupancy of particular ion exchange sites in metal-containing zeolites. Zeolites are particularly attractive, especially since site isolation alone is not enough — one must also have optimal site densities per unit area of catalyst surface.

In acid catalysis by zeolites the effect of site isolation is well known. The catalytic activities of HZSM-5 and dealuminated Y-type zeolites are linearly related to their framework aluminum contents. This proportionality indicates that every active site is nearly equally active. The active sites in high Si-Al zeolites are not only homogeneous but are “in a state of an ideally

Figure 5. Structures of UO_3 , USbO_5 , and $\text{USb}_3\text{O}_{10}$ and (bottom row) Cation Positions in $\text{USb}_2\text{O}_{10}$. (Adapted from Grasselli and Suresh, 1972).

Figure 6. Unit Cell Structure of $\text{USb}_3\text{O}_{10}$ Showing Cation and Anion Positions.
 (Reprinted from Grasselli and Suresh, 1972, by permission of Academic Press).

dilute solution" (Haag and Chen, 1987; Rabo and Gajda, 1990). This is a classical example of site isolation in a solid catalyst.

Another feature of site isolation that is perhaps as crucial as the effect of physical separation from other sites is the ability to truly modify the electronic properties of the isolated metal. Isolated metals by their nature differ electronically from metal particles since they do not have a band structure. Instead, their atomic orbitals are mixed with those of their non-metallic, nearest neighbors into metal-ligand molecular orbitals. As a result, the electronic properties of the nearest neighbor atoms and their geometric disposition can have a marked and real effect on the reactivity of the site isolated metal. Metals confined to the ligation spheres of molecular catalysts are the epitome of site isolation. It is well known that in these systems the metal's reactivity, and hence the catalyst's activity and selectivity, is highly dependent upon the choice of ligands. This has been done already in metal-containing zeolites. Recently, small isolated clusters of palladium have been reported to form in NaY and 5A zeolites (Beutel *et al.*, 1993).

Site isolation in solids is the best approach to reproducing the specificity and control offered by homogeneous molecular catalysts. The design of catalysts for specific reactions will require site isolation. It has been reported that for the reduction of carbon monoxide by hydrogen, supported bimetallic catalysts comprised of rhodium and an early transition metal oxide from Groups IV to VI or lanthanum oxide have higher selectivity toward methanol and other alcohols than do catalysts comprised of just rhodium, which tend to produce methane (Figure 7).

Several groups have considered this to be due to a textural promotion of rhodium by the early metal oxide rendering it ultra- or atomically dispersed. This is the ultimate in textural promotion, and when considered at the molecular level of the active site, may prove to be another example of site isolation, but in this case for a reduction step rather than for an oxidation step.

2.4.1.4 Multifunctionality

For complex reaction mixtures such as those encountered in petroleum refining multisite catalysts are useful and even preferred. In these systems, because of steric demands or other constraints associated with the complexity of the reactant matrix, different sites may be required to carry out generically the same chemical steps, for example, hydrogenation or desulfurization. In some instances even for simple, not complex reactant feeds, the reaction pathway from reactant to final product demands that several generically different reactions be coupled together. In these instances there is a need for multifunctional catalysts in which the different sites carry out generically different reaction steps. In fact, for some catalysts each functional type of site may actually be distributed, so these systems are both multifunctional, multisite catalysts. The classic example of an industrial catalyst that is multifunctional is the petroleum reforming catalyst. In this system two separate functions, one for dehydrogenation of hydrocarbons by supported metals and the other for skeletal isomerization of unsaturated hydrocarbons, are combined to work together (Mills *et al.*, 1953). By working in concert, the rates of skeletal isomerization are markedly increased since the latter steps require a carbenium ion intermediate to proceed, and

Figure 7. Site-Isolated Versus Sintered Rhodium on an Oxide Support Surface.

this is efficiently produced from an unsaturated hydrocarbon (Figure 8). Transport and reaction between the two kinds of sites was probed explicitly by combining a dehydrogenation catalyst (Pt/SiO_2) with an acid catalyst ($\text{SiO}_2\text{-Al}_2\text{O}_3$) (Weisz and Swegler, 1957). It is irresistible to describe this multifunctional effect as synergy, since either function alone would lead to quite different ends at quite different rates. More recently, metal-containing zeolites also have been shown to be able to do this kind of coupled chemistry.

It seems logical that if the synthesis and control of separate uniform sites for generically different chemistries can be accomplished, then it also eventually should be possible to synthesize and assemble these sites on the same material to produce well-defined multifunctional catalysts that are true nanoscale devices.

2.4.1.5 New Solid Acids and Bases

Zeolite solid acids are ubiquitous as catalysts for a wide range of processes that lead either to carbon-carbon bond breaking or making steps. It is likely that further advances in this arena will come through more complete control of pore sizes especially at the large end of the range ($> 7.4\text{\AA}$).

Figure 8. Transport and Reaction of n-Alkanes Between Metal and Acid Functionalities and Example of Bifunctional Catalysts.
(Adapted from Gates et al., 1979).

At the same time, many other molecular sieving materials are now available and will lead to new catalysts for acid catalyzed reaction. These systems will include the aluminophosphates with the full range of isomorphically substituted analogues, synthetic clays, and layer structures and heretofore unanticipated materials such as MCM-41.

Interestingly, much less has been accomplished in the area of solid-base catalysis (Pines, 1981; Tundo, 1992). Some reactions such as isomerizations and hydride exchanges have been reported to occur. Most catalysts in this category have been prepared by supporting basic oxides or carbonates, liquid metals, or organic bases in suitable solids. More recently side chain alkylation of toluene to ethylbenzene has been investigated over alkali-metal exchanged and phosphorous-doped zeolites (John *et al.*, 1992).

Oxidative coupling of methane especially to produce ethane and ethylene can be carried out with lithium metal supported on MgO . Intercalated alkali metals in graphite also are catalytically active for various reactions but they suffer from short lifetimes, thermal instabilities, and oxygen sensitivity (Bartlett and McQuillan, 1982). New forms of carbon, particularly carbogenic molecular sieves with ultramicroporosity, like that of zeolites and other molecular sieves but with little or no inherent acidity, should be ideally suited for the dispersion and stabilization of alkali metals for base catalysis. Fullerene carbons offer the opportunity to prepare crystalline carbon structures with free volume and molecular sieving properties.

2.4.1.6 Numeric and Heuristic Computing for Design

Numerical models of catalytic phenomena that are well-described by continuum level analyses are proving to be exceptionally useful for the optimal design of catalyst structures. These models have been employed, for example, to optimize the pore structure of particular catalysts, used in SCR, HDM, and other applications (Beeckman and Hegedus, 1991; Hegedus and Pereira, 1990; Pereira *et al.*, 1988a; 1988b) in order to squeeze out the highest efficiency possible. The processes captured by these numeric models are inherently deterministic and so can be handled explicitly. Thus the advantage of this approach is that it allows the catalyst design engineer to utilize the full power of modern computational methods to describe the problem with all its inherent complexity at a level previously unrealizable.

In contrast, even the simplest cases of molecular sieving or reaction phenomena defy complete analysis and simulation since they occur on length and time scales well below the continuum limit, as explained earlier in this chapter. Although good efforts are under way to bring higher level theory to these problems, they are still in the research stages and provide little help to the practitioner of catalysis faced with an actual design problem. Despite the lack of rigorous numeric models for reactions at active sites, catalysis experts have and do continue to design novel catalysts with new components and functions. This is done largely through the use of heuristics — design rules that are assembled through analogy and experience (Foley *et al.*, 1992). The type and level of heuristics that any one expert or group of experts may employ depend upon their training, exposure to other disciplines, and experience base in heterogeneous catalysis. True experts are considered to be insightful because they are able to establish a path forward that can be implemented with high likelihood of success. The insights attributable to specialists derive largely from their ability to recast the problem at hand and to attack it heuristically, at least at the initial stages of the research. Their success is largely dependent upon the quality and sophistication of their heuristics which are both personal and cumulative over time (Figure 9).

The value then of an expert in the industrial setting is his or her ability to derive a solution to a problem creatively so that a novel result is produced expediently, so that the time and cost required to derive the result can be minimized. Two problems immediately come to mind. Despite similarities in training, some individuals are more effective than others. Yet in many cases this higher effectiveness or insight cannot be readily transferred to others with less experience. This raises the second problem. When the highly effective individual expert discontinues practice, the heuristics that led to higher effectiveness and deeper insights may be lost. A mechanism needs to be established to codify as much as possible, if it is possible, heuristics employed by experts so that they are transferable and not lost.

Another trend that needs to be dealt with is the crush of information that can be routinely produced in research programs. One need only follow the literature of heterogeneous catalysis to realize that with automation and better instrumentation, catalysis researchers are able to produce unprecedented amounts of new information. Information is not knowledge and information alone is difficult to apply; it must be reviewed and distilled for its key elements. At the same time, information storage and retrieval must be handled in new ways in order to

Figure 9. Sources of Catalysis Heuristics for Design.

(Adapted from Foley et al., 1993).

facilitate its usefulness and to ensure that it is not inadvertently lost, especially at the current costs of research.

With these trends in mind, it is reasonable to begin to carry out research aimed at the use of nonnumeric or heuristic computing in catalysis research and development. Knowledge bases and expert systems may provide new approaches to codifying the rules that experts use implicitly when considering problems in heterogeneous catalysis design and synthesis (Hu *et al.*, 1991). This seems even more imperative as the field becomes more interdisciplinary, since specialists with different backgrounds working in catalysis must know more than that provided by the limits of their traditional training. Hybrid systems that use heuristics to describe those phenomena that cannot be modeled explicitly and rigorous numeric models for those phenomena that are deterministic may be particularly useful and important (Dumesic *et al.*, 1987; Banares-Alcantara *et al.*, 1987; 1988; Kito *et al.*, 1984). In other disciplines heuristics and deterministic models are combined quite satisfactorily to describe real problems that are too complex to handle *ab initio*.

Transfer of expertise, assimilation of information, and higher productivity are all potential outcomes of this new approach to computing in catalyst research and design.

2.4.2 Enabling Sciences in Catalyst Design and Synthesis

Catalyst design and synthesis is necessarily interdisciplinary and it defines the intersection of three otherwise distinct and separate disciplines: chemistry, chemical reaction engineering, materials and surface science. The exploration and development of the new concepts and effects in catalysis described in the previous section will require the further implementation and application of methods and techniques developed by these enabling sciences.

2.4.2.1 Inorganic and Organometallic Chemistries

The development of new catalytic systems that can carry out separation and catalysis, or that provide uniform isolated sites will require that advances be made in materials synthesis. This can be accomplished partially by incorporating the latest advances in organometallic and inorganic synthesis, but these methods must be pushed beyond the current horizons and limits of the traditional discipline. Catalysis synthesis involves developing architectures on length scales uncommon in molecular syntheses. Therefore, new techniques based on conventional methods will need to be developed in order to synthesize supramolecular architectures. Hence, the challenge of catalyst synthesis can be a driver for the new field of supramolecular synthesis.

To the extent that supramolecular synthesis is aimed at the design of catalysts rather than sensors or nanoscale electronic devices it should be embraced as a legitimate part of catalysis research in the future. However, much can be learned from advances that will be made in supramolecular syntheses devoted to these other fields of application. Cross fertilization between research aimed at new materials that provide molecular recognition, molecular level logic, and catalysis is to be expected and encouraged.

2.4.2.2 Chemical Kinetics and Reaction Engineering

Pharmaceutical design and synthesis is facilitated by the use of computation chemistry methods from *ab initio* quantum methods to highly parametrized molecular mechanics. As catalyst materials preparation becomes synthesized with the drive for supramolecular architecture, site isolation and multifunctionality, computational methods will be more relevant, applicable, and necessary for design. Hence it will be crucial to incorporate more computational chemistry in chemical reaction engineering. To do this will require a sustained and earnest effort on the part of those chemical reaction engineers in catalysis to become molecular reaction engineers.

Eventually, it is possible that molecular level models for individual reaction steps can be incorporated into models for reaction networks which in turn are utilized in the full description of a reactor in a particular process. Nesting of models from the molecular level up to the macroscopic level of the units will advance no faster than the hands employed to advance computing power, both in terms of hardware and algorithmic methods. However, research should be done on this frontier so that computing in catalysis can be as up-to-date as is technically feasible.

2.4.2.3 Materials and Surface Science

Surface science has and will continue to advance the level of understanding of molecular interactions at well defined interfaces through experimental and theoretical analysis of structure. A frontier that is just beginning to open up is the use of materials science methods as employed in other technologies, such as electronic materials, in the synthesis of well-defined catalyst materials. High to low vacuum methods from molecular beam epitaxy to low pressure organometallic vapor deposition offer exciting new ways to prepare more complex model systems that are well suited to high vacuum and other emerging methods of analysis. These new synthesis techniques combined with new techniques for analysis like atomic force and scanning electron microscopy offer unparalleled opportunities for surface and materials scientists to begin to do rigorous syntheses that can lead to a deeper knowledge of the subtleties of structure and function in catalysis.

2.7 SUMMARY AND RECOMMENDATIONS

The drive to new energy efficient and low cost, zero waste solutions to chemical process technologies is fueling the drive for new research in catalysis science and technology. The science of catalysis has overtaken the technology of catalysis, and future advances in technology are as likely to result from first principles application as they are from pure empiricism and discovery.

This trend brings with it the need for catalysis preparation to become a science in its own right, thus it is appropriate to consider catalysis materials preparation as a problem in supramolecular synthesis. In this way, catalysts can be viewed as nanoscale reactors with specifiable structures and functions.

As catalysis synthesis becomes more controlled and scientific, hence predictable and reproducible, it is natural to consider the problem to be one of materials design at the nanoscale. Along with this view comes the need for modeling in order to guide design, to streamline experimentation, and to accelerate innovation. Computation at all levels will be required to bring *ab initio* design to its full fruition in catalysis.

Surface and materials science have provided valuable new tools for the analysis of catalytic steps and for the characterization of interfacial systems. With the advances that have been made in the fabrication of nanoscale devices with materials synthesis techniques, the field is poised to make major strides in bringing these new approaches into catalysis. In this way, surface and materials methodologies can provide new routes to the synthesis of advanced structures and more complex model systems.

More specifically, it is recommended that research thrusts be aimed over the next ten years at new concepts and effects in catalysis especially:

Combined catalysis and separation

- ▶ Shape selectivity and molecular recognition
- ▶ Site isolation
- ▶ Multifunctionality
- ▶ New solid acids and bases
- ▶ Numeric and heuristic computing for design

These topics are at the forefront of current catalytic science and technology and hold the promise for major advancements over the next ten years.

Beyond these topics, integration of the enabling sciences of inorganic and organometallic chemistries, chemical reaction engineering and computation, and materials and surface science must be integrated more fully into the science of heterogeneous catalysis.

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Chapter 3

CATALYST CHARACTERIZATION: STRUCTURE/FUNCTION

Gary L. Haller and Wolfgang M. H. Sachtler

3.1 INTRODUCTION

The fundamental concepts of electronic structure and bonding that are at the basis of all chemistry are also at the root of understanding the structure and reactivity of catalyst sites. A specific aspect of catalysis by solids is, however, that we are less interested in their bulk structure than in the interfaces between two phases. Novel theoretical and experimental methods have opened the gates to this new two-dimensional world which includes solid/gas, solid/liquid, and solid/solid interfaces. Often one solid phase consists essentially of small clusters, each comprising only a few atoms but interacting simultaneously with another solid, the support, and with molecules of the surrounding fluid. The ability of coordinatively unsaturated atoms at this interface to quickly form chemical bonds which are also swiftly broken again, is an essential criterion for catalysis.

The main classes of catalysts used in energy applications are: zeolites, metals, and transition metal oxides. Crudely speaking, we can say that the chemical functions associated with these catalysts are acidity, oxidation, and reduction, from which it will be surmised that the chemical and physical techniques needed to characterize these classes of materials will be quite different. Thus, one way in which this discussion might be organized would be along the lines of the kind of material being characterized. Instead, we have chosen to use a more conceptual organization, illustrated with examples of materials and techniques, the selection of which may be more indicative of our personal experience than the relative importance in the field of catalysis.

It will be the objective of this chapter to present some examples of catalyst characterization which are on the frontier of what we can do, which reveal apparent contradictions between findings of well characterized surfaces and practical catalysts, or which are illustrative of where progress is needed in instrumentation or concepts of characterization. From these, we will arrive at some recommendations for catalyst characterization which will be important in the future. These will not necessarily be associated with any particular catalyst or reaction, but will seek lines of research to develop new concepts, approaches, or techniques which will have some generality. It would not be useful to attempt to catalogue techniques of surface characterization, but representative examples will be used to focus on the problems of catalyst characterization and attributes that will be required for progress.

It will be presumed that the ultimate goal of all catalyst characterization is to identify and describe Taylor's active centers (Taylor, 1925), *i.e.*, the catalytically active sites. Several rather obvious corollaries follow. Identification would best be accomplished *in situ* under the conditions of temperature and pressure in the range where the catalyst would be used. Moreover, as the performance of any catalyst is mainly of interest during the *steady-state* of the

catalyzed reaction, catalyst characterization should, ideally, be done in the presence of all reactants, products, and intermediates. For instance, we see little value in studying clean transition metals or their oxides as potential catalysts for HDS if it is certain that under HDS conditions these metals or oxides will be quantitatively converted to metal sulfides. Likewise, the surface composition of numerous metal alloys is known to change in the presence of a reacting gas. It should also be kept in mind that surface reconstruction in the presence of a reacting gas is a very common phenomenon for small particles; consequently, the structure and the shape of supported particles will often change when the catalyst is exposed to the reacting gas or fluid. Quite generally, it is important to distinguish between the *catalyst precursor* and the *true catalyst*; the transformation of the former into the latter often occurs during the first stages of the catalyzed reaction.

To assure kinetic significance of the site or adsorbed intermediate associated with the site, the spectroscopy used should be capable of time resolution that allows transients on the time scale of reaction to be followed, and the kinetic response of a reactant and/or product should be followed simultaneously (Tamaru, 1978). Because catalytic reactions may always be assumed to be more sensitive probes for the site than are physical techniques, we also need to think of new chemisorptive and model reaction probes for catalyst characterization to complement spectroscopy.

Perhaps it is useful to begin by discussing what might be the most important aspects of sites to be characterized. Of course, we would like to know as much as we can about both the nature of the sites and their concentration. From the point of view of understanding the chemistry, the nature or structure would appear to be more important. However, most of the time we put a premium on site density since that will allow us to compare catalysts between two laboratories. It is understood that almost always we have to be content with a measurement of surface atom density which does allow a quantitative comparison between laboratories but almost certainly has little to do with the actual site density involved in the reaction. That is, we usually measure the adsorption sites by a chemisorption probe which is assumed to have a 1:1 stoichiometry with the sites, *e.g.*, H_2 dissociation on metals at room temperature. We are aware of the friction involved here since there is ample evidence that the stoichiometry assumed, *e.g.*, $H/M = 1$, is only rarely correct and even when it is, it would not be under the conditions of reaction (Kip *et al.*, 1987). Even qualitatively this chemisorptive titration can be misleading for very small particles. In the range of metal particles consisting of only a very few atoms, H_2 chemisorption has been found to decrease with increasing dispersion, if the latter quantity is derived from Extended X-ray Adsorption Fine Structure (EXAFS) data (Xu *et al.*, 1992).

There are one or two exceptional cases where the adsorption site density used to normalize rates between laboratories may be close to the active site density. The most obvious is the use of N_2 chemisorption on Fe at the reaction temperature to measure the active site density for the NH_3 synthesis reaction (Topsøe *et al.*, 1981). Here it is known that the adsorption of N_2 is the rate limiting step in the reaction, so that if one uses the adsorption isotherm at reaction temperature, one assumes that the observed adsorption site density must be a reasonable approximation to the correct one (although it will still be an overestimate, because under reaction conditions the steady-state coverage will be lower). Another case where the measured site density must be

about right is that observed by ^{27}Al NMR for n-hexane over a ZSM-5 zeolite (Haag *et al.*, 1984), since the n-hexane cracking activity correlates with Al in the framework over several orders of magnitude, and the acid sites are known to be associated with Al. Still, this kind of site density cannot be simply extended to other zeolites, *e.g.*, to Y-zeolite, since it is known that in this case the activity for cracking passes through a maximum when the Al site density is varied (Carvajal *et al.*, 1990). From the point of view of characterization, we might conclude that site density is not inherently very revealing except in so far as the order of magnitude will limit some possibilities, for example, if it is as large as 10^{15} sites/cm² on a metal surface, the site cannot plausibly involve more than a few atoms.

In these examples only one type of site is of relevance in each catalyst. For instance, in the NH_3 synthesis catalyst the active sites are certain ensembles of Fe atoms, whereas, in the cracking catalyst protons of high Brønsted acidity are crucial. In many catalysts the situation is, however, more complex because two or more types of sites are involved in the catalytic reaction. Some catalytic systems can be described as "bifunctional"; in these catalysts different steps of a catalytic reaction make use of different sites, for instance, in petroleum reforming (de-) hydrogenation steps are catalyzed by Pt sites and carbenium ion reactions by acid sites. In some catalysts the sites are essentially independent of one another; reaction intermediates are supposed to "shuttle" between metal sites and acid sites (Mills *et al.*, 1953). This may be an oversimplification for catalysts such as Pt supported in acid zeolites, as there are indications that Brønsted acid protons and metal clusters form metal-proton adducts (Homeyer *et al.*, 1990). In these complexes the metal atoms are electron-deficient (DallaBetta and Boudart, 1973), because the positive charge of the proton will be shared with the adjacent metal atoms.

When a catalyst ingredient modifies another site by some chemical interaction it is called a "catalyst promoter" or, if the catalytic activity is lowered, a "poison". Promotion of the iron in the ammonia synthesis catalyst by alkali ions is a classical example. Although the primary function of inert oxides such as Al_2O_3 or SiO_2 is to increase the dispersion of the active material supported by them, these supports can also have a promoting function, that is, change the turnover frequency or the selectivity of the catalytic process. For structure-sensitive reactions it suffices that the support affects the geometry of the supported particles of the catalytically active material. Chemical bonding between metal particles and ions of the support, often called chemical anchoring (Jiang *et al.*, 1988), will stabilize a high dispersion of the active material; for extremely small particles electronic changes at the metal/gas interface, caused by the Volta potential at the metal/support interface, have also been visualized. Expressions such as a "strong metal-support interaction" have been proposed for these phenomena (Tauster *et al.*, 1978). The chemical interaction can imply a rather drastic rearrangement of atoms; for instance, for Pt (Mériaudeau *et al.*, 1982) or Ni (von Engels *et al.*, 1981) supported on TiO_2 it has been shown that under reduction conditions the metal becomes partially covered with a Ti suboxide, while Ti^{3+} ions are concentrated near the metal particles (Bonnevot and Haller, 1988).

These examples illustrate the importance of chemical interactions between an active site and its environment. Most catalyst modifiers have been found empirically; in some cases the nature of this interaction was later clarified by using physical characterization methods, but reliable predictions are not possible with the present state of this science. An important objective of

catalyst characterization is, therefore, to identify not only the active sites but also their interactions with the environment in and below the catalyst surface. A long-term goal is to use this knowledge in a predictive manner in order to prepare superior catalysts "by design".

3.2 SOME WAYS TO CHARACTERIZE SITES

We are going to focus on physical methods of characterizing sites, but before we move into this, we need to remind ourselves of the catalytic chemical adage about site characterization, *i.e.*, that a catalytic reaction is more sensitive and specific than any physical technique. One cannot dispute this, but it is worth adding that it is not always easy to deduce structural information from chemisorption or the reaction itself. Carefully chosen probe catalytic reactions can rank activity and selectivity of a group of catalysts and, when the probe molecules are appropriately complex and combined with isotopic labeling, can also determine the mechanism and the structure of adsorbed species. (See R. L. Burwell (1990) and references therein for progress on what he has labeled the organometallic zoo described by such experiments). In most cases, probe reactions cannot indicate why a catalyst is good or bad, so complimentary spectroscopic analysis is always needed.

For purposes of illustration, we will only consider very simple molecules in the examples given below. Here we can point to a case study which started with a simple combination of chemisorption (hydrogen) and reaction (ethane hydrogenolysis) and evolved to include several complimentary spectroscopies (infrared, Mössbauer, X-ray absorption, *etc.*) and produced a commercial catalyst, the Exxon Pt-Ir/Al₂O₃ reforming catalyst (Sinfelt, 1983). It is interesting to note that the catalytic test reaction which was used most in this development is an undesirable side reaction, but this does not suggest itself as a general strategy to be used.

3.2.1 Classical Site and Kinetic/Reaction Probes

Perhaps the most widely used chemisorptive site probe is some generalized base to determine the strength/density of acid sites. The use of infrared spectroscopy with appropriate probe molecules to quantify acidity has been recently reviewed by Knözinger (1993) and will not be further discussed here. For this approach to be useful, one must have some chemical model for the site and, of course, the concepts of Brønsted and Lewis acidity are such essential parts of fundamental chemistry that there is no need to describe them. However, a specific structure for any site is still helpful, and perhaps the most widely known and accepted site picture that we have is that of the bridging hydroxyl for Brønsted acid sites in silica-alumina (Hansford, 1947).

Experimental evidence on the chemistry of acidic sites has been only recently emerging. New concepts have been also proposed recently to explain the fundamental cause of the great difference in acid activity between crystalline zeolite and amorphous silica-alumina gel (Rabó and Gajda, 1989-90).

A somewhat more powerful approach (than simple chemisorption) is to use a catalytic reaction to probe the sites. Traditionally, cumene cracking and toluene disproportionation have been used as probes "counting" Brønsted acid sites. Often this means building some particular structure into the reactant molecule which will then reflect some aspect of the site structure by virtue of how reactive the molecule is. Here organic chemistry offers an almost unlimited variety from simple things like primary, secondary, and tertiary hydrogen (or carbon) to the complexity of optical activity. (See Rooney, 1993, for some excellent examples of the use of molecular structure to probe sites). As a recent example of this approach using what might be called a classical reaction, the deuterium exchange pattern of methyl cyclopentane was used to analyze the electronic effects of support on supported Pt (Baird *et al.*, 1992). The H/D exchange of cyclopentane has been used to distinguish mono-atomic Pt sites from multiatomic Pt_n sites. On the former sites the exchange occurs *stepwise*, whereas larger metal ensembles preferentially catalyze the *multiple* mode of isotope exchange (Lei and Sachtler, 1993).

3.2.1.1 Reaction Selectivity as a Probe for Acidity

Several catalytic reactions have been developed which provide a relative, but quantitative measure of solid acidity. Among the latter is the recently reported reaction of 2-methyl-2-pentene, advanced by Kramer and McVicker (1985). The isomerization of 2-methyl-2-pentene combines a double bond shift (which requires relatively low acid strength, *i.e.*, it occurs on essentially all acid sites) and a methyl shift (which requires relatively high acid strength). The fact that double bond isomerization occurs on essentially all acid sites allows this reaction to effectively act as a normalization of the site density when the selectivity of the methyl shift relative to double bond shift is considered. Thus, this reaction may be considered a measure of site strength while other reaction rate probes will be some convolution of site density and site strength. This reaction has several advantages as a probe for acidity. It involves a single reactant, the acidity correlates with selectivity (between the methyl and double bond isomerization) rather than rate, it spans a wide range of solid acidity, and it correlates with the commercially important measure of cracking activity, the MAT number (Kramer and McVicker, 1986).

3.2.1.2 n-Hexane Cracking as a Probe Reaction

Even a relatively simple reaction can be diagnostic in the right hands. Haag *et al.* have developed the cracking of n-hexane on HZSM-5 such that it can now be used as a probe reaction to characterize other acid catalysts (Haag *et al.*, 1991). The general mechanism for acid catalyzed reactions envisions the addition of a proton to the molecule, the rearrangement of the protonated species, and the removal of the proton. For example, we can write for the isomerization of cyclopropane ($c-C_3H_6$) to propene ($n-C_3H_6$) on solid acid HA:

This is a quite general mechanism and can be applied to many molecules. When applied to a paraffin, one arrives at a non-classical penta-coordinated carbonium ion. This leads to what is called the monomolecular cracking mechanism (Haag *et al.*, 1991). As noted by Haag *et al.* (1991), one kind of evidence for this mechanism is that $C_6H_{15}^+$ formed from n-hexane on zeolite catalysts, *e.g.*, HZSM-5, produces the same distribution of products as when this same ion is produced in the gas phase via chemical ionization by CH_5^+ in an ion cyclotron resonance mass spectrometer. The conditions which favor this mechanism are high temperature and low paraffin partial pressure and/or low conversion. The latter assures low olefin concentrations (as products). When significant olefin concentrations exist in the feed or are formed by the monomolecular cracking mechanism, these are more easily protonated than the paraffin and lead to the classical (bimolecular) mechanism involving a carbonium ion chain reaction, which for n-hexane may be written:

This is referred to as a bimolecular mechanism, because the step (4) involving rearrangement of the carbonium ion and β -scission occurs very rapidly and the rate determining step is the hydrogen transfer reaction of step (3). The conditions at which the bimolecular reaction predominates are low temperature and high olefin concentration. In practice, both mechanisms may contribute to varying extents, depending on the composition of the feed and the reaction conditions. As discussed by Haag *et al.* (1991), the overall rate (which is a sum of the two mechanisms) can be formulated such that in two limiting cases they produce apparent first order kinetics. However, the apparent first order rate constant represents the rate limiting formation of penta-coordinated carbonium ion (in the limit of high temperature and low olefin concentration) and formation of tri-coordinated carbonium ion (in the limit of low temperature and large olefin concentration).

3.2.1.3 n-Hexane Aromatization as a Probe

To this point, the probe reactions discussed have been ones where a particular property, for example, acidity was being sensed.¹ Overall knowledge of the mechanistic details of a reaction can be used to identify a new catalyst with a different mechanism for the same reaction and this,

too, can be a powerful characterization approach. This is nicely illustrated by the n-hexane to benzene reaction which is one reaction among many that occur on conventional reforming catalysts. The original proposal of Mills *et al.* (1953) for reforming of alkanes has been confirmed and elaborated on by many researchers and is now found in standard textbooks on catalysis (Gates, 1992), that is, it is well understood and widely accepted. Thus, if the attributes of a catalyst needed to convert n-hexane into benzene, *i.e.*, both dehydrogenation and acid sites, and the intermediates involved, *i.e.*, methyl-cyclopentane, are found not to exist for a new n-hexane to benzene catalyst, it may safely be concluded that a new mechanism is at work. This is the case for the Pt/L-zeolite aromatization catalysts.

Many of the important observations and characteristics of Pt/L-zeolite aromatization catalysts were presented in the original publication of Bernard (1980). It was noted (i) that benzene selectivity was a strong function of conversion, (ii) that at the same conversion, L-zeolite was superior to other zeolites tested, (iii) that the K^+ cation exchange of other zeolites did not render them competitive with L, (iv) that introduction of acidity into Pt/L-zeolite degraded the selectivity, (v) that n-hexane conversion to benzene was faster than methylcyclopentane conversion to benzene (which is not the case on a conventional bimetallic reforming catalyst) and (vi) that the Pt site density was rate controlling (while it is usually acid site density in conventional reforming catalysts). Observation (i) indicates that comparison of supports must be done at the same conversion (but that is standard good practice for any catalytic comparison) and (ii) and (iii) suggest there is something special about KL-zeolite. Observations (iv) and (v) argue against a conventional bifunctional mechanism and (vi) is direct evidence for monofunctionality involving Pt.

3.2.1.4 Competitive Hydrogenation as an Electronic Probe

Often there is a need to sense the local electronic perturbation of a metal particle and the effect of this restructuring on catalysis. The shift in the infrared frequency of the C-O stretch of chemisorbed CO has often been used for this purpose (Peri, 1984). However, CO vibrational frequencies are often affected by dipole coupling (as a function of coverage) to a greater extent than they are by electronic perturbations. A reaction probe which has been developed and demonstrated is the competitive hydrogenation of benzene and toluene (Tri *et al.*, 1982). Hydrogenations are generally considered structure insensitive (Boudart *et al.*, 1968), and this is advantageous if it is the electronic nature of the metal particle that we are trying to probe. The competitive hydrogenation of aromatics is governed by their relative adsorption coefficients, and these in turn reflect the local electronic charge on the metal particle. In the competitive hydrogenation of toluene and benzene, toluene is the better electron donor and therefore is expected to form stronger π -bonds with Pt. As pointed out by Tri *et al.* (1982), it is the ratio of adsorption equilibrium constants $K_{t/b} = (K_{\text{toluene}})/(K_{\text{benzene}})$ which one wishes to measure because the rate is a product of the adsorption constants and rate constants. Because both toluene and benzene are π -electron donors and their ionization potentials are known, it is possible to predict how $K_{t/b}$ would vary with charge on the Pt cluster, while the effect on the rate constant is not so obvious. This parameter can be determined kinetically by measuring competitive benzene hydrogenation as a function of partial pressures of toluene and benzene at a temperature where both reactions are zero order in aromatic reactant. This probe reaction has

also been used in the analysis of the sites in the Pt/L-zeolite aromatization catalyst (Larsen and Haller, 1989).

3.2.1.5 Hydrogenolysis as a Probe in Bimetallic Catalysts

There are many industrial catalysts that are based on the use of two metals. These catalysts present a particularly difficult characterization task because often the two metals will have quite comparable physical and chemical properties. This is the case for Pt-Re/ Al_2O_3 which is, after exposure to a sulfur-containing gas, a widely used commercial reforming catalyst. In the total absence of traces of sulfur, both metals catalyze hydrogenolysis, but Pt-Re alloys are much more active for this reaction than either Pt or Re. This high specific activity of the bimetal particles can be used as a probe for alloying. The hydrogenolysis of cyclopentane has been demonstrated to be a reliable probe for the existence of bimetal particles in catalysts which contain both Pt and Re (Augustine and Sachtler, 1989). Electron microscopy is not very helpful, because it does not distinguish atoms of similar mass, such as Re and Pt. Likewise, the fact that Re and Pt have about the same number of electrons gives them similar backscattering functions and makes EXAFS analysis highly problematic (see below). Here then is another example where catalysis is the most sensitive way to characterize an important structural parameter (the formation of alloys) of the catalyst.

A useful probe discriminating between metal catalyzed hydrogenolysis and bifunctional (*i.e.* metal + acid) catalysis is the conversion of methylcyclopentane. In the absence of acid sites, a transition metal such as Pt or Pd catalyzes hydrogenolytic fission of one C-C bond in the ring. With some catalysts, the three possible ring opening products, n-hexane, 2-methylpentane, and 3-methylpentane are formed in ratios strongly deviating from statistics, as has been shown by Gault (1981). Such distribution provides valuable information on the site geometry, possibly also on its electronic structure (Lerner *et al.*, 1992). In the presence of acid sites, the bifunctional reaction of ring enlargement is catalyzed, with cyclohexane and benzene as the products. If formed in ratios deviating from the thermodynamic equilibrium ratio, this information is possibly indicative for sites which combine metal particles and Brønsted acids into a common *metal-proton adduct* (Bai and Sachtler, 1991; Lerner *et al.*, 1993).

For bimetal/zeolite catalysts such as Pt + Cu in NaY prepared by ion exchange and reduction, the addition of Cu to the Pt particles lowers the hydrogenolytic catalysis as a consequence of the well-known *ensemble effect*. Simultaneously, the enhanced concentration of protons, which are generated during reduction of both metals, favors the bifunctional catalysis of ring enlargement (Moretti and Sachtler, 1989).

3.2.2 Development of Surface Science for Catalytic Studies

The study of single crystal surfaces cleaned and maintained in ultra-high vacuum and investigated either in the field electron or the field ion microscope or with a variety of novel spectroscopies (Auger Electron Spectroscopy, Photoelectron Spectroscopy or Electron Loss Spectroscopy) or with Low Energy Electron Diffraction forms a very important part of surface science (Koel and Somorjai, 1985). Important new concepts have been identified by means of

these techniques, for example regarding the kinetics, dynamics of ad- and desorption, the effect of defect sites, the structure of adsorbed species, and the participation of subsurface atoms. In the past decade, much attention has been focused towards developing these new techniques to a state of high reliability and precision. For the future it is hoped that they will increasingly be applied to samples and conditions which simulate real catalysis. One strategy is to combine these techniques with high pressure reactors, so that a crystal can be shuttled between the ultra-high vacuum chamber and the reactor. This approach has already provided us with new inspiring models (Rodriguez and Goodman, 1991). Unfortunately, very little of this work has involved *in situ* analysis under reaction conditions because the probe particles require a good vacuum to operate. Infrared reflection absorption is an exception (Evans *et al.*, 1993) but is most frequently used in the before and after reaction mode of the other spectroscopies. What is suggested here is that there should be effort expended to develop photon based surface science that will allow true *in situ* analysis on well defined and characterized surfaces.

By way of an example of replacing of an electron surface science tool with an analogous photon tool, we cite the recent work on photon scanning tunneling microscopy (Ferrell *et al.*, 1992). The photon STM provides images of both insulators and conductors, but requires that the surface be either thin or not too strongly absorbing at the wavelength used. STM provides better spatial resolution but poorer spectroscopic resolution, that is, they are complementary tools. The photon STM has the potential to combine with vibrational spectroscopy, for example, resonance or surface-enhanced Raman. Other photon surface science tools under development include second-harmonic (and sum frequency) generation through nonlinear optical processes at a surface.

The need for photon (or some equivalent) surface science approach that will allow analysis under reaction conditions on well defined surfaces (probably characterized by current electron based surface science) is great. In addition to this general need, there are listed below some specific areas where new developments in surface science would be most welcome.

3.2.2.1 Oxide Surfaces

Surface science has made very significant contributions to our understanding of elementary steps on metals, but we need to see similar progress on oxides. Oxides are more difficult to study by surface science techniques for many reasons. Some oxides are difficult to grow as large single crystals. They are more prone to defects and can become non-stoichiometric at even modest temperatures in ultra-high vacuum. Of course, the fact that they are mostly insulators can compromise many of the electron spectroscopies by virtue of the static charge that results from electron emission, and the HREEL's spectra are compromised by the huge optical phonon losses in the oxide surfaces. Both the promise and problems are evident in a recent CO and CO₂ study on Cr₂O₃(111) (Kuhlenbeck and Freund, 1992). While they add complications to the experiments, all of these problems can be overcome and many laboratories have projects underway, for example, Evans *et al.* (1993) have presented a study of Rh on single crystal TiO₂(110) which combined many of the conventional surface science tools with reflection absorption infrared spectroscopy (Evans *et al.*, 1993).

3.2.2.2 High Coverages

While there have been many experiments performed under steady-state, high pressure conditions on single crystals, the vast majority of surface science experiments are performed in vacuum or at very low partial pressures. The resulting low coverages can completely alter the selectivity and dominant reactions. While this can still be interesting surface chemistry, it would be even more interesting to use surface science to learn about practical reactions (at relatively high pressures and surface coverages).

In some recent work it has been shown that methyl radicals on Ni(111) readily recombine with subsurface H atoms to form gas phase methane (Johnson *et al.*, 1992) while the dominant reaction is decomposition of the methyl radicals with surface H atoms rather than recombination. One suspects this is the result of the rather low H surface coverages that can be accomplished in these experiments and that the decomposition would be inhibited at high surface coverages of H. Of course, one approach is to get the high coverages the same way as they are obtained in real catalysis, that is, raise the pressure, but this means that *in situ* analysis has been given up.

Sometimes it may be possible to simulate high pressure by increasing the local coverage by other means. For example, Campbell *et al.* (1988) have found that high pressure conditions are simulated by postdosing Bi onto Pt(111). This forces species such as adsorbed H or hydrocarbon fragments into higher local coverages where they react as if at high pressures. Clearly, this is not a general solution and we need to find innovative ways around this problem.

3.2.2.3 Kinetic Characterization on Single Crystal/Model Catalysts

Of course, there are other reasons to go to high pressure other than just coverage considerations. This also makes possible kinetic characterization of the surfaces. While such studies might use kinetic probe reactions, the minimum we might expect to learn is whether the rate on the single crystal or model surface was comparable to that on high area conventional catalysts. This would then ensure that whatever surface science characterization was possible would be relevant to the steady-state catalysis. A recent example of such an investigation was reported by Coulter and Goodman (1992). They investigated oxidative dimerization of methane on thin-film MgO and Li/MgO (on which electron spectroscopies could also be performed) and showed that kinetics on the model catalysts gave about the same rates as the polycrystalline Li/MgO under similar conditions.

3.3 TIME RESOLVED SURFACE SPECTROSCOPY

While many stable adsorbed species have been identified by various spectroscopies, there is no guarantee that they play any role in the reaction, even if they originate from one of the reactants. One approach to determine if a given species is kinetically significant, that is, if it forms and reacts on a time scale sufficiently fast to sustain the steady-state reaction, is to perform a transient experiment. Tamaru (1964) first proposed this principle, and its summary was provided in 1978 and 1991 and more recently by Frennet (1993). The most effective approach

is to have the transient occur effectively at steady-state by a switch in one or more of the reactants, isotopically labeled, and follow the evolution of the isotopically labeled intermediates on the surface, for example, by infrared spectroscopy, or in the gas phase by mass spectrometry. Of course, a better experiment is to follow both the surface concentration and the gas phase simultaneously, but few of these experiments have been performed. A recent example using mass spectrometry to follow an isotope transient to estimate the rate coefficients for chain initiation, propagation, and termination during Fischer-Tropsch synthesis over Ru/TiO₂ is given by Krishna and Bell (1993).

Reutt-Robey *et al.* (1988) have reported a particularly elegant example of time-resolved infrared spectroscopy applied to what is expected to be a true elementary step. The law of mass action only applies to surface reactions involving two (or more) surface species only if one or more of these species diffuse on the surface rapidly on the time scale of reaction. In the case of CO oxidation on Pt, the rate at high temperature can be shown to be proportional to the product of coverages, $\Theta_{\text{CO}}\Theta_{\text{O}}$. Because oxygen atoms are known to diffuse slowly at reaction temperature, it is presumed that CO must diffuse rapidly. Just how rapidly this diffusion is on a microscopic dimension (20 atom length) has been shown by following the diffusion of CO initially on a Pt(111) terrace to a step. This can be followed by reflection infrared spectroscopy because the absorption frequency of CO on the terraces is different from CO on step sites. This migration was followed with a temporal resolution as fast as 5 msec and, by varying temperatures, a diffusion barrier of only 4.4 kcal/mol was determined. While there are several examples of diffusion over macroscopic dimensions, it is microscopic experiments, such as this, which are probably the most important for catalytic kinetics. The macroscopic diffusion will necessarily average over defects where the diffusion rate is very low because the fast diffusing species are likely to desorb before they can diffuse over a macroscopic distance (and therefore contribute little to reaction). This has recently been demonstrated for CO diffusion on supported Pd using ¹³C NMR (Becerra *et al.*, 1993). On the smallest clusters the diffusion activation energy was 6 ± 2 kcal/mol but decreased to 4 ± 1 kcal/mol for the large particles (12% exposed by CO chemisorption) which presumably have a lower defect density.

In the example of CO surface diffusion on Pt given above, the elementary step has been slowed down by lowering the temperature to the point where it could be followed. This is probably a reasonable thing to do for migration, but for a chemical reaction the mechanism might change; so we are in need of time resolved surface spectroscopies with much better time resolution. If it is possible to repeat the transient very rapidly, then it is possible to work out algorithms where data are collected at the same time into the transient and then to construct a spectrum at that "time". This approach has been used by looking at the infrared emission of vibrationally excited desorbed CO₂ from a Pd surface (Mantell *et al.*, 1985). The transient was a pulse of reactant directed at a surface. The pulse was about 200 μs and spectra could be obtained at spacings of about 30 μs through the transient using an efficient data collection algorithm that collects data continuously and then shuffles it into a matrix in which all the data at a given time into the transient could be transformed into a spectrum. In principle, this approach could be applied to other spectroscopies. Time-resolved measurement on a picosecond time scale has been demonstrated using infrared lasers to saturate and monitor the recovery of infrared absorptions

on surfaces (Casassa *et al.*, 1986). While this approach has not yet been applied to reactions on surfaces, this appears to be technically possible.

3.4 NEEDED SPECTROSCOPIC ATTRIBUTES

Most practical catalysts are either comprised of amorphous materials or small crystalline particles and, consequently, do not possess long-range order. Moreover, the existence of long-range order does not in itself assist in the characterization of the relevant properties of the catalysts. For example, many industrially important oxidation catalysts contain particles of metal oxide that are large enough to exhibit diffraction patterns, but the bulk structure does not necessarily enlighten us about the surface structures which are relevant to catalysis. Thus, techniques which are element specific and provide local structural information without the requirement of long-range order are very desirable. The element specificity is important so that we might tune to different components and interrogate them with respect to the surrounding order. Techniques which have these properties are NMR, X-ray absorption, EXAFS, X-ray absorption near-edge structure (XANES), and Mössbauer spectroscopies. As it happens, the wavelengths of the electromagnetic spectrum used by these spectroscopies are either very short (hard X-ray or γ -ray) or long (radio frequency) so that these spectroscopies do not require a vacuum and can be used at reaction pressures, and under some circumstances, at reaction temperatures. Unfortunately, this same property makes them bulk techniques so that special precautions must be taken to make them surface sensitive, for example, have the element of interest entirely exposed to the reactants (as in zeolites) or in very small particles so that essentially all atoms may be exposed to the reactants in the fluid phase.

We have already referred to the recent NMR investigation of CO on Pd with regard to the information provided on the activation energy for surface diffusion (Becerra *et al.*, 1993). But even for a site about which we know a great deal, the a-top and bridged-bonded sites of CO, this study provides several kinds of new information. The Knight shift informs us that the bridged-bonded site results in more interaction between the conduction electrons and those on the C than does the a-top site, that the bridged-bonding site is somewhat weaker and, at least at full coverage, is the dominant site on which migration occurs (although not simply because of the lower enthalpy of adsorption). While this is clearly not direct information on the active site, it is necessary structural information about the chemisorbed reactant and the site that bonds it.

While NMR is providing a wealth of new structural information on zeolites, oxide catalysts, adsorbed species on metals, *etc.*, the challenge is to make this spectroscopy truly applicable under reaction conditions. That is, the trend in solid state NMR is toward improved resolution by ever more complex motion of the sample, for example, magic angle spinning, dynamic angle spinning, double-rotation (Wu *et al.*, 1990), and this motion of the sample does not make it easy to imagine the sample as a steady-state reactor. An alternative to discrete Fourier transformation of NMR data that has been proposed is the maximum entropy method (Jones and Hore, 1991). While the maximum entropy method would normally be used with magic angle spinning to improve resolution, perhaps this or other new line shape analyses can be developed that will permit NMR of the catalyst during reaction.

More direct information on active sites on CoMo/Al₂O₃ HDS catalysts has been obtained by Mössbauer spectroscopy (Candia *et al.*, 1982). Mössbauer spectroscopy of the cobalt, an experiment that involves the preparation of radioactive samples, shows that hydrodesulfurization activity parallels the formation of a particular cobalt species that does not resemble any of the known bulk cobalt sulfides (Candia *et al.*, 1982). The same result appears in spectra of supported and unsupported mixtures of sulfided molybdenum and cobalt and has led the Topsøe group to propose a species they call "CoMoS" as the site of the hydrodesulfurization activity.

The attributes of synchrotron radiation, particularly as applied to EXAFS and XANES of catalysts, has been briefly reviewed by Joyner (1993). He has emphasized the need for *in situ* measurements in parallel with catalyst activity and selectivity measurements. Recently, both EXAFS and XANES have been used to follow formation of bimetallic particles using *in situ* temperature programmed reduction (TPR). Bazin *et al.* (1990) have followed the formation of Pt-Rh and Pt-Re on γ -Al₂O₃ using EXAFS and Jentys *et al.* (1992) combined XANES with TPR. The EXAFS measurements have the advantage that they provide directly structural parameters (coordination numbers, internuclear distances), but the resolution is greatly degraded by Debye-Waller effects, even at modest temperatures. XANES has the advantage that the spectra do not suffer from Debye-Waller degradation, but we do not have a good theory to interpret the electronic information that is, in principle, contained in the spectra. An approach which has much in common with XANES, but may have advantages when the whiteness intensity is not a linear function of oxidation state, is the measurement of the shift in the X-ray absorption edge, from which the binding energy can be monitored *in situ* in a TPR experiment (Hilbrig *et al.*, 1992).

A simple EXAFS analysis of a single first coordination shell with one kind of atom can result in both accurate internuclear distances and good approximations of the coordination numbers. However, there is a great deal of skepticism about the results for more complicated analyses which are common for real catalysts. The task is particularly difficult when one attempts multiple shell fits with more than two atoms of similar mass, for example, Pt-Re/Al₂O₃ catalysts and, indeed, different laboratories have come to quite different conclusions. There is a clear need for laboratories to exchange data, to share analysis programs, to set standards for the data to be used and to otherwise organize the application of the use of X-ray absorption analysis if it is to deliver on its potential for catalyst characterization.

3.5 THEORY

The continuing reduction in cost and increase in speed of computing has brought "theory" into the laboratories of the novice as well as the expert. The word theory is placed in quotes here to imply that we take the catholic definition that includes everything from reaction modeling to molecular modeling/molecular graphics to quantum chemistry. However, this does not imply that all aspects of theory are at the same stage of development. Chemical reaction engineering, where the focus is on the analysis of the reactor and pellet design, is widely applied in industry and is a mature science. Kinetic modeling is at a similar stage with regard to the necessary mathematics, but this is not the case with regard to parameter estimation that relies on sources other than experimental measurement. Dumesic *et al.* (1993) have introduced a systematic

synthesis of experimental data, theoretical principles, and appropriate correlations to quantitatively formulate elementary reaction steps in what they have designated "microkinetics of heterogeneous catalysis". In the extreme, this faces the same problems that confront other theoretical efforts at the atomic scale.

The real frontier for theories of catalysis occur where the focus is on the atomic scale and where the simulation of catalyst properties and the dynamics of elementary processes is the goal. Lombardo and Bell (1991) provide a recent review of theoretical models of adsorption, desorption, diffusion, and reaction of metal surfaces, and van Santen (1991) has published a comprehensive monograph which covers both metal and oxide (including zeolite) catalysts. However, in all of this work the theoretical calculations make an implicit assumption of some knowledge about the structure of the adsorption or reaction site that is to be theoretically simulated. It may not take into account the relaxation or changes in structure that accompany adsorption and reaction at the site; and thus, there is no guarantee that the lowest energy configuration of a given possibility is achieved. Thus, if this is the criterion by which the presumed site is selected among several possibilities considered, the conclusion will be flawed, and of course the original set of possibilities may be conditioned by constraints of feasibility so that it does not include the real site. Some constraints can now be eliminated when simulating the structure of active sites in zeolites or other sites composed of low atomic number atoms. For most metals, this is still a difficult task because the large number of electrons in transition metals requires algorithms that are too computationally intensive to permit the inclusion of relaxation effects. (For a recent survey of theoretical models in common use today for electronic structure of transition metal systems, see Zerner, 1991). Even though one is forced to assume the structure of the active site at the outset, these theoretical simulations can yield insights into what might happen at the molecular scale that are not accessible by other means. Such theoretical simulations, particularly when coupled with experimental attempts to verify the results, are to be encouraged.

3.6 RECOMMENDATIONS

Our recommendations for catalyst characterization are placed into two groups. The first group of six are general in nature. The second group applies to characterization techniques and is more specific, although the particular techniques are mostly illustrative.

3.6.1 Recommendations for Catalyst Characterization

Catalysis is by definition a kinetic phenomenon. Thus, it is the sites on which the elementary reactions are occurring that will be most fundamental to our understanding of catalysis. We should always attempt to study the catalyst in the act of turning over, that is, while reaction is occurring at steady-state.

- *There is a need to identify sites more precisely, both in the catalyst as prepared and in the steady-state of the catalytic reaction, that is, in the presence of reactants and products under the conditions of temperature and pressure of the catalytic reaction of interest.*

- *As active sites often comprise more than one atom, the design of an optimum catalyst requires a detailed knowledge of the ensemble size and of the chemical interaction of these atoms with their environment, including support, promoters, chemical anchors, and catalyst poisons.*

While our interest is in the characterization of catalytic sites in action, often insight into the nature of these sites can be provided by the study of the precursors to the active catalyst. This is true for all kinds of catalysts, including zeolites, mixed oxides, and supported metals, although the nature of precursor chemistry is very different. For example, the precursor chemistry of supported metals is particularly important not only to understand the nature of the final metal particles but also to make the catalyst preparation reproducible. We are almost wholly ignorant of the inorganic chemistry that transpires between a metal ion in solution and the resulting metal particle supported on an oxide (or other) surface. A statement that a given weight loading of metal on a particular support was prepared by "incipient wetness impregnation" can disguise many known and unknown effects. There may be dissolution of the support, retention of the anion by the support, migration of the precursors (into or out of the pores) which will be affected by the drying temperature, initial reduction temperature, rate of reduction, *etc.*

- *Complete characterization of catalyst sites (and description of catalyst preparation) should include the complete inorganic chemistry of catalyst preparation.*

We need new surface spectroscopic techniques which are element specific, provide local structure where no long-range order exists, and can be applied under reaction conditions. These would be more nearly ideal if they were also surface specific.

- *Whatever techniques we contemplate, making these techniques applicable under reaction conditions and developing time resolution will be important and will pose essential challenges which should be given our continued attention.*

We have already noted that chemical catalytic probes are by definition the most sensitive probes of catalytic sites, but this sensitivity does not necessarily provide the detailed site structural information that is sought. Every physical technique for catalysts characterization will have some particular strengths and weaknesses. A given technique may be more or less surface sensitive, for instance, ion scattering spectroscopy is more surface sensitive than X-ray photoelectron spectroscopy. The parameter measured may be a nonlinear function of coverage,

for example, infrared intensity of CO on metals, or provide better information on surface symmetry or morphology than composition, *e.g.*, LEED and STM.

- *Characterization of catalyst sites should always involve complementary physical (spectroscopic) and chemical (chemisorption and/or catalytic kinetic) techniques*

of characterization and use as wide a combination of physical characterization techniques on the same catalyst as may be practical.

We need to have the two approaches used in a complementary way. For example, the competitive hydrogenation of benzene and toluene was described as a reaction that qualitatively probed for the charge on small metal particles. It should be possible to design model systems on which both this reaction and a direct measure of the charge on the particles could be measured, for instance, by the XPS binding energy shift, so that the catalytic reaction could be calibrated against the physical method. It could then be used on catalysts where the changes were too small to measure directly by the physical technique, but by the calibration, the property could be reported on a quantitative basis. While the use of model reactions is among the oldest techniques we have for characterizing catalysts, it would be useful to have a modern review and critique of the many reactions that have been tried. This could serve as a reference for future developments.

The extension of the present level of theoretical analysis to treat very large systems is essential for low symmetry problems represented by surfaces.

- ▶ *New theoretical approaches which are atomically based and can treat site dynamics that accompany adsorption and catalytic turnover need to be developed.*

3.6.2 Recommendations for Surface Analysis

Certain physical techniques, such as X-ray absorption, have become widely used and have admitted potential for characterizing catalysts. However, the analysis is complex and not well understood by many users, and much of the work to date has not been cross-checked for reproducibility. There is also widespread skepticism about conclusions drawn from this work.

- ▶ *The community needs to agree on standard analysis programs, methods of assessing uncertainty, and minimum standards for experimental data that are analyzed and published, e.g., for X-ray absorption spectroscopy.*
- ▶ *We need new photon based surface science spectroscopies which can be applied to surfaces at high coverage and under reaction conditions. We seek surface science improvements that will make application to nonmetals routine.*
- ▶ *We need new and improved element specific spectroscopies that can determine local surface structure in high area catalytic materials. As a specific example, we need improved lineshape and data analysis for solid state NMR, along with continued improvements in field strength and dynamic probes.*

Until STM is routinely used in such a way that compositions as well as images are obtained via either experimental improvements or coupled theory, it will be analogous to the early contributions of LEED where symmetry was easy and obvious, but true structure required the development of a firm theoretical underpinning. There is a recent and promising STM report

in this regard where it was demonstrated that polyanion arrays (on a graphite surface) with different compositions could be distinguished by a kind of density of states analysis (Watson *et al.*, 1992).

- *New surface analysis techniques should provide both symmetry/morphological and chemical composition.*

Some work has been done to develop a method of elemental analysis to accompany STM involving inelastic tunneling to obtain vibrational frequency analysis as a function of position. The development of such a method of compositional analysis should be given a high priority, since the transient isotope switch approach may be applied in the steady-state of the reaction to identify the true active sites on catalyst surfaces on an atomic scale (Tamar, 1993).

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Chapter 4

CATALYST PERFORMANCE TESTING

Heinz Heinemann

4.1 INTRODUCTION

The ultimate objective of a catalyst testing program is the evaluation of the catalyst for performance in a commercial process. Development of the catalyst usually begins with small samples tested in laboratory-scale equipment. It is, of course, desirable that the testing results from such small equipment simulate with considerable accuracy the performance in a large-scale commercial unit. The characterization of a catalyst in terms of its activity is obviously a qualitative measure of the ability of the catalyst to carry out a particular chemical transformation under specified conditions. Speed of reaction and specificity or selectivity are prime considerations. Testing of a catalyst for activity implies a range of experiments varying widely in the degree of sophistication of both the experimental equipment employed and the interpretation of information obtained (Anderson, 1985). It is therefore necessary to distinguish clearly what information is required and to what ultimate use it is to be applied. According to Anderson and Pratt, the most common objectives are:

- ▶ Routine quality control tests conducted by the manufacturers or users of a catalyst which may involve a reaction carried out under standardized conditions on individual batches or samples of a particular catalyst type.
- ▶ Rapid screening of a large number of catalysts to establish an order of merit for a particular reaction. Such experiments are often carried out in relatively simple apparatus and under mild conditions. Interpretation may be based on the determination of a single reaction parameter.
- ▶ More detailed comparison of several catalysts. This may involve testing under conditions covering the likely range of commercial application to identify the optimum performance area of each. Evaluation may be based on a number of criteria, and the resistance to known poisons and the reaction atmosphere determined.
- ▶ The determination of the mechanism of a specific reaction, possibly involving the use of labelled molecules and sophisticated analytical equipment. This information may assist in the formulation of a suitable kinetic model or provide valuable clues in the search for improved catalysts.
- ▶ The determination of the detailed kinetics of a reaction over a particular catalyst. The kinetics of deactivation or regeneration could also be of interest. This information may be needed to enable the design of a commercial plant or demonstration unit to be performed.

- ▶ The continuous long-term operation of the catalyst in such a way as to simulate commercial reaction conditions. It is usually performed in a reactor having a similar configuration to the planned commercial system, and may consist of an individual module (for example, a single full size reactor tube) or of a reduced scale version of the full-size reactor.

It is very important to identify at the beginning of a catalyst study the key catalytic problem in a given process. This will determine the correct method of investigation.

Four factors are usually identified as being the most important:

- ▶ Activity
- ▶ Selectivity
- ▶ Life
- ▶ Cost

While catalyst activity is often emphasized, other properties, such as selectivity, tendency to carbon formation, catalyst stability, poisoning resistance, or the impact of different feedstock characteristics may be more important.

Laboratory testing of a catalyst will usually concentrate on one or more of the first three of the above listed criteria, one of which will be most important for the particular application. Economic factors, while ultimately determining the potential use of the catalyst, cannot usually be obtained from catalyst testing other than from catalyst life data. Catalytic activity can often be defined as the turnover rate or turnover frequency which describes the number of molecules that react per active site per unit time. The problem with this excellent definition is that it is frequently not possible to obtain an exact estimate of the number of active sites on the surface or in the bulk of the catalyst. Other measures in use are: the reaction per unit mass or volume of catalyst; the reaction rate determined in the presence of concentration or temperature gradients; temperature required to obtain a given conversion or yield; reaction conversion of product yield achieved under a given set of reaction conditions; reactant space velocity required to achieve a given conversion or yield at specified conditions; the rate constant derived from a kinetic study of the system (*Catalytica*, 1987).

To determine selectivity it is important to obtain close to 100% material balances. It is also important to identify the by-products and to follow the change of product distribution with time.

Aging of the catalyst with corresponding decline of conversion and/or selectivity will occur in most catalytic reactions. Rates of aging and potential catalyst regeneration to full activity must be investigated.

No catalyst testing is better than the analytical facilities available for analyzing the major product and by-products. Gas chromatography often coupled with mass spectrometry are the most common means of product analysis today. With increasing emphasis on environmental concerns, the need for greater and greater sensitivity of analytical tests has increased. An example of this need is demonstrated by the fact that the sulfur content of fuels 30 years ago was expressed as fractional percentages, whereas it now often required to be in parts per billion. One may expect this trend to continue.

A major problem in testing catalysts for potential use by evaluating them in bench scale equipment is the likelihood of possible heat and mass transport limitations which can occur in large scale equipment and which do not always show up in bench-scale testing. This will be discussed in a later section.

4.2 CATALYST TYPES

There are three major forms of catalysts used in heterogeneously catalyzed reactions:

- ▶ pelleted or extruded catalysts
- ▶ fluid bed catalysts
- ▶ suspension or slurry catalysts

Catalysts used in commercial operation often cannot be used in the same form and size for catalyst performance testing.

In fixed bed commercial reactors, catalyst particle size will often be determined by pressure drop considerations. A test reactor will have a much smaller diameter and probably cannot accommodate the same particle size. Smaller particles will have higher surface area and be less diffusion limited than large particles. Means have to be found to extrapolate from one particle size to another.

Similarly, it is often difficult if not impossible to simulate fluid bed operation in a small bench-scale reactor. Again, there is a likelihood of differences in particle size but also a major difference in catalyst age. While the performance of a fresh catalyst in both commercial and laboratory sized units may be similar, a commercial fluid bed reactor will have a distribution of catalyst particles of different age. This is due to the continuous recirculation of the catalyst after regeneration and to the addition of a small percentage of fresh catalyst. This is very difficult to simulate in a small reactor.

Slurry or suspension catalysts may be simulated reasonably well as far as activity and selectivity are concerned. There are, however, problems of potential catalyst disintegration after extended periods of time which are not likely to show up in relatively short-term tests.

Occasionally it is helpful to study the activity of a single pellet at high mass velocity. This is usually done in a single pellet Berty-reactor with a thermocouple imbedded in the pellet.

4.3 MECHANICAL AND PHYSICAL TESTS OF CATALYSTS

Proper catalyst specifications for mechanical and physical properties are as important as activity and selectivity (Bertolacini, 1989). Poor resistance to attrition and crushing can cause pressure drops and expensive unit shutdowns in refining and petrochemical operations. Setting reasonable specifications depends on the development of reliable test procedures and well characterized reference materials for method development. Statistical control processes can be used to eliminate test variations to reduce off-specification catalysts.

Catalyst stability (Farrar, 1982), attrition resistance (Farrar, 1983), and crushing strength (Farrar, 1984) are most important. Broken catalyst particles in fixed bed reactors cause increased pressure drop by bridging interstices between catalyst particles which can plug the bed with debris. Fixed bed catalysts are prone to breakage when they are loaded into reactors. High pressure, high temperature, and high space velocity feed throughputs exert strain on catalyst particles requiring that catalysts be prepared in different shapes to resist fracture, spalling, and disintegration. Catalyst strength is crucial in tubular cooled or heated reactors, because catalyst breakage will result in maldistribution of flow and overheating (or overcooling) of tubes.

Important tests to measure potential catalyst breakage during operation are single-pellet and bulk crushing strengths. These tests measure the resistance to a compressing force and are used for quality control by the catalyst producer. Bulk crushing measures the ability of the catalyst to support the weight of the catalyst bed. A test is now under consideration for standardization (Bradley, 1988; Bertolacini, 1989). A mechanically driven piston apparatus giving reproducible crushing results has been described by Bearer (1974) as has been a procedure for measuring catalyst attrition resistance (Dart, 1974). Overall, twenty-five standards have been developed by the American Society for Testing Materials, Committee D-32-Catalysts, which include tests for attrition, crushing strength, particle size distribution, and vibrated apparent packing density (*A.S.T.M. Standards on Catalysts*, 1988).

Catalysts in slurry or ebullating bed reactors are subject to attrition. They must resist high turbulence from high gas velocities as well as erosion by solids in the feedstocks. No standard tests seem to have been developed for this particular application.

Fluid bed catalysts must withstand the effects of several thermal stresses during reaction and regeneration. They must also be resistant to attrition in pneumatic lift operation. Their ability to resist excessive sintering is described in a different chapter.

Characteristics of catalysts such as surface area, pore size distribution, crystallinity, metal dispersion, and surface acidity are important parameters which can distinguish good catalysts from bad ones. Tests for these characteristics are described in other chapters of this report.

In general, mechanical characteristics of catalysts are most important for catalysts ready to go into commercial use. In catalyst research for new or improved catalysts, existing or novel processes, activity, selectivity, and life performance will have to be established before it becomes important to test the catalysts for their mechanical characteristics. However, even the best performing catalyst is no good if it cannot stand up to the climate in the reactor.

4.4 ACTIVITY, SELECTIVITY, AND LIFE TESTS

A first objective of catalyst activity and selectivity testing is usually a preliminary screening of a number of new and existing catalysts to establish a ranking of "performance" for a given reaction (*Catalytica*, 1987). Relatively few candidate catalysts need to be investigated beyond this stage. While the initial tests are usually performed in relatively simple laboratory reactors, and the catalyst ranking is often based on a single easily determined performance parameter, it must be kept in mind that the relationship between performance simulation in a laboratory reactor and performance in a commercial reactor is not always well established and is subject to disguises by heat and mass transfer. Preliminary test screening is usually followed by a cursory screening of parameters that affect the reaction, followed by a more detailed comparative evaluation of catalysts with confirmed potential. Dautzenberg (1989) has presented guidelines for an effective catalyst testing program. He emphasizes the importance to define an objective for the catalyst testing program before starting experimentation. A well designed, appropriate experimental strategy will enhance the effectiveness of the program. Statistically derived experimental strategies and a statistical design of experiments will greatly reduce the number of experiments to be performed while providing the desired information.

The choice of an appropriate test reactor is of the utmost importance. Many reactors and their performance characteristics have been described in the literature and are well summarized in Chapter 11 of Satterfield's book (1980) and Chapter 6 in Anderson's book (1985). Anderson *et al.* (1985) state, "Perhaps the most important physical distinction which may be made amongst laboratory reactors is between batch and continuous systems. Nowadays greater use is made of continuous reactors in catalytic studies. It is now relatively rare that catalytic kinetic studies are made in batch reactors, and these systems are mostly used in preliminary screening tests for reactions where high pressures necessitate the use of autoclaves. In such cases catalysts are usually evaluated simply in terms of measured conversion under fixed reaction conditions and reaction time".

Commercial continuous reactors are generally complicated by the presence of several flow modes and radial and longitudinal gradients of concentration and temperature both within and between catalyst particles (Figure 1). In laboratory reactors, however, strenuous efforts are usually made to eliminate these effects in order that information obtained might be absolutely unambiguous. A classification of laboratory reactors taken from Anderson and Pratt (1985) is presented in Figure 2. Reactor selection depends on both the nature of the reaction system under study and the purpose of the work, subject to the constraints of available time and money. A generalized

Figure 1. Large Diameter Trickle Reactor with Poor Flow Distribution
(From - F. M. Dautzenberg, 1989)

Figure 2. Laboratory Reactors
(From - J. R. Anderson and K. C. Pratt, 1985)

preferred reactor selection for different phases of catalyst and substrates is shown in Table 1 (*Catalytica*, 1987). It is always most important to gather the desired information in a reproducible and efficient manner.

It is necessary to have an energy balance, a mass balance for each independent reaction constituent, and a phase balance for each phase of the reaction whether it be gas, liquid, or solid. Isothermal operations simplify the energy balance, and a design is desirable that minimizes pressure drop and is not complicated by the effect of concentration gradients. Continuous rather than batch or semi-batch operation is usually preferred because of the impossibility of uncoupling the main kinetics from deactivation in batch mode and because of the difficulty in defining the actual reaction time in batch operations.

Plug flow reactors and continuous stirred tank reactors are usually preferred over batch or fluidized bed or trickle bed reactors. The complex hydrodynamics in fluidized bed and trickle bed column reactors do not permit an accurate assessment of intrinsic catalyst behavior. However, laboratory trickle bed reactors can be designed to compare catalysts. They are also suitable for life testing of catalyst samples but are generally not good tools for determining reaction kinetics. Methods for evaluating fluid catalytic cracking catalysts have been described in numerous publications, only two of which are referred to here (O'Connor, 1974; Moorehead, 1974). Hydrodynamic properties needed for scale-up of fluidized bed processes can sometimes be obtained from small scale equipment by maintaining strict geometrical similitude and using appropriate dimensional groups for proper scaling (Glicksman, 1984; Fitzgerald, 1984).

The plug flow reactor is particularly efficient for screening solid catalysts in a single fluid phase. The choice of an integral versus a differential plug flow reactor depends on the objectives of the testing. The integral reactor has a number of advantages which make it commonly used. Large conversions reduce analytical problems and lead to more accurate data. Integral reactors are also easy and cheap to build compared to recycle reactors which may be complex. Differential reactors have the advantage that mass and heat transfer influences are usually absent at low conversions and low heat release. Because of the uniform conditions in the bed, most of the parameters of interest can be studied separately. Uniform fluid properties in the bed make true plug flow easier to achieve and in any case, because of the low conversions, the existence of radial velocity profiles does not cause significant departures from the ideals of plug flow. However, because of the small conversions required in a differential reactor, analytical difficulties and therewith the possibility of large errors may arise. While plug flow reactors are preferred for solid-gas and solid-liquid phases, stirred tank reactors are preferable for catalyst screening for solid-gas-liquid phases and for gas-liquid and liquid-liquid phases. A continuous stirred tank reactor is important for evaluation of kinetic parameters and for life tests.

In plug flow reactors gradients in concentration and/or temperature can exist between different locations in the reactor (intra-reactor gradient), between the bulk fluid, and the fluid-catalyst interface (interface gradient), and within the pores of a solid catalyst (intra-particle gradient).

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Reactor Selection

<u>Objective</u>	<u>Phases</u>				
	<u>Solid-Gas</u>	<u>Solid-Liquid</u>	<u>Solid-Gas-Liquid</u>	<u>Gas-Liquid</u>	<u>Liquid-Liquid</u>
Catalyst screening	PFR	PFR STR (batch)	STR (semibatch)	STR (semibatch)	STR (batch)
Parameter screening	CSTR	CSTR	STR (semibatch)	STR (semibatch)	STR (batch)
Reaction network characterization	CSTR	CSTR	Trickle bed CSTR	CSTR	CSTR
Kinetic parameters	CSTR	CSTR	Trickle bed CSTR	CSTR	CSTR
Catalyst life tests	CSTR PFR	CSTR PFR	Trickle bed CSTR	CSTR	CSTR
Catalyst optimization	CSTR PFR	CSTR PFR	Trickle bed CSTR	CSTR	CSTR
Scaleup	PFR Fluidized bed	PFR Slurry	Trickle bed Slurry	Bubble column	CSTR
Commercial operation	PFR Fluidized bed	PFR Slurry	Trickle bed Slurry	Bubble column	CSTR
Process improvement	PFR Fluidized bed	PFR Slurry	Trickle bed Slurry	Bubble column	CSTR

PFR Plug Flow Reactor
 STR Stirred Tank Reactor
 CSTR Continuous Stirred Tank Reactor

Table 1

Assessing the contributions from such gradients requires experimental measurements sometimes supplemented with generalized mathematical criteria. Effective elimination of interferences from the various possible gradients requires appropriate reactor selection, design, and operation. Freedom from transport disguises is an essential criterion for effective catalyst testing in small-scale reactors. Only after the intrinsic catalyst properties are quantified, should the complexities of transfer phenomena be addressed. The ideal reactor is one in which temperature, concentration, and pressure do not vary in space or in time. These conditions are fulfilled completely only in a continuous stirred tank reactor. In a plug flow reactor, isothermal operation is critically important for generating quantitative information about catalyst performance in a laboratory reactor.

Heat transfer coefficients cannot be reproduced in laboratory scale reactors and therefore radial gradients are not observable. It is not enough to study initial rates in gradientless reactors. One must emphasize knowledge of rates at different conversion levels and particularly at close to equilibrium.

Catalyst aging is a phenomenon which can change greatly from catalyst to catalyst. Aging can be caused by different phenomena, such as: accumulation of by-products on the catalyst surface or in catalyst pores (coke); poisons even in very small amounts in the feed; sintering of surfaces at high temperatures; surface rearrangements during reaction; *etc.* Frequently, aging cannot be observed except after fairly long runs. In batch reactors catalyst activity and catalyst decay cannot be independently evaluated. Continuous reactors allow the separation of time scales for reaction and decay. It is also possible to determine changes in catalyst surface and structure by spectrographic techniques. Much work has been done on accelerated aging tests to avoid the necessity of evaluating catalyst performance over long periods of times (days, weeks, or months). One of the best known cases is the steaming of fluid bed cracking catalysts at high temperatures for different periods of time (Satterfield, 1980). However, a great deal of experience is necessary to permit proper correlation between accelerated aging tests and actual aging at normal operating conditions. In reactor tests, aging can usually be observed by changes in conversion and product distribution over a period of time. It is also generally true that most catalysts exhibit different (usually higher) activity when first coming on stream than during a long period of fairly level operation. Of course, this indicates an initial rapid aging probably due to deactivation of specific active sites by poisoning. The most desirable catalytic reactions and catalysts are those that give 100% selectivity to the desired product, thus avoiding interference with a catalyst by by-products formed during the reactions.

In general, it is apparent that catalyst performance testing is a complex, time consuming, and costly effort. It is subject to many pitfalls and must be carried out according to a carefully planned sequence and with careful selection of the right reactor and right operating conditions. In recent years, automation of catalyst testing equipment has enabled workers to test more catalysts on an around-the-clock basis. Combination of computer controlled testing units and computer interacted gas chromatography presents the possibility of obtaining a very large number of data with relatively little manpower requirement. However, it also diminishes direct observation of unexpected phenomena by experienced scientific personnel, and it provides such an abundance of data that it is often difficult to select the important ones and to plot trends.

4.5 MODEL COMPOUNDS

Catalyst characterization can be of considerable assistance in the performance testing of catalysts. The more that is known about the chemical composition and the surface properties of a catalyst, the easier it is to interpret differences in performance between closely related catalysts. This is particularly true for multifunctional catalysts where an understanding of the active sites responsible for specific steps in a reaction sequence will help in interpreting aging and poisoning effects during performance testing. Good understanding will also help in synthesizing new or modifying existing catalysts.

In recent years much emphasis has been put on surface and bulk characterization of catalysts by spectrographic techniques, ranging from infrared spectroscopy, X-ray diffraction, nuclear magnetic resonance, X-ray photoelectron spectroscopy, and many other techniques to quite recent work on scanning tunneling microscopy. This is discussed in a different chapter of this report. However, there are methods of chemical characterization which can throw much light on catalytic mechanisms and therewith on the performance of catalysts. Studies with pure compounds frequently permit identification of specific catalyst sites. This has been demonstrated as early as 1956 for the reforming of petroleum naphthas (Ciapetta, 1958). Dual functionality of platinum-alumina catalysts was first demonstrated using pure organic model compounds to distinguish between acid and metal functions (Mills, 1953). Pines (1960) has published numerous papers characterizing catalysts and their functions by studies of the behavior of model compounds. More recently, the capability of a catalyst has been measured by chemical identification of the bonds which are broken, using a complex organic compound for modeling (Farcasiu, 1991).

While an ideal catalyst will have perfect selectivity, in practice a catalyst produces unwanted products or mixtures of substances. At an early stage in the study of kinetics the existence of parallel and consecutive reaction pathways in chemical reactions can be identified, often by studies with model compounds. The simplest first order rate expressions are then easily integrated to give the variation of product distributions with contact or reaction time. Much more elaborate networks are necessary to describe actual catalytic processes.

Hydrocarbon feeds contain many dozen components, and it is useful to attempt a kinetic analysis in a compromise that acknowledges that different types of organic compounds behave in analogous ways allowing them to be lumped together to give a network similar to that for a pure compound. Development of a network model leans heavily on existing knowledge of catalyst behavior plus experimental work.

The advent of new techniques in surface science has in recent years stimulated much work on an understanding of the structural and chemical properties of surfaces. While the science of catalysis has traditionally advanced as a consequence of new experimental techniques, theory has begun to play an increasingly important role. The availability of powerful computers for extensive calculations has enabled graphical display of results of both experimental surface science and theoretical studies (Salmeron, 1991). This information is becoming helpful in guiding the design of novel catalysts, interpreting experimental measurements, and understanding

the way in which catalyst composition and structure affect its activity and selectivity (NRC Report, 1992). *Catalyst by design* is a goal, the attainment of which is gradually becoming more likely. Future catalyst evaluation would be greatly simplified if catalyst performance could be fully predicted from its structural, electronic, geometric, and bond strength characteristics. A major obstacle to this accomplishment will be the difference in temperature and pressure conditions of the surface science measurements and the actual operating conditions during catalytic reactions. It can be assumed that major changes in surface characteristics occur at operating conditions and in the presence of substrates during catalysis.

4.6 ANALYTICAL REQUIREMENTS

As has been discussed earlier in this chapter, almost all catalyst testing for performance in catalytic reactions is being carried out in one of several possible laboratory reactors. The reactions are studied at temperatures and pressures which correspond to those expected to be used in commercial applications and with feed streams which either correspond to those available to industry or simulate components of these feed streams, such as pure organic compounds. Feed streams are metered by volume and weight, as are effluent streams from the reactor. Analysis of feed and effluent streams is usually achieved by gas chromatography, mass spectrometry, and infrared or ultraviolet absorption (Bland, 1967). Fractionation of liquid streams is sometimes required prior to more detailed analysis.

It is essential that excellent mass and weight balances be obtained around the reactor. This may at times require adding an inert internal standard (*e.g.*, a rare gas) to the feed and relating charge components and effluent components to this standard. Since the catalyst may absorb or have deposited on it by-products from the reaction (*e.g.*, coke), it is necessary to have gravimetric analysis of the catalyst before and after reaction as well as identification of the deposits on the catalyst. Only then can a weight balance be complete.

With increasing demand for catalytic processes to control environmentally harmful products and with better knowledge of the effect of very small amounts of poisons on catalysts, it has become necessary to increase the sensitivity of analytical procedures into the parts per billion range. Sulfur analysis, for instance, in petroleum naphtha streams has required continually increasing sensitivity. The analysis of NO_x in combustion exhaust streams prior to and after catalytic reaction also must be in the parts per million range and is usually carried out by chemiluminescence.

New analytical techniques are constantly being developed for greater and greater sensitivity and for components in gas and liquid streams which have not previously been analyzed. New analytical methods will be required in the future as catalytic processes are being developed for environmental control purposes. A particularly difficult consideration is the fact that the concentration of harmful components, which must be chemically reacted with other potentially harmful compounds (*e.g.* $\text{NO} + \text{ammonia}$ over vanadia-titania catalysts), can be constantly changing and must be monitored continuously to maintain stoichiometry of the reactants.

For conventional catalyst performance testing, particularly of petroleum refining catalysts, units are commercially available which combine reactor testing with gas chromatographic and mass spectrometric analysis of products controlled by integrated computers. Increasing sensitivity requirements make this sort of equipment more complex and consequently much more expensive.

4.7 DISCUSSION

The major part of this chapter is concerned with test procedures of catalysts used in or intended for the petroleum refining, petrochemical, and chemical industries. Existing test procedures which are commonly also suitable for new catalysts involve laboratory tests for the catalyst performance under conditions simulating commercial operations and laboratory tests for the mechanical and physical characteristics of the catalysts. While the performance tests allow selection of superior catalysts for a specific purpose and an evaluation of performance over a range of operating conditions, they are often complex, require expensive testing and analytical equipment, and are time and manpower demanding. Numerous tests are required to optimize the performance of a given catalyst. Since the cost of a catalyst decreases with its increasing life (amount of product formed per unit of catalyst), it is always important to estimate the relative lifetime of competing catalysts. While accelerated aging tests have been developed in many cases, they cannot totally substitute for very long runs in laboratory or pilot plant units. It is easier to extrapolate catalyst life in case of a gradually declining activity than it is in the case of catalyst poisoning, which may lead to feed breakthrough after considerable periods of level onstream production.

A better understanding of the nature of active sites on a catalyst for a particular reaction, of both the number of sites and of site strength, could assist in the development of better performance and life test procedures. A major obstacle to the use of current knowledge in this area is the fact that most observations of surface characteristics are made at conditions which are far removed from those existing during the actual catalytic reaction. In fact, it is likely that the catalyst surface and its active sites at operating conditions and in the presence of substrates differ from those observed at ambient or low temperature and vacuum conditions. There is therefore a major incentive to study catalyst composition, structure, and characteristics at the conditions of the catalytic reaction. Knowledge thus acquired could likely lead to simpler and faster performance tests.

During the last decade or so, there has been a major shift from catalyst research and applications for industrial manufacturing improvements based on profitability alone to consideration of environmental impacts and the use of catalysts in primary prevention of pollution (removal of pollution forming components prior to catalysis) and in secondary prevention (removal of pollutants after catalysis) (Cusamano, 1992). In many cases this trend has required novel sampling and analytical methods. It is expected that, as new processes are developed, new testing and analytical methods will have to follow. It is, of course, impossible to predict the type of tests required unless and until the catalytic process is developed.

Analytical procedures for testing catalyst performance will have to make greater use of more sensitive spectrographic and novel analytical tools. Sensitivity into the parts per billion range

will be a requirement in the future; thus, research to develop new instrumentation with this sensitivity will be required.

Modeling of catalyst characteristics and theoretical interpretation of surface and adsorbate bonding may eventually lead to a better design of catalysts, and with it to an early understanding of catalyst performance. Research in this direction must be encouraged. As catalysis progresses from an art to a science, prediction of performance should become possible.

4.8 RECOMMENDATIONS

- ▶ Research on correlations between laboratory and commercial size reactors to enable faster scaleup time and possibly avoid pilot plant construction.
- ▶ Research on accelerated catalyst aging techniques to reduce performance testing time.
- ▶ Research on surface properties and diffusional characteristics of catalysts at operating conditions and in the presence of reactants and products to permit deduction to rapid scaleup.
- ▶ New analytical techniques will have to be developed to ensure performance testing to meet increasingly severe specifications.

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Chapter 5

REACTION KINETICS/REACTOR DESIGN

Jens Rostrup-Nielsen

5.1 INTRODUCTION

Reaction kinetics is an important tool for industrial catalysis. It provides the basis for reactor design and it may contribute to the understanding of reaction mechanisms and thereby supply ideas to formulate new catalysts and to explore new reaction paths.

Reactor and reaction engineering was added to catalysis during the 1950s and, with the introduction of computers, it developed to perfection, "the noble art of modelling", although most of it was still based on Langmuir assumptions and Hougen-Watson kinetics.

From the late 1960s, surface science made its substantial input to the understanding of catalysis, which almost transferred catalysis into "the noble art of characterization".

Industrial catalysis needs both elements. Research and development in catalysis requires a multi-disciplinary effort concerning the manufacture of the catalysts, the study of the catalyst's impact on the chemical process, and the scale-up of results to industrial reactor design. It is important that there is a close interaction between fundamental catalysis and reaction engineering (see Figure 1).

The traditional scheme has been to start doing basic research to create ideas for applied research, and to complete the applied research before beginning development and engineering. A more effective approach is to work with overlapping phases, meaning that the applied research is supplemented by fundamental studies.

As an example (Rostrup-Nielsen, 1993a), the testing at semi-industrial scale, at industrial mass velocities, and heat transfer rates may well provide results that are relevant for engineering of industrial units. But in addition, practice has shown that it is often at this scale that the secondary phenomena such as unforeseen deactivation phenomena are best recognized. On the other hand, the progress in surface science has provided a basis for a detailed understanding of poisoning phenomena. This knowledge can be used in characterizing the spent catalysts from pilot plants and forming the basis for a new approach in catalyst development, and thereby the cycle is closed. The interaction between the two fields may help in focusing the fundamental studies on the relevant problems.

Figure 1. Essential Connection Between Basic Research and Pilot Plant Operation.

5.2 REACTION KINETICS

5.2.1 Paradox of Heterogeneous Catalysis

With the introduction of the chemical reactor, engineering procedures were developed to establish rate expressions from experimental work by using the Langmuir/Hinshelwood approach for formulating possible mechanisms and their equivalent rate equations (Hougen *et al.*, 1959; Froment *et al.*, 1979).

$$r = \frac{(\text{kinetic factor}) \cdot (\text{driving force})}{(\text{adsorption group})} \quad (1)$$

The rate equation showing the best fit or the minimum residual squares of conversion was chosen and often this was taken as proof for the mechanism behind the expression. This could easily be misleading because even if it made the mechanism plausible, the fit by itself could be no proof of its assumptions.

Also, it was shown that many of the rate data could be expressed by simple power rate expressions (Weller, 1956).

$$r = k \cdot p_A^\alpha \cdot p_B^\beta \cdot p_C^\gamma \quad (2)$$

which could reflect the simpler Freundlich isotherm. This isotherm is related to the Langmuir isotherms by the approximation:

$$\frac{Ap}{1+Ap} \sim B \cdot p^n, \quad 0 < n < 1 \quad (3)$$

Therefore, one should be careful in describing conclusions about reaction sequences from the form of the kinetic expression only (see Figure 2).

Figure 2. Kinetics Alone Cannot Explain Mechanism.

In principle, the different isotherms represent different distributions of adsorption sites, reflected by different variations of the heat of adsorption with coverage. Nevertheless, it was shown that even when assuming a wide distribution of heat of adsorptions, the resulting kinetics would be close to that obtained when assuming that the reaction took place only on the most active sites (Boudart *et al.*, 1984). This is the background for what was termed the "paradox of heterogeneous catalysis" (Boudart, 1956), stating that irrespective of the complexity of the catalytic surface, very often kinetic data can be represented by the Langmuir isotherm even though assumptions are far from reality.

It was shown that many reactions can be represented by simplified reaction sequences when it is possible to assume or identify a most abundant surface intermediate (MASI) and either a rate determining step (rds) or two irreversible steps (Boudart *et al.*, 1984). On this basis, simplified kinetic expressions can easily be derived.

Many early kinetic studies were influenced by uncontrolled mass and heat transfer restrictions. Such kinetic information was of little use for scale-up to industrial conditions or for determining reaction mechanisms. The interaction between catalytic reaction and diffusion was analyzed in depth (Froment *et al.*, 1979; Satterfield, 1970), including the complex impact on the selectivity

of catalysts. Today, most kinetic studies are carried out on catalyst powder in reactor systems, resulting in gradientless conditions. If experiments are to be carried out on catalyst pellets, it is essential to use full size pellets and that the conditions reflect industrial mass velocities and heat transfer rates.

The reaction engineering methods resulted in computer models capable of describing the complex interaction between intrinsic kinetics and mass and heat transfer inside the pellet and in the film surrounding the catalyst pellet. These models were included at an early stage in reactor engineering models for design (Kjær, 1972; Froment *et al.*, 1979).

In conclusion, kinetics and reaction engineering was developed almost to perfection 25 years ago, and reaction engineering was considered a mature field of science.

5.2.2 Breakdown of the Simplified Approach

The simplified approach has proven powerful for many industrial reactions. Nevertheless, irrespective of high sophistication of the mathematical modelling of chemical reactors, most work was still based on semi-empirical Langmuir-Hinshelwood kinetics. However, the simplified Langmuir-Hinshelwood approach breaks down in a number of situations. The "rds" as well as the "masi" may change through the reactor as a function of conversion or temperature. If it changes with conversion, it will also change inside the catalyst pellet, if the effectiveness factor is low.

Also, one may speculate about the meaning of * in the kinetic sequence. Surface science has provided information on the atomic scale, which may justify a more detailed approach to kinetics.

The size of the ensemble required may change with conversion and temperature. Also, the surface may be reconstructed under reaction conditions (Somorjai, 1991; Ruan *et al.*, 1992), depending on the composition of the gas at various positions in the reactor. The supported liquid phase catalyst for SO₂ oxidation for sulphuric acid may be considered as an extreme. The composition of the vanadium-potassium salt melt changes not only through the reactor, but also inside the catalyst pellet (Villadsen *et al.*, 1978).

Surface science (LEED, STM, *etc.*) has demonstrated that the structure of the adsorbed layer does not reflect random adsorption. On the contrary, the typical picture is the formation of island structures. Hence, the "mean field" assumption behind rate equations stating that the rate of a surface reaction between two adsorbed species is proportional with their surface coverages.

$$r = k \theta_A \theta_B \quad (4)$$

may reflect a simplified picture of the real situation. It may be more likely that reactions take place at the edges of surface islands (Ruan *et al.*, 1992; Lang *et al.*, 1992).

The reaction may also show oscillations on the surface as observed recently for CO oxidation on palladium (Ehsasi *et al.*, 1992). In conclusion, there are several reasons that the simplified Langmuir-Hinshelwood approach may break down (see Figure 3).

- ▶ rds/masi
- ▶ Required "ensemble" may change with conversion, temperature
- ▶ Catalyst structure
- ▶ "Mean field" assumption may not reflect situation

Figure 3. Breakdown of Simple Approach.

5.2.3 Kinetics and Surface Science — Micro-Kinetics.

The classical way of overcoming the situation described above is to use steady state kinetics with no assumption of a rate determining step. This approach easily leads to complicated equations with a number of constants difficult to determine in catalytic reactions. However, progress in surface science has provided strong tools for estimating the kinetic constants of the various reaction steps.

Work on ammonia synthesis (Stoltze *et al.*, 1985) is one example of bridging the gap between surface science at ultra-high vacuum and industrial conditions, which is based on a well-known process with a well-established rate determining step. For reactions with a less established basis, it may be helpful to use "*in situ*" techniques where the catalyst structure or the surface intermediates are studied under reaction conditions by exposing the catalytic reactor to radiation such as X-rays from Synchrotron radiation (for EXAFS), gamma-rays (from Mössbauer spectroscopy) and infra-red (for FTIR), *etc.* Recent work has shown examples of "direct" observation of surface reactions by STM and AFM.

The "*in situ*" approach is illustrated by the selective catalytic reduction over a vanadium/titania catalyst:

This reaction was studied in a FTIR cell (Topsoe *et al.*, 1991) working as a catalytic reactor. The FTIR-spectra indicated that the same adsorbed ammonia species are present on the surface, but no adsorbed NO-species. These observations were used at first to formulate a simple kinetic model for the SCR-reaction involving a rate-determining step of gaseous NO reacting with adsorbed ammonia being in equilibrium with the gas phase.

The model results in the rate expression (Topsøe *et al.*, 1991; Dumesic *et al.*, 1993a).

$$r = k_2 \cdot P_{\text{NO}} \cdot \frac{K_1 \cdot P_{\text{NH}_3}}{1 + K_1 \cdot P_{\text{NH}_3}} \quad (7)$$

However, more detailed studies (Dumesic *et al.*, 1993a) involving a variety of experimental techniques (TPD, TPR and *in situ* FTIR) lead to a more complex mechanism involving a change of the active site during the reaction sequence:

resulting in the following rate equation:

$$r = k_2 \cdot P_{\text{NO}} \frac{(k_2/k_3) K_1 \cdot P_{\text{NH}_3}/P_{\text{NO}}}{1 + (k_2/k_3) K_1 \cdot P_{\text{NH}_3}/P_{\text{NO}} + (k_2/k_3) \cdot k_{-2}/k_3 P_{\text{NO}} + K_1 \cdot P_{\text{NH}_3}} \quad (7)$$

which approaches first order kinetics at low concentrations. The nature of the two sites (* and $\rightleftharpoons$) and their transformations during the reaction cycle were identified by spectroscopic studies (N. Topsøe, to be published).

The input from surface science to micro-kinetics has made it meaningful to solve the steady state rate equations, which is possible with modern computer techniques (Dumesic *et al.*, 1987; Stewart *et al.*, 1993). Micro-kinetics analysis (Dumesic *et al.*, 1993b) of various reaction sequences is a useful tool to combine the kinetic data with information from related kinetic studies (TPD, tracer studies, *etc.*) with data from surface science (sticking coefficients, surface bond energies, *etc.*).

The pre-exponential factors for the elementary steps in the reaction sequence may be estimated by using transition state and collision theory, and thermodynamic consistency may be achieved by statistical mechanics for estimating equilibrium constants (Dumesic *et al.*, 1993b).

There is a need to assess the effects of surface nonuniformity directly by measurements of heats of adsorption versus coverage (micro-calorimetry). It would be beneficial to measure surface coverages and collect kinetic data simultaneously (Dumesic, 1993) to obtain information on the surface chemistry at steady state. It may help to identify the slow steps and it may also give an input to assess whether the "new field assumption", *e.g.* whether Equation (4) is applicable. It is also required to carry out isotopic tracer studies over a wider range of reaction conditions to allow a more quantitative analysis of data. This would provide a powerful tool to extract reliable rate constants (Dumesic 1993).

The micro-kinetic analysis should be considered a tool for providing a consistent description which may then form the basis for formulating more predictive rate equations for reformulation of the catalyst or for exploration of new reaction paths. The consolidation of spectroscopic kinetic and surface chemical data may provide a basis to study new catalytic cycles and new catalyst systems. This "micro-kinetic synthesis" (Dumesic *et al.*, 1993b) requires a multi-disciplinary effort and it may also serve to bridge the work in catalysis research groups with the work of highly specialized groups in surface science.

Figure 4. Micro-Kinetic Analysis.

5.2.4 Kinetics of "ppm Reactions"

The breakdown of the simplified approach is evident in particular for processes in which one component should be completely removed down to a ppm-level. These types of reactions are becoming more important in environmental processes such as selective catalytic reduction for removal of NO_x , catalytic combustion of carbon monoxide, hydrocarbons and other organic compounds in waste gas streams.

The oxidation of carbon monoxide on noble metals has been studied in detail on well-defined surfaces of platinum (Ertl, 1983). The reaction order changes from minus one at high CO coverages to first order at very low partial pressures of carbon monoxide, which reflects a change in reaction mechanism. The availability of oxygen was critical at high CO coverages, meaning that the inhibited adsorption of oxygen was the rds. At low CO coverages, the rate took place between adsorbed carbon monoxide and oxygen at the periphery of islands of adsorbed oxygen atoms with the surface reaction becoming the rds.

The simplified kinetics may well assist in establishing rate equations for the extreme conditions, but it may hardly lead to a description of the wide transition zone. Also, Langmuir kinetics cannot explain the oscillations observed recently (Ehsasi *et al.*, 1992) at very low pressures.

The interaction between diffusion restrictions and intrinsic kinetics becomes complex as the concentration of the reactants approaches zero (Rostrup-Nielsen, 1993b, in press). Table 1 shows how the impact on the effectiveness factor depends on the reaction order of the intrinsic reaction. A zero order reaction becomes diffusion limited, whereas a second order reaction of stoichiometric mixtures is determined by intrinsic kinetics. The relative rates have been estimated in Table 1 for a high conversion process assuming identical intrinsic rates at the reactor inlet (Rostrup-Nielsen, 1993b, in press). The actual rates were estimated assuming as an example $\theta=0.3$ for the first order reaction. It is demonstrated that wrong kinetics can lead to estimated rates at high conversion being more than one size of order wrong.

Table 1.
Relative Rates in High Conversion Processes (Rostrup-Nielsen, 1993b in press).
Same Intrinsic Rate at Reactor Inlet. $\eta = 0.3$ for first order reaction.

Intrinsic Reaction Order	-1	0	1	2
Thiele modulus Φ_L *	$1/C$	$1/\sqrt{C}$	-	$\sqrt{C}$
Effectiveness factor, $\eta < 0.3$	$a \cdot C \sqrt{k_{-1}}$	$a \sqrt{k_0 C}$	$a \sqrt{k_1}$	$a \sqrt{k_2/C}$
Lim $\eta \rightarrow$ for $C \rightarrow 0$	0	0	const.	1.
Reactor Inlet $X=0\%$				
— Intrinsic rate	1.0	1.0	1.0	1.0
— Actual rate	1.5	1	0.3	0.1
Reactor Exit $X=99\%$				
— Intrinsic rate	100	1	0.01	10^{-4}
— Actual rate	0.02	0.01	0.003	10^{-4}

$$* \quad \Phi_L = d_{p,s} \sqrt{k_i/D_{eff}} \cdot C^{(m-1)/2} = a \cdot \sqrt{k_i/C^{1-n}}$$

The change of reaction order with conversion can have substantial impact on the estimated catalyst volume as illustrated in Figure 5. The tentative conversion profiles are based on identical intrinsic rates at the reactor inlet. The first order reaction remains first order irrespective of diffusion restrictions, whereas the effective reaction order of the second order reaction will start at less than two (ca. 1.5) and increase to two as intrinsic kinetics take over.

Figure 5 also shows the effective rate for the SCR-reaction using the simplified mechanism (Eq. 7). The SCR-reaction with stoichiometric concentrations of reactants starts with a reaction order close to one and approaches second order, according to Equation (7). As mentioned above, the simplified model is not sufficient and kinetics should rather be expressed by Equation (9).

Figure 5. Tentative Concentration Profiles Assuming Different Reaction Orders.
(Rostrup-Nielsen, 1993a, in press) (dotted lines: no diffusion restrictions)

This emphasizes the need for reaction expressions covering a much wider range of gas compositions, in particular, with only traces of reactants being present. Steady state kinetics as shown in Equation (9) may be required to describe the complex transitions described in Figure 4.

5.2.5 Complex Reaction Schemes

Although very complex reaction schemes can be described by the state-of-art methods in reaction kinetics (Froment *et al.*, 1979), this is true mainly for reaction systems for which the intrinsic kinetics of the individual reactions are linear. In the case of nonlinear kinetics, there are still problems to be solved for reactions involving multi-component mixtures (Sapre and Krambeck, 1991). Nonlinear kinetics reflects the situation where the probability of reaction of any molecule depends on the other type of molecules in its surroundings. It means that lumped kinetics as applied in many hydrocarbon reactions may be misleading (Astarita *et al.*, 1992). In particular, this creates a problem for reactors not showing uniform behavior (*i.e.* other than plug flow, batch type). A better understanding of the kinetics of the conversion of multi-component mixtures is also required in view of legislation focusing on the control of the molecular composition of fuels.

5.2.6 Research Needs

The breakdown of the simplified approach in reaction kinetics may not be critical to conventional reactor design, but it may well become important for future industrial practice because of high demands to complete conversion and maximum selectivity caused by environmental requirements.

Micro-kinetic analysis may provide a useful tool for a more detailed kinetic description. It may also solve the problem of the rds/masi changing with conversion by giving meaningful input to steady-state kinetics.

However, there is a need for more research into the methods and underlying theories. Collision and transition state theories may not be sufficiently advanced to estimate kinetic parameters for all the chemical processes on the catalyst surface (Dumesic *et al.*, 1992). There is a need to apply the micro-kinetic approach to important reactions in the energy conversion processes and to the "ppm" reactions in environmental catalysis to provide a better design basis and to explore new reaction paths. There is a need to study reactions rather than characterize sites.

So far, micro-kinetic analysis has been based mainly on the assumptions of a "mean field" and a well-defined reaction site. Some attempts have been made to include ordered lattice structures in a classical adsorption model, but more work is required (Alstrup *et al.*, 1987). As an alternative, Monte Carlo simulations of surface reactions (Alstrup *et al.*, 1987; Deem *et al.*, 1992) may include the complexity of surface chemistry and the violation of the "mean field" assumption. Much more work is needed.

Also, the micro-kinetic methods should be refined to include the information that the active site (ensemble) may change with the temperature and the conversion (and composition of the gas phase). Work in this field is almost "nonexistent".

Surely, these improvements would lead to complex computer algorithms rather than simple rate expressions, but they may result in more predictive methods for reactor design.

There is a need to provide a better description of reaction schemes showing nonlinear intrinsic kinetics work to eliminate the risks involved in using "lumped kinetics".

5.3 REACTOR DESIGN

5.3.1 State-of-the-Art

The introduction of computer methods has allowed more precise designs of chemical reactors by using models to solve the heat and mass balances to various degrees of sophistication (Froment *et al.*, 1979). The one-dimensional pseudo-homogeneous models consider only plugflow in the axial direction and do not account for gradients around and inside the catalyst

pellets. The two-dimensional models include the radial gradients in the reactor as well, which is important when heat transfer to the reactor tube is decisive for the reactor design. At an early stage, it was possible to include the gradients inside and around the catalyst pellets in first order heterogeneous models (Kjaer, 1972). Two-dimensional heterogeneous models still require long computer time, but there are recent examples (Wagner *et al.*, 1992).

The mathematical modelling of the ammonia synthesis reactor (Jarvan, 1970; Dybkjaer, 1986) is one example of how it was possible with a first order heterogeneous model to analyze the feedback from industry. With this input and the precise knowledge of the reaction kinetics, pore structure, *etc.* it was possible to model a new radial flow converter having a very complex flow pattern, and to scale up directly to industry. Another example is the use of a two-dimensional pseudo-homogeneous model to analyze full-size monotube pilot runs on steam reforming and CO₂-reforming to provide a design basis for tubular reformers operating much closer to carbon limits, resulting in more economic manufacture of syngas (Rostrup-Nielsen *et al.*, 1993). A two-dimensional model was also applied to simulate thermocracking reactors with their very complex kinetics (Froment, 1992). This was coupled to modelling of the furnace taking into account the position of each burner and the flue gas flow pattern.

Although much more complex than fixed bed reactors, the knowledge of fluidized bed reactors has improved significantly over the last decade (Kunii *et al.*, 1991). "Fluidization is not such a black art and if we keep careful tab of our uncertainties and get the needed information for scale-up, we should be able to design fluidized bed successfully". The scale-up of the Mobil MTG-process to fluidized bed (Grimmer *et al.*, 1988) and the development of a fluidized bed isobutane dehydrogenation process (Sanfilippo *et al.*, 1992) are more recent examples.

It might then be concluded that chemical reactor engineering has become a mature field of science. This is not true. As an example, there are big problems related to the reactor engineering of reactions in complex multi-component mixtures. A lumped kinetic function is not a true kinetic equation, and therefore it cannot be used directly to analyze reactors other than plug flow and batch reactors (Astarita *et al.*, 1992).

Moreover, the challenges to chemical reactor technology have changed. The chemical process industry is faced with environmental requirements which will necessitate the design of reactors for much higher conversions and much better selectivities. This is necessary to minimize the release or removal of products to a degree which would not be economic without considering the environmental requirements. First, this situation opens room for new reactor concepts such as catalysis combined with separation or reactors utilizing transient operation. Secondly, the use of catalysis to clean flue gases and other waste streams requires catalyst shapes and reactor configurations which are not typical for the process industry. Safety concerns require better models to predict how reactors will operate in run-away or rapid shut-down mode.

The challenges to reactor engineering are summarized in Figure 6.

- ▶ Safety concerns require better models to predict how reactors will operate in run-away or rapid shut-down mode
- ▶ New reactor concepts to push conversion and selectivity
- ▶ Environmental catalysis to clean waste streams
- ▶ Reactor modeling of transient operation

Figure 6. New Challenges to Reactor Engineering

5.3.2 Separation Catalysis

By combining catalysis with separation, it is possible to push a thermodynamic equilibrium by removing one of the products. Also, it is possible to add one of the reactants at controlled rates.

Catalytic reactive distillation is practiced at large scale in the manufacture of MTBE (Dokerty *et al.*, 1992). Pure MTBE leaves the bottom of the reaction distillation column and a methanol/ C_4 azeotrope is leaving the top. The heat of reaction is used in the distillation. This principle might be used for other processes, where the temperatures for the distillation of the reaction can be made to coincide by adjusting the pressure. Reactive distillation may be attractive whenever a liquid phase reaction must be carried out with a larger excess of one of the reactants (*e.g.* alkylation). With reactive distillation, it may be possible to operate closer to stoichiometry (Dokerty *et al.*, 1992).

Condensation of a reaction product was utilized in a gas phase reactor for methanol synthesis (Boegild-Hansen *et al.*, 1991) to push the equilibrium, and it was possible to achieve almost complete conversion of the stoichiometric syngas into methanol.

Combining catalytic reactors with membranes has the potential to greatly improve several important processes (Westertorp, 1992; Hsieh, 1991), such as dehydrogenation of alkanes, the manufacture of styrene, and steam reforming of hydrocarbons. These endothermic reactions require high temperatures to push the chemical equilibrium. When using membrane catalysis, it would be possible to carry out the reactions at lower temperatures, withdrawing the hydrogen product through the membrane. So far, the dense (monolithic) palladium membranes appear too costly, although it has been claimed (Gryaznov, 1992) that the thickness can be reduced from the conventional 50 microns to 2.5 microns in a composite membrane with a corresponding high hydrogen flux of $10 \text{ m}^3/\text{m}^2/\text{h}$. Still, it is a challenge to materials science to make these thin membranes tight and stable.

The use of porous ceramic membranes (Westertorp, 1992; Hsieh, 1991) results in lower selectivity but larger permeabilities. Both reactants may diffuse through the membrane and there appears to be a relatively narrow window of operation, because the permeation rate of the component to be removed should be larger than reaction rate, whereas the permeation rate of the other reactants should be lower than the reaction rate.

This situation might be improved by zeolite membranes, introducing shape selectivity as a separation parameter (Geus *et al.*, 1991; Haag *et al.*, 1991). The ceramic membranes may also be used to control addition of, for instance, oxygen in partial oxidation reactions (Westertorp, 1992).

Other principles for separation catalysis (Westertorp, 1992) are chromatographic reactors, product selective adsorbents, and high temperature fuel cells (Vayenas *et al.*, 1991).

5.3.3 Transient Reactors

The use of periodic flow reversal in adiabatic fixed bed reactors for an exothermic reaction has the potential to eliminate complex heat transfer equipment inside the reactor at the same time as the reaction is equilibrated at low temperature (Westertorp, 1992; Matros, 1989).

For large-scale high pressure syntheses, such as ammonia and methanol syntheses, the transient principle results in too expensive equipment, because the required reactor volume is higher than in the conventional layout. Also, the principle means that the catalyst is poisoned from both ends. The principle appears advantageous for low pressure applications, such as catalytic combustion of waste gas, streams containing organics (Matros, 1989; Jensen *et al.*, 1991), and in some cases for sulphuric acid manufacture (Matros, 1989). The increased reactor volume may be compensated for by the elimination of an expensive feed effluent heat exchanger.

The application of pulse reactors utilizing higher selectivities in a transient region of the reaction is still a field to be explored.

5.3.4 New Catalyst Shapes

Traditionally, catalysts are supplied as pellets in the shape of spheres, cylinders, or rings. The catalyst shape is related to effective activity, pressure drop, and heat transfer as well, all parameters that are essential for reactor optimization. Small pellets result in high activity but high pressure drop as well. Monoliths have been introduced to solve this problem, in particular for low pressure processes, with auto exhaust catalysts as the classical example. For large scale applications, such as catalytic reduction of NO_x in power plants, square cross-section monolithic catalysts are usually installed. The flow pattern in monolithic catalyst beds results in a complex pattern for film diffusion control of the catalytic reactor (Ullah *et al.*, 1992). This is particularly true when monoliths have noncylindrical channels.

Development in materials science has made it possible to place the catalyst on construction materials forming "catalyzed hardware". It is tempting to place the catalyst on a heat transfer surface, thus eliminating the heat transport over the gas film at the internal tube wall in the conventional design. Catalyzed hardware for internal reforming in a high temperature fuel cell is one example (Rostrup Nielsen *et al.*, 1991), but the principle has potential for many other applications, such as methanation (Pennline *et al.*, 1979) and methanol synthesis (Curry-Hyde *et al.*, 1986). For selective partial oxidations, catalyzed hardware would mean a better temperature control and reduced "particle" size, both leading to higher selectivities at the same time as pressure drop will be low.

5.3.5 Complex Reactor Systems. Fluid Mechanics

The flow pattern in these reactors with new catalyst shapes can be very complex and far from the plug flow usually assumed in the reactor design models (Balling *et al.*, 1989). More input from fluid mechanics should be included in the design models as, for instance, applied in the Harwell program, FLOW 3D (CFDS, 1992). This is true also for trickle bed reactors. More knowledge is required to model these reactors, in particular on the "physics at the particle level". A list of research topics (Ng *et al.*, 1987) include studies using the method of Computer Aided Tomography to verify the simulated flow features at the particle level.

5.3.6 Heat Input to Endothermic Reactions

Heat transfer surfaces are expensive; hence, process economy can be improved by new means of heat transport. Also, hot reactor walls may contribute to reducing catalyst selectivity. In syngas manufacture, attempts have been made to replace the expensive fired tubular reformer with heat exchange reformers where flue gas or hot gas from an oxygen fired secondary reformer exchanges heat in an endothermic steam reforming process (Rostrup-Nielsen, 1993c, in press). This results in an increase of heat exchange efficiency from 50 to 80% of the fired duty (Stahl *et al.*, 1985). In dehydrogenation of isobutane, the heat transfer may take place by heating up the catalyst by the circulating fluidized bed (Sanfilippo *et al.*, 1992). More advanced ideas involve the circulation of an inert fluidized powder, blown through a stationary catalyst bed (Westertorp, 1992). Other ideas involve coupled reactions, for instance, combustion of hydrogen in a membrane dehydrogenation reactor supplying the heat for the dehydrogenation (Gryaznov, 1992).

5.3.7 Simultaneous Gas Phase and Catalytic Reactions

A number of reactions of potential interest involve simultaneous reactions in the gas phase and on the catalyst. Examples are catalytic combustion (Ahn *et al.*, 1986) for gas turbines, oxidative coupling of methane (Lunsford, 1993), and catalytic steam cracking (Albright *et al.*, 1983). Better modelling (Ahn *et al.*, 1986) is required of these complex reactions. Two-dimensional models are required to include the impact of radial temperature gradients on the kinetic severity function (Albright *et al.*, 1983) of the homogeneous reactions in steam crackers. This function describes the residence time temperature history of the reactants in a way that is consistent with reaction kinetics.

5.3.8 The Need for Explorative Process Engineering

It is important at an early stage to establish a preliminary flowsheet for a new catalytic process and to identify the constraints and the room for improvements and breakthrough. As an example, a future methanol synthesis (Rostrup-Nielsen, 1993a, in press) may only present a breakthrough if it is able to accept the normal CO₂-content (ca. 5% in the synthesis gas). Otherwise, the savings in the synthesis may easily be compensated for by the more expensive syngas manufacture, which at present amounts to ca. 70% of plant costs. Another example is the direct conversion of methane into a methanol or by oxidative coupling to ethylene. A preliminary flowsheet analysis shows that a minimum requirement to selectivity can easily be identified (Rostrup-Nielsen *et al.*, 1992). In simple terms, the direct methane conversion processes should have a CO₂-yield substantially below 20 C-atom% to represent a breakthrough compared to the indirect route.

There are several constraints in the reactor design for oxidative coupling (Dautzenberg *et al.*, 1992). A fluidized bed appears feasible to control heat transfer, whereas a multi-tube reactor would have impractical dimensions.

For oxidative coupling, it is also important to identify how to incorporate product separation and use of product ethane. As an example, one interesting approach has been the use of a fluidized bed reactor using the endothermic pyrolysis of recycle ethane as a cooling agent for the reaction (Edwards *et al.*, 1991).

5.3.9 Research Needs

The new challenges to reactor engineering require more research in a field which had been developed almost to maturity.

There appear to be several opportunities in coupling catalysis with separation and, in particular, for membrane catalysis there is an obvious need for more experimental work (Westerterp, 1992; Hsieh, 1991).

The low permeation rate should be improved by several sizes of order. Fouling problems must be overcome, and there is a need for better design to supply or withdraw heat to and from large-scale membrane reactors as well as a need to solve the difficulty of keeping pressure difference across the membrane to almost zero in large-scale industrial reactors.

The large-scale monolithic reactors, as well as trickle bed reactors, require a much better understanding of the fluid mechanics to provide better design models. This is true also for nonconventional applications of catalysis in connection with catalytic combustion for gas turbines, internal reforming in fuel cells, the application of catalyst inside engines, *etc.* In general, one would see the shape of the catalyst and the reactor approach each other, for instance, by the use of "catalyzed hardware". This calls for new reactor modelling.

Many important large-scale reactions in energy conversion involve syngas or coal gas with high partial pressures of carbon monoxide. These gases involve the risk of serious corrosion attack by metal dusting (Grabke *et al.*, 1987). This is a phenomenon which is only partly understood. More research is required into the mechanism to predict design criteria for various construction materials.

Reactor studies and innovative flow sheeting need to be included in the planning of fundamental studies on new processes in order to better identify constraints and room for breakthroughs.

5.4 RESEARCH RECOMMENDATIONS

(see also 5.2 and 5.3.9)

5.4.1 Reaction Kinetics

► Micro-kinetic studies

- Further development of methods to transfer information from a variety of surface science techniques into computer models of advanced reaction sequences.

► Nonlinear kinetics

- Development of better basis for describing the reaction of multi-component mixtures.

5.4.2 Reactor Design

► Separation catalysis

- Materials development
(stable Pd-membranes, ceramic membranes, zeolite membranes)
- New reactor concepts
(low temp. steam reforming, dehydrogenation of alkanes and ethylbenzene)
- Reactor systems for better temperature control

► Modelling

- Fluid mechanics and catalytic reactors
- Simultaneous gas phase and catalytic reactions
- Complex reaction networks in complex reactor systems
- Reactor performance at transient conditions

- ▶ **Construction materials**
 - Metal dusting corrosion in CO-rich gases
- ▶ **Innovative flowsheet analysis**
 - Encouragement to collaboration between science and engineering groups in order that constraints and room for improvements are identified at an early stage.

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Chapter 6

CATALYSIS FOR INDUSTRIAL CHEMICALS

J. E. Lyons and G. W. Parshall

6.1 INTRODUCTION

The chemical industry in the U. S. produces a spectrum of materials that find their way into all other industries and into products used in every household. The industry employs about 1.2 million workers. These individuals produce about \$140 billion worth of materials ranging from household detergents to pharmaceuticals to polymer-based plastics, fibers, and films.

A major segment of the chemical industry business is an array of about thirty organic chemicals and polymers that are used in applications that touch our lives daily. These chemicals are produced on a huge scale (Tables 1 and 2) and, collectively, are worth over \$60 billion. They are largely commodities produced to meet standard specifications and are sold primarily on the basis of price. Because the scale of production is so large, they are a major factor in the chemical industry's effort to develop manufacturing technology that meets the environmental expectations of modern society.

Catalysis is a major technology used in the manufacture of commodity chemicals. The chemicals produced by catalytic processes are highlighted in Tables 1 and 2. In addition to these organic chemicals and polymers, the two largest scale inorganic chemicals, sulfuric acid (88.6 billion ppy) and ammonia (34.0 billion ppy), are produced by catalytic processes. Catalytic technology is a key to both the economic competitiveness and the environmental acceptability of this major sector of the American economy. Looking to the future, catalysis can also play a significant role in sustaining this industry by providing the technology to use feedstocks other than petroleum and natural gas. Heterogeneous catalysis in particular will be critical in processes to utilize abundant raw materials like coal and renewable biomass-derived feedstocks.

In this chapter we seek to define research objectives in heterogeneous catalysis which, if achieved, will enable the production of major industrial chemicals with greater energy and feedstock efficiency and with improved environmental friendliness. We outline both current manufacturing processes and potentially advantageous advanced technologies that may improve the ways that commodity chemicals and polymers are produced. Based on input from experts in industrial heterogeneous catalysis, we identify potential technologies from which advanced manufacturing processes may be developed. These technological goals, in turn, define research objectives that may be appropriate subjects for consideration. The essential research needs are prioritized in Section 6.4.

Table 1.
1991 U. S. Production of Major Organic Chemicals
Products made by catalytic processes shown in boldface.

PRODUCT	U. S. PRODUCTION (billions of pounds)*	VALUE (\$ billions)**
Ethylene	39.23	8.23
Propylene	22.02	3.30
Benzene/toluene	18.58	2.41
Ethylidenedichloride/vinyl chloride	13.92 (11.7)	1.70
Methyl t-butyl ether	9.60	1.73
Ethylbenzene/styrene	9.22 (9.01)	2.16
Methanol	8.65	0.58
Terephthalic acid/dimethyl terephthalate	7.66	2.30***
Formaldehyde (37%)	6.43	0.71
p-Xylene	5.43	1.11
Ethylene oxide/glycol	5.24 (4.93)	2.36
Cumene/phenol/acetone	4.28 (3.49/2.13)	1.69
Acetic acid	3.61	1.19
Butadiene (polymer grade)	2.91	0.55
Propylene oxide	2.75	1.58
Acrylonitrile	2.65	0.93
Vinyl acetate	2.65	1.17
Cyclohexane	2.31	0.39
Adipic acid	1.56	1.09
n-Butanol	1.31	0.52
Isopropanol	1.30	0.47
Caprolactam	1.28	1.14
TOTAL	172.59	37.31

* *Chemical and Engineering News*, June 1992

** *Chemical Marketing Reporter*, November 1992

*** Industry sources

Table 2.
1991 U. S. Production of Major Synthetic Polymers. *(Sources as in Table 1.)*

Polymer	Production (billions of pounds)	Value (\$ billions)
Polyethylene* (low dens.)	11.58	3.94
Polypropylene	10.20	3.67
Polyethylene (high dens.)	9.22	3.13
Polyvinyl chloride	9.17	2.38
Polyester	5.52	3.64
Polystyrene	4.96	2.03
Nylon *	3.11	3.89
Phenolics	2.66	1.3
ABS	2.29	1.42
TOTAL	58.71	25.40

* Prepared partially by catalytic processes. Polymers in bold face made entirely catalytically.

6.2 COMMODITY CHEMICALS AND POLYMER INTERMEDIATES

Essentially all the highlighted chemicals in Table 1 are manufactured by well established catalytic processes. Some of the processes are very efficient in their use of energy and feedstocks and offer only modest incentives for research in catalysis. For example, the manufacture of acetic acid by carboxylation of methanol proceeds in nearly quantitative yield under mild processing conditions (Parshall, 1992). The source of both the methanol and the CO used in this process is synthesis gas (CO/H₂), which may be made from almost any hydrocarbon or, potentially, from biomass. Although improved catalysts may play a role in better processes for methanol and synthesis gas (Mills, 1993), only incremental opportunities exist for improving the synthesis of acetic acid or its derivatives. These improvements are likely to be achieved through advances in engineering rather than through fundamental studies in catalysis.

In contrast to the efficiency of the methanol carboxylation process, many other catalytic processes to make the chemicals in Table 1 offer great scope for improvement. Some of the potential incentives are:

- ▶ Improvement in utilization of a current feedstock, particularly petroleum. The opportunities for improvement are especially great for oxidation processes. Generally, an improvement in feedstock utilization yields environmental benefits such as reduced waste production and pollution.
- ▶ Substitution of an abundant or renewable feedstock. The benefits are most substantial for petroleum-based chemicals such as adipic acid and caprolactam.
- ▶ Reduction of severity of reaction conditions. The attendant reduction in energy consumption saves fuel and reduces the output of carbon dioxide, a major contributor to global warming.
- ▶ Reduced production of toxic, corrosive, or environmentally damaging chemicals and by-products. The incentives are especially great for reduction of halogen- and nitrogen-containing by-products in the manufacture of nitriles and CFC replacements.

Each of these areas is discussed below along with recommendations for technology development and research needed to capitalize on the opportunity.

6.2.1 Utilization of Current Feedstocks

The chemical industry has a huge infrastructure of process facilities based on petroleum feedstocks. Ultimately, these facilities are likely to be replaced by new generations of plants based on abundant or renewable feedstocks, but the cost in time and capital to replace the existing plants dictates that major changes in feedstocks have to occur gradually over a period of decades. (The conversion of vinyl monomer technology from acetylene to olefin feedstocks is instructive. Even though acetylene is expensive in both dollars and energy, some acetylene-based plants are still operating thirty years after the introduction of catalytic processes to make vinyl acetate and acetaldehyde from ethylene.) As a result, improvements in current processes through the use of better catalysts can lead to substantial savings in the use of feedstocks such as petroleum. These savings can support the competitiveness of American industry and promote energy independence.

6.2.1.1 Oxidation Processes

Probably the largest area for improved feedstock utilization is in the oxidation of hydrocarbons to alcohols, ketone, epoxides, and carboxylic acid derivatives, as illustrated in Figure 1. The yields of many oxidations, especially those based on free radical processes, leave much to be desired.

- ▶ The oxidation of cyclohexane to cyclohexanol and cyclohexanone, which are major intermediates for making adipic acid and caprolactam, generally proceeds in 70-80% yield. The subsequent oxidation to adipic acid using nitric acid as an oxidant gives very high yields, but produces nitrous oxide, an atmospheric pollutant, as a byproduct. The conversion of cyclohexanone to caprolactam by conventional technology yields massive amounts of ammonium sulfate as a low value coproduct.

Figure 1. New Catalysts Have the Potential to Simplify Current Multistep Processes to Single-Step, Energy-Efficient Transformations of Alkanes to Commodity Chemicals.

- The homogeneous catalytic oxidation of butane to acetic acid is still carried out on a very large scale even though the yield of the desired product is only 45-50%. Some formic and propionic acids are also recovered, but the production of carbon oxides as byproducts is substantial. They arise both directly from the oxidation and from the energy production for the extensive distillation needed to separate the carboxylic acids.
- The oxidation of butane to maleic anhydride also gives low (ca. 50%) yields in conventional heterogeneous catalytic processes but, in contrast to the acetic acid process, there is little recovery of other useful products. The main coproducts are carbon oxides.

- ▶ The oxidation of ethylene to ethylene oxide occurs in 85-90% yield, but the co-production of carbon oxides is substantial because the process is conducted on such a large scale.
- ▶ Another major class of industrial oxidations is the two-step heterogeneous catalytic production of either acrylic acid from propylene (overall yield > 85%) or methacrylic acid from isobutylene, also in high yield. The combined production of acrylate and methacrylate monomers from these catalytic technologies exceeds one billion pounds per year in the U. S. alone.

Other important large-scale oxidation processes (Table 1) include the heterogeneous catalytic oxidation of methanol to formaldehyde, the homogeneous catalytic oxidation of p-xylene to terephthalic acid, and the epoxidations of propylene to propylene oxide, which can employ either heterogeneous or homogeneous catalysts. Since these three processes are over 95% selective to the desired products, there is less room for improvement in their catalytic reaction chemistry than in those oxidations mentioned above.

In all the highlighted examples, catalyst improvements can lead to greater selectivity in the formation of desired products with attendant economic and social benefits. More selective conversion of hydrocarbon feedstocks clearly reduces the consumption of valuable hydrocarbon resources. It also reduces energy consumption in product purification, typically by distillation. The reduction in by-products minimizes waste disposal problems. When the by-product is carbon dioxide, as in the oxidation of butane to maleic anhydride, the global warming potential is reduced.

6.2.1.2 Advanced Oxidation Processes

Hydrocarbon Feedstocks — Because the cost of feedstocks can be as much as 60-70% of manufacturing costs, a very direct way to lower the cost of making a commodity chemical is to find a way to use a less costly raw material. The feedstocks for most commodity chemicals and polymers are olefins or aromatics. Much of the cost of these materials arises from the high temperature endothermic processes (reforming, dehydrogenation, cracking) to make them from less expensive saturated hydrocarbons, as shown in Table 3. As shown in Figure 1 above, many current processes start with an energy-intensive endothermic step that produces an unsaturated feedstock which, in turn, undergoes a reaction to introduce a functional group into the molecule.

Multifunctional Catalysts to Transform Aliphatic Feedstocks — Figure 1 shows potential new developments in multifunctional catalysts that could do both steps in transforming an alkane into a functionalized commodity chemical. One current system mentioned in 6.2.1.1 is that in which butane is dehydrogenated, oxidized, and cyclized to produce maleic anhydride in a single catalytic process. The formation of an unusually stable five-membered cyclic anhydride is among the driving forces for the technical success of this reaction. Although the reaction has been practiced commercially for some time, it is still being improved significantly (Stadig, 1992; Centi, 1993).

Table 3.
Production of Hydrocarbon Monomers for Fuels and Chemicals.

	MMM Lb/Yr*	Manufacture
Olefins		
Ethylene	39.2	Alkane Cracking
Propylene	22.0	Dehydrogenation
Isobutylene	(n.a.)	Dehydrogenation
Styrene	9.0	Dehydrogenation
Butadiene	2.9	Dehydrogenation
Aromatics		
Benzene	11.8	Reforming, dealkylation
Toluene	6.8	Reforming, hydroforming
Xylenes	6.5	Reforming
Ethylbenzene	9.2	Alkylation, reforming
Cumene	4.3	Alkylation, reforming

* *Chemical and Engineering News*, June 1992.

Acrylic and methacrylic acids are currently produced from relatively costly olefins (Figure 1). Recent work is pointing the way to multifunctional heterogeneous catalysts that promote direct exothermic reactions between the respective alkanes and dioxygen to produce these acids in a single step (Ai, 1992; Kuroda, 1992). Early results, though promising, have not yet produced the selectivities needed for a commercial process. Continued work could revolutionize this area of catalytic oxidation. It would be extremely valuable to understand the role of each of the many metallic ions added to the basic metal oxide structure of the oxidation catalysts (Gellings, 1992). New catalyst characterization tools like those discussed in Chapter 3 could be very helpful in this regard.

As with the acrylic and methacrylic acid processes, direct air oxidation of methane to methanol or formaldehyde would be valuable for conservation of both energy and hydrocarbon feedstocks. The direct oxidation would obviate the need for discrete steam reforming and methanol synthesis steps (Kennedy, 1992). Direct ammoxidation of propane to acrylonitrile has also been achieved

in modest yields on a laboratory scale (Centi, 1992). Development of practical catalysts for such one-step reactions will eliminate costly two-step routes with energy-intensive, endothermic, initial steps, and will produce energy as a valuable by-product of the exothermic one-step processes.

Alcohols from the Selective Oxidation of Alkanes — Alcohols such as methanol, ethanol, isopropanol, and *tert*-butyl alcohol are produced in enormous quantities today (Table 1). Direct oxidation of the light alkanes present in natural gas and in low-value refinery streams would be a valuable addition to current chemical process technology. Despite extensive research on reactions such as the selective oxidation of methane to methanol mentioned above, there are no commercially practical catalysts that have the required selectivity. Instead, alcohols are produced by traditional two-step processes in which an initial energy-consuming first step generates a reactive intermediate which is then converted to the alcohol in a second process step, as illustrated in Figure 2.

Methane to Methanol

Propane to Isopropyl Alcohol

Isobutane to t-Butyl Alcohol

Figure 2. New Catalysts Can Provide Direct Processes for Alternative Motor Fuels and Reformulated Gasolines.

Recent research, drawing on experience in enzymatic and homogeneous catalysis, provides clues to the design of heterogeneous catalysts that may have the necessary selectivity to make one-step oxidations of alkanes to alcohols commercially feasible. For example, "design catalysts" with oxo centers on the surfaces could be patterned after enzymatic species that are selective for alkane oxidation (Lyons, 1991). In another recent development, highly electrophilic metal centers catalyze selective oxidations such as the liquid phase oxidation of methane to methanol (Periana, 1993). Heterogeneous catalysts embodying these principles could exhibit enzyme-like selectivity while affording practical benefits, such as process simplicity, easy product recovery, and low corrosivity.

Other examples of multistep processes to produce commodity chemicals include the manufacture of phenol, ethylene glycol and propylene glycol. New processes for the direct hydroxylation of aromatic rings (Kitano, 1992; Kunai, 1988) to phenols and the direct dihydroxylation of olefins (Myers, 1987) with oxygen appear promising, although substantial advances in catalytic technology are required. The contrasts between the current multistep processes and the potential one-step technologies are dramatic:

Phenol Manufacture

Current: Benzene + propylene $\rightarrow$ cumene

Cumene $\rightarrow$ cumene hydroperoxide $\rightarrow$ phenol + acetone

Potential: Benzene + dioxygen $\rightarrow$ phenol + energy

Propylene Glycol Manufacture

Current: Isobutane $\rightarrow$ *tert*-butyl hydroperoxide (TBHP)

Propylene + TBHP $\rightarrow$ Propylene oxide $\rightarrow$ Propylene glycol

Potential: Propylene + dioxygen + water $\rightarrow$ Propylene glycol

Oxidative Dehydrogenation — Although the development of simple one-step functionalization processes like those described in the preceding paragraphs can have wide commercial application, it will always be necessary to generate olefins from aliphatic feedstocks. Olefins and arenes are among the most versatile classes of intermediates for making organic chemicals. Catalytic dehydrogenation is the current technology for conversion of paraffins to olefins, but it presents many challenges, especially for the less reactive lower alkanes. These dehydrogenations are highly endothermic and require that large quantities of heat be added to the reactors at very high temperatures. Equilibrium conversions are not high, and the elevated temperatures reduce selectivity. Loss of catalyst activity and coking are also significant problems.

Unlike simple dehydrogenation, oxidative dehydrogenation is not thermodynamically limited, because the reaction is driven to completion by oxygen as a hydrogen acceptor. Oxidative dehydrogenation is exothermic and, therefore, does not require the provision of large quantities of external heat to the reactor. The heat released in the reaction, along with the presence of oxygen, reduces coking. The oxidative dehydrogenation of butane to *n*-butenes has recently

been applied industrially, and attempts are under way to extend this technology to propane. Much more research is required, however, before oxidative dehydrogenation can be applied on a large scale to a wide variety of light aliphatic feedstocks. Active, selective catalysts that can operate under practical industrial conditions could provide breakthrough advances in light olefin manufacture. A special case with attractive potential is dehydrogenative coupling of methane to ethylene (Fox, 1993; Pereira, 1993).

Energy Production from Commercial Oxidation Reactions — Oxygenates make up most of the commodity chemical monomers that are produced from hydrocarbon feedstocks. Of the twenty largest volume monomers that contain elements other than carbon and hydrogen, sixteen contain only oxygen as the hetero element. Whenever a hydrocarbon and oxygen react, energy is produced, as in the industrial process chemistry shown in Figure 3.

Figure 3. Current Production of Oxygenates *via* Oxygen.

The energy produced in these reactions is very significant. Oxygen is an inexpensive oxidant but is difficult to control for selectivity because many of its reactions proceed by nonselective free radical processes. Industrial oxidation processes often use several steps to accomplish what could be done in a single step if a suitable selective catalyst was available, as illustrated in the examples above. Such single step processes could not only lower feedstock costs but could also supply the energy needs of a whole process and, in some instances, make the oxidation process a net exporter of energy.

6.2.1.3 Other Functionalizations of Hydrocarbons

In addition to the oxidations enumerated above, there are other ways to introduce functional groups into hydrocarbons that can have substantial economic and environmental benefits. Most are oxidative in character and can benefit from new developments in oxidation catalysis. The knowledge bases developed by studying reaction mechanisms and catalyst structures for oxidations should support innovation in catalyst development for direct functionalizations of the types described below.

One class of chemistry that is ripe for innovation in the short term is the introduction of fluorine substituents without the intermediacy of organochlorine compounds. There is a strong incentive to reduce the production and handling of organic chlorine compounds because of their environmental impact (Hileman, 1993), both in destruction of stratospheric ozone and in pollution of groundwater. At present, nearly all production of aliphatic fluorine compounds involves chloro compounds as intermediates. For example, most of the hydrofluorocarbons (HFCs) being developed as replacements for the ozone-destroying CFCs are made from chlorinated ethylenes. The leading refrigerant candidate, HFC-134a (1,1,1,2-trifluoroethane), is made from tri- or tetrachloroethylenes in multistep processes:

These processes are effective in producing the desired compounds, but are inefficient in that they produce huge quantities of HCl that must be recycled or neutralized. In addition, they require the production and handling of large quantities of chloroolefins.

A much more desirable approach to the manufacture of HFCs and fluoroolefin monomers would be based on the direct oxidative fluorination of hydrocarbons. This chemistry is illustrated by the oxidative fluorination of ethylene to vinyl fluoride:

This sort of reaction would closely parallel the oxidative chlorination of ethylene to vinyl chloride and the oxidative acetoxylation reaction used to manufacture vinyl acetate monomer. The current catalytic technologies for these latter processes would provide starting points for exploration of oxidative fluorination.

The replacement of organochlorine intermediates can be an important general topic in catalysis, going far beyond the interest in improved fluorocarbon syntheses. For example, many aromatic isocyanates are made by the reaction of aromatic amines with phosgene. Extensive work on the reactions of aromatic nitro compounds with CO indicates that it may be desirable to prepare aromatic isocyanates with these ingredients if the current catalysts can be improved (Parshall,

1992). Similarly, aliphatic isocyanates can be prepared by dehydrogenation of alkylformamides. In both cases, replacement of phosgenation by a CO-based process eliminates the hazards of handling phosgene and the environmental consequences of using organochlorine chemistry. Many other processes using organochlorine intermediates can be replaced by selective oxidation reactions like those described above. A prototypical example would be the direct oxidation of benzene to phenol. This reaction would replace the high temperature alkaline hydrolysis of chlorobenzene used by some phenol manufacturers.

Another class of reactions that will benefit greatly from innovations and improvements in heterogeneous catalysis is the introduction of nitrogen functionality into organic molecules. Nitrogen-containing compounds such as acrylonitrile, caprolactam, hexamethylenediamine, and arene diisocyanates are essential monomers for major polymers such as acrylics, nylons, and polyurethanes. In addition, simple amines such as aniline and dimethylamine are intermediates for a wide range of organic products including pharmaceuticals, crop protection chemicals, dyes, and pigments.

Most approaches to organic nitrogen compounds are very indirect. For example, aniline is made by a sequence of energy-consuming reductions and oxidations. First, N_2 is reduced to ammonia, then the ammonia is oxidized to nitric acid, which is used to nitrate benzene to nitrobenzene that, in turn, is reduced to aniline. Simplification of this sequence could greatly reduce the energy consumption involved in hydrogen generation and in repeated purifications of intermediates. One potential innovation would be the direct oxidative amination of benzene to aniline:

Development of catalysts for this kind of reaction could build on the catalysts for direct hydroxylation of benzene (Kitano, 1992; Kunai, 1988), mentioned earlier.

Nitriles derived from HCN are major building blocks for many important amines and carboxylic acids, for example:

Currently, HCN manufacture is carried out by the Andrussov process in which methane and ammonia are reacted over a precious metal catalyst at very high temperatures, at which HCN is the most thermodynamically favored product. A potentially significant advance would be the co-oxidation of ammonia and methane with a catalyst that would provide high yields even at moderate temperatures. Such a process would be closely analogous to the propane-based synthesis of acrylonitrile mentioned in Section 8.2.1.2 (Centi, 1992). Development of such processes for ammoxidation of alkanes would save energy and improve the economics for production of a range of nitriles and products derived from them.

Another major nitrogen-containing monomer is caprolactam, the building block for nylon-6 (Tables 1 and 2). It is made conventionally by an acid-promoted Beckman rearrangement of cyclohexanone oxime, in which the oxime unit is isomerized to an amide function:

Because a stoichiometric amount of sulfuric acid is used to bring about the isomerization, large volumes of dilute acid must be neutralized on completion. The low value coproduct, ammonium sulfate, must be dealt with. Development of a solid acid that would function as a true catalyst for the oxime rearrangement would be a major advance in this technology (Cusumano, 1992). The acid catalyst would have the same potential to improve the technology for manufacture of methacrylic acid and its esters. Currently, acetone cyanohydrin is hydrolyzed and dehydrated to form methacrylic acid with strong sulfuric acid. The reaction produces large volumes of dilute sulfuric acid containing ammonium sulfate. A catalytic solid acid might eliminate the dilution aspect as well as permit the recovery of ammonia from hydrolysis of the cyanohydrin. Developments in solid acid catalysis based on aluminosilicates and aluminophosphates could lead to major energy savings and reduced by-product formation (with concomitant environmental benefits) in both the caprolactam and methacrylate processes. Work on catalysts for these processes can build on research on solid acid catalysts for petroleum refining (Chapters 1 and 9).

A potentially valuable addition to the catalytic syntheses of polymer intermediates would be the development of catalytic chemistry to add ammonia or water to primary olefins or dienes in anti-Markovnikov fashion (*i.e.*, with the NH_2 or OH substituent on the terminal carbon of the olefin or diene). Success in the addition of ammonia to 1,5-hexadiene would provide one of the best possible syntheses of 1,5-hexanediamine, key ingredient in nylon manufacture. It would avoid the need to make and hydrogenate adiponitrile, which is produced using HCN or acrylonitrile, both of which are made by high temperature processes involving large inputs of hydrocarbon or energy. A closely analogous objective would be the anti-Markovnikov addition of water to primary olefins to give primary alcohols, many of which are made by hydroformylation/hydrogenation today. A special case with large economic value would be the selective addition of water to butadiene to form 1,4-butanediol or tetrahydrofuran. Success in this reaction would replace the relatively unselective oxidations of butane or benzene currently employed.

The difficulties in attempting to catalyze the selective addition of water or ammonia to olefins should not be underestimated. The reactions are only marginally feasible from a thermodynamic viewpoint - conversions of less than 10% can be expected at 100°C . The equilibrium becomes much less favorable above 100° and is only modestly affected by increase of pressure. Normal acid catalysis gives almost exclusively the unwanted Markovnikov isomer with the NH_2 or OH substituent on a secondary carbon.

From the viewpoint of trying to develop catalysts for these useful addition reactions, industrial homogeneous catalysis can provide many helpful conceptual inputs. Coordination of an olefin to a cationic metal complex facilitates the addition of a nucleophile such as ammonia or water and may "steer" the substituent to the desired carbon (Knoth, 1975). Oxidative addition of the

N-H bond of ammonia to a low valent transition metal complex can give a hydrido metal amide that, under some conditions, can add the N-H bond across the C=C bond of an olefin (Casalnuovo, 1988). It is also known that radical mechanisms for the addition process (*e.g.*, HBr plus a radical initiator) can give the desired anti-Markovnikov additions to olefins. Concepts such as these, borrowed from homogeneous catalysis, can provide the basis for exploration of heterogeneous catalysts for olefin additions. Indeed, a good starting point for such studies may be "anchoring" homogeneous catalysts to solid support materials.

Given the mechanistic information available from homogeneous catalysis of addition reactions, these reactions may be good candidates to test the design of new catalytic materials. This topic may be a fertile field for collaboration between industrial scientists and their colleagues in the national laboratories and the DOE-supported university programs. Past industrial research in the area has been largely empirical, but the government and academic groups could bring many strengths in fundamental chemistry that would be needed for catalyst innovation.

6.2.2 New Feedstocks

The preceding sections have dealt primarily with processes to use hydrocarbon feedstocks more efficiently. These feedstocks derive principally from petroleum and natural gas, which are likely to be the dominant feedstocks for the chemical industry for the next 20-30 years. Because these carbon sources will become scarcer and more expensive, we must also look to alternative feedstocks that will be available for the indefinite future. Some obvious sources are coal, shale oil, and tar sands that are abundant in North America, although they suffer disadvantages in terms of being more difficult to process than the current feedstocks. Eventually, however, even these resources are likely to be exhausted or, at least, difficult to utilize economically.

Plant-derived materials, both oils and cellulose such as corn cobs, wood chips and bagasse (sugar cane residues), constitute carbon-containing feedstocks that are renewable by photosynthesis. These materials are referred to as biomass. Other forms of biomass that seem inexhaustible in the sense that they are produced constantly are the organic by-products of modern society like garbage, paper and plastic trash, and sewage sludge. Waste materials, both the cellulose and those of human origin, are particularly attractive to consider as feedstocks because they are cheap and widely available. The cost, apart from collection and transportation, is essentially equivalent to their fuel value if they were to be burned in a boiler or incinerator to recover their energy content as heat or electricity. The collection and transportation costs cannot be overlooked, however, because the sources such as farms and households are scattered, and collection systems are not always well developed. Another complication is that waste products such as garbage, trash, and sewage are heterogeneous materials. Sorting and preprocessing may be uneconomical as is often observed in recycling operations.

For economical processing of heterogeneous wastes, generic processes are required to obviate the need to sort the mixtures. Those available in the near term generally do not involve heterogeneous catalysis. Some examples are the collection of methane-rich gases from landfills and the acid-catalyzed hydrolysis of cellulosic wastes. The methane collection approach to produce a useful feedstock is being tested in a small facility near Denver in which landfill-

generated gases are converted to syngas which, in turn, is converted to diesel fuel (Mills, 1993). In the longer term, it may be more attractive to convert solid organic wastes to syngas directly by high severity reforming processes like those used for the gasification of lignite. The syngas produced from biomass (or coal or shale oil) by reforming is a versatile feedstock for the manufacture of fuels (Chapter 9) and chemicals. As discussed below, innovations in catalytic technology for the use of syngas can have a major impact on the production of industrial chemicals and polymer intermediates.

Another way to use biomass as a renewable feedstock is to produce crops specifically for chemical production. One historical example is the production of palm, cottonseed, and other vegetable oils as intermediates for the manufacture of soaps, detergents, and margarine. Another is the growth of grain and sugar cane for production of ethanol to be used as a fuel and as a chemical intermediate. In this example, the primary processing technology is fermentation. With both vegetable oils and fermentation ethanol, however, subsequent processing steps commonly involve catalytic reactions such as hydrolysis, hydrogenation, or oxidation. The catalysis of these specific reactions is well developed and does not seem appropriate for major research support.

6.2.2.1 Catalytic Processes Using Syngas

Synthesis gas (syngas), a mixture of carbon monoxide and hydrogen, is now produced from various carbon sources including methane and coal. As mentioned above, it can also be made from many abundant forms of biomass. Many current industrial processes use syngas as a basic building block for manufacture of commodity chemicals (Figure 4). All are highly optimized and very efficient. These processes, apart from methanol synthesis, utilize soluble catalysts.

Figure 4. Production of Major Organic Chemicals from Syngas.

The usage of homogeneous catalysts reflects the fact that carbon monoxide reacts with most transition metals to give soluble or volatile metal carbonyl derivatives. It has been extremely difficult to "anchor" catalytic complexes to a support so that the catalytic metal is not leached from the support during extended reaction periods. The "anchoring" of catalytic molecular complexes to insoluble supports is a major challenge in design of heterogeneous catalysts for reactions involving CO as a reactant.

Syngas, whether derived from fossil or renewable feedstocks, is an extremely versatile source of chemicals. Major industrial chemicals such as methanol, formaldehyde, and acetic acid derivatives are currently made in one or two steps from syngas. Potential catalyst improvements for methanol synthesis could make these processes even more attractive. Other potential industrial processes simply await improvements or inventions in syngas conversion. Figure 5 shows an array of oxygenated products that can, in principle, be made solely from syngas in reactions that have been demonstrated in the laboratory, but have not been commercialized on a significant scale. Some examples are production of ethanol and acetaldehyde by homologation of methanol and synthesis of ethylidene diacetate for conversion to vinyl acetate. Direct synthesis of ethylene glycol from syngas would have a substantial economic and energy conservation impact (Pruett, 1977). In all these cases, improvements in catalyst properties could lead to use in new economical, energy-conserving processes. In these reactions, as in the oxidative carboxylation processes discussed below, development of heterogeneous catalysts may be essential to provide catalysts with the chemical and physical properties needed for industrial application. Success would open the way to use of abundant or renewable feedstocks for production of some of the largest-scale chemical products made today.

Figure 5. Potential Product Network Based on Syngas.

6.2.2.2. Oxidative Reactions of Syngas-Based CO

Although most commercial technology utilizing syngas is reductive in nature, there are large opportunities for new chemistry based on oxidation of CO (Figure 6). Most of these opportunities are apt to involve multifunctional heterogeneous catalysts, somewhat analogous to the multifunctional catalysts for oxidation of hydrocarbons discussed earlier in this chapter. In fact, many of the oxidative processes for CO are likely to incorporate similar metal oxides as co-catalysts or catalyst supports.

Figure 6. Potential Commercial Processes Based on Syngas.

The oxidative reactions of CO and alcohols to give dialkyl oxalates and carbonates, as shown in Figure 6, are currently practiced commercially (Parshall, 1992). Ube Industries carries out the reaction of CO with 1-butanol and 1-butyl nitrite (as an oxidizing agent) in the presence of a palladium catalyst to give primarily dibutyl oxalate along with small amounts of dibutyl carbonate. Dialkyl carbonates can be made the major products with copper catalysts. Dimethyl carbonate, a substitute for the highly toxic phosgene in many reactions, is produced this way by Enichem. Both of these syntheses may be carried out with either homogeneous or heterogeneous catalysts. Most of the chemistry in Figure 6 has been demonstrated with soluble catalysts, but it seems likely that practical applications will depend on the development of multifunctional heterogeneous catalysts. The heterogeneous catalysts should reduce the corrosion problems that are associated with palladium chloride-based liquid phase systems and should simplify product separation from catalysts.

Newly designed catalyst systems can sequentially coordinate and assemble mixtures of reactants like those shown in Figure 6 (Lyons, 1991). Advanced catalyst design makes it possible to control the numbers and positions of the CO entities that will be oxidatively added to a hydrocarbon substrate. The practical challenge is synthesis of long-lived, active, selective catalyst species on the surfaces of useful supports. The supports may play a co-catalytic role in activating dioxygen or some other practical oxidant needed for a truly catalytic process.

Both for conventional syngas reactions and for promising new oxidative reactions of CO, we need better understanding of the interactions of CO with solid surfaces. Despite decades of work on the mechanism of the Fischer-Tropsch reaction (Hindermann, 1993) and on CO binding to metals, the sheer complexity of these processes prevents design of new catalyst systems. The challenge is especially great in oxidative carboxylations because exploration of these reactions has been limited and because two different kinds of catalysis (CO activation and oxidant generation) must interact constructively (Hsu, 1986; Lyons and Hsu, 1987). Fortunately, knowledge gained from studies of hydrocarbon oxidation catalysis should apply to oxidative carboxylation catalysis. The metal oxide catalysts discussed for C-H activation may be useful as active supports for metallic CO activation sites. A wide variety of organometallic species on metal oxide supports have been characterized (Zecchina, 1993), but this field of research seems very promising for enhanced understanding of syngas catalysis.

6.3 POLYMERS

As noted in Table 2, many of the largest scale polymers are produced by catalytic processes. Polyolefins are commonly made using supported organometallic catalysts related to the Ziegler-Natta catalysts first developed for such processes, but are far more efficient than the originals. Successive generations of olefin polymerization catalysts have improved in efficiency to the point that they no longer need to be removed from the finished product. Ingenious engineering has led to gas phase processes that rain out polymer pellets nucleated on individual catalyst grains. With the latest "single-site" catalysts being based on metal oxide-supported metallocene complexes, excellent control of molecular weight and tacticity is obtained. In many ways, the development of the olefin polymerization catalysts is a model of intelligent catalyst design based on mechanistic understanding, characterization of catalyst-support interactions, and understanding of process engineering requirements (Burdett, 1992).

Despite the economic value of polymers to the U. S. economy (about \$25 billion per year for the polymers in Table 2), research on polymerization catalysts is probably a low priority for the U. S. Department of Energy. Some factors in this conclusion are:

- ▶ The opportunities for energy and feedstock savings are small because polymerization processes commonly proceed in high conversion and nearly quantitative yield. There are, however, significant opportunities for energy and feedstock conservation in the manufacture of polymer intermediates, as discussed in Section 6.2.
- ▶ The environmental impact of the polymerization catalysts themselves is small, especially as chromium-based ethylene polymerization catalysts are replaced by new,

environmentally innocuous catalysts. There is still a desire to replace antimony catalysts used in the manufacture of polyesters, but this problem is being addressed by the chemical industry.

- The potential contribution to the competitiveness of U. S. industry is also small because the current processes are so efficient and because many U. S. firms continue to enhance this technology.

The major areas in which research could assist U. S. polymer producers lie in improved process technology for polymer intermediates (Section 2) and in characterization of metal oxide surfaces that may be used as catalyst supports. Many of the characterization issues discussed in Chapter 3 are just as relevant to polymerization catalysts as to the catalysts used in petroleum refining. Fundamental information leading to the understanding of surface phenomena on "real catalysts" could be valuable. Researchers in surface characterization should be alert to the implications for polymerization catalysis. In a complementary sense, knowledge of the chemistry of supported organometallic polymerization catalysts should be transferable to the design of catalysts for many other applications.

6.4 SUMMARY OF RESEARCH NEEDS

The catalytic developments that can have the greatest impact on production of industrial chemicals fall into two major categories:

- Selective oxidation and functionalization of hydrocarbons. Because the feedstocks for these processes are largely petroleum and natural gas, this objective is short-term in the sense of benefiting the chemical and petroleum industries in the next 20 to 30 years.
- Heterogeneous catalysis for reactions based on synthesis gas. These catalyst developments are longer-term because they use a feedstock that can be derived from abundant or renewable carbon sources, such as coal and biomass. However, success in this area can also have near-term impact because synthesis gas is currently available from petroleum and natural gas. Major opportunities exist in the development of chemistry and technology for oxidative carboxylation reactions.

The potential energy/feedstock impact of success in these two areas can be estimated. Success in the targets identified for selective oxidation catalysis may lead to savings of about 8.5 million barrels of petroleum and natural gas liquids per year. This amount is about one percent of the annual total petroleum used for chemical feedstocks or about half as much petroleum as the U.S. consumes in one day for all purposes. While the chemical feedstock savings are small compared to those attainable in the fuels area, the economic impact would be substantial. [Basis for the estimate: The oxygen-containing chemicals in Table 1 consume about 50 billion ppy. of hydrocarbon feedstocks. An average 5% yield increase in each of their manufacturing processes would save 2.5 billion ppy. of petroleum and natural gas. Some processes, such as the oxidations of butane and cyclohexane, might afford 10% yield increases. Others, like the

oxidation of p-xylene to terephthalic acid, are unlikely to give yield increases above 2%. A 5% average seems plausible.]

In contrast to the modest feedstock savings realistically expected from improved catalysts for hydrocarbon oxidation, larger but more speculative savings may be forecast for catalyst developments in the use of syngas or bio-derived feedstocks. It may be reasonable to set a goal of annually shifting 1% of the chemical industry's feedstock needs from petroleum to syngas or renewable feedstocks. Substituting abundant or renewable raw materials for an additional 8.5 million barrels of petroleum each year would have a large cumulative effect. Over the course of four decades (a reasonable transition period for such a large and varied industry), the feedstock savings would rise to about 5% of total U.S. petroleum consumption.

The research required in both areas centers on better understanding of metal oxides, both as oxidation catalysts in themselves and as supports for metals. Catalyst-support interactions may be critical in the metallic catalysts.

6.4.1 Selective Oxidation and Functionalization Catalysts

We recommend that highest priority be given to the synthesis, characterization, and catalytic evaluation of catalysts for the selective oxidation of hydrocarbons, especially alkanes, with air or oxygen. In particular, greater understanding is required in the catalytic functions that lead to activation of dioxygen and of hydrocarbons.

Selective oxidation catalysis can yield major savings in energy and feedstocks, both through improvements in existing processes such as the oxidation of butane to butadiene or maleic anhydride, and through invention of new processes to convert hydrocarbons to functionalized organic compounds. Many current hydrocarbon oxidations operate by free radical mechanisms that are relatively unselective. We know, however, that metalloenzymes and analogous homogeneous catalysts can attain high selectivities by generation of unique oxidants such as $M=O$ species, and through controlled binding of the hydrocarbon substrate. Similarly, there is a large body of empirical knowledge about existing catalysts that can be used to develop new catalysts if the necessary scientific foundation can be developed. For example, the catalysts developed by Sohio for the ammoxidation of propylene to acrylonitrile are basically bismuth molybdates, but the optimum commercial catalyst contains traces of many other metal ions that contribute to its stability and selectivity. Understanding the role of these additives could go far toward intelligent design of new catalysts. Interestingly, the catalyst-support interactions appear to be just as important for metal oxide-supported metal oxide catalysts as for oxide-supported metals (Owens, 1993).

Integrating insights from diverse sources with new information from structural and computational studies of metal oxides can yield major benefits in the development of new, environmentally friendly processes that will conserve energy and feedstocks. Some examples of replacing complex, multistep processes are the following:

[HFC-152a is an attractive replacement for ozone-depleting CFC's in applications including refrigeration and air conditioning.]

6.4.2 Catalysts for Synthesis Gas Reactions

We recommend exploration of heterogeneous catalysts for reactions of carbon monoxide, especially the relatively undeveloped oxidative carboxylation reactions.

Syngas (CO and H₂ in varying proportions) can be produced from a wide variety of carbon sources and is now used extensively in manufacture of major industrial chemicals such as methanol, acetic acid, and the oxo alcohols. Broadening the process applications of syngas to a wider range of organic chemicals could lead to a "syngas economy" for the chemical and petrochemical industries. Developing the catalytic technology for a syngas economy would ease the transition from petroleum and natural gas feedstocks to abundant and renewable feedstocks, because the "downstream" process technology would be the same once the syngas is generated. In the conversion of syngas, it is preferable to produce oxygenated fuels/chemicals with a value exceeding that of the corresponding hydrocarbon products. This strategy increases overall thermal efficiency and provides products specifically responsive to future needs for high efficiency and environmental concern.

Development of heterogeneous catalysts for CO reactions is a critical step in the transition to the syngas technology. Most current CO-based processes, apart from methanol synthesis and the Fischer-Tropsch technology, employ homogeneous catalysts. These soluble catalysts have many virtues, but difficulties in separating the catalysts from product mixtures limit the range of products to which they can be applied. Development of heterogeneous catalysts, which have many advantages in terms of process engineering, would facilitate the conversion to syngas as a feedstock. Because of the remarkable ability of CO to convert transition metals to soluble or volatile species, the "anchoring" of catalytic species to supporting materials presents special challenges as well as significant opportunities. Fortunately, the base of mechanistic information on heterogeneous catalysts for CO reactions is growing rapidly (Hindermann, 1993).

Oxidative carboxylation reactions, in particular, offer opportunities for innovative new processes that would conserve energy and feedstocks. For example, the oxidative carboxylation of alkanes to esters would provide new classes of economical and efficient oxygenates for fuels.

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Chapter 7

CATALYSIS FOR ELECTRICITY APPLICATIONS

G. Alexander Mills and Jens Rostrup-Nielsen

7.1 OVERVIEW: SCOPE, STATUS, ENVIRONMENTAL ISSUES, RESEARCH OBJECTIVES

This chapter defines the status and opportunities for new catalytic technology, to provide more efficient and economic generation of electricity from carbonaceous fuels and, particularly, to provide enhanced environmental protection. Not included in this discussion are fuel cell catalysis and non-catalytic research by DOE and others to improve efficiency by (hot) stack gas cleanup or turbine improvements.

While the application of catalysis to electricity generation is relatively recent, it has assumed growing importance and shows much potential. A driving force for the provision of new technology is increasingly severe requirements for environmental protection, particularly those limiting emission of oxides of nitrogen and sulfur in combustion gases. Carbon dioxide emissions pose a serious concern as well, and may assume major importance in the future.

Electricity generation and use represent a major segment of our energy activity. About one-third of the world's energy fuels are consumed in generating electricity, and this proportion represents a wide variety of fuels. In contrast, virtually only one fuel, petroleum, is used in the transportation energy sector. A variety of fuels offers a range of important technical opportunities, including the chance to use our non-petroleum resources — coal, gas, and biomass. Another significant difference between the electrical and transportation sectors is the difficulty in importing electricity, except from Canada, compared to the relative ease of shipping liquid petroleum from abroad. Two-thirds of the fuels' heating value is lost in the generation of electricity; hence, there is an important opportunity to improve energy efficiency.

New U.S. government regulations are having a major impact on technology used by utility companies. Compliance with some new regulations faces industry with profound economic consequences. Currently, in some states a utility company must purchase electricity from an outside source if this is cheaper than electricity that would be generated in a newly constructed plant. Also, electrical transmission companies are required to transmit electricity through/over their systems in return for a fee for their services. This is done to provide the public with the most economic electricity available.

New environmental regulations, driven by a desire for environmental improvements, are causing profound *technological* changes. The Clean Air Act Amendments of 1990, CAAA, are broad-based, applying not only to acid rain (the primary target) but also to ozone nonattainment, air toxics, and visibility. Electric utilities, mobile and industrial sources are all subject to emissions

control provisions within the CAAA. The electric utility industry is most affected in the near term by the reduction of SO₂ and NO_x, required to meet acid rain provisions (Title IV), and by control of NO_x for ozone nonattainment (Title I). However, provisions for air toxic emissions in Title III and visibility in Title VIII may have significant impacts, especially in the longer term.

The CAAA requires reduction of SO₂ to half of 1980 levels. By the year 2000, annual SO₂ emissions must be reduced to 8.5 million tons and placed under a permanent emissions cap. During the first phase, 1995-9, the highest SO₂ emitters, a group of 110 power plants, must limit their emissions to below 2.5 pounds per million Btu of fuel. Beginning in the year 2000, all remaining generating units greater than 25 MW in size will be affected (Torrens *et al*, 1990) with emissions reduced further. The impact of the CAAA on utilities presents a host of new technical challenges, introduces business risks, changes the cost of electrical generation, and calls for organizational responses. The costs of clean air compliance are major in magnitude. The costs of acid rain control requirements are estimated to approach \$7 billion annually, once fully implemented in the year 2000.

There are fundamental differences in the chemistry of NO_x and SO₂ and consequent options for their pollution alleviation. NO_x is derived in part from nitrogen contained in the fuel and in part from the reaction between air nitrogen and oxygen in the high temperature combustion chamber. While low-NO_x burners can minimize NO_x formation, at present the main NO_x control technology is achieved by both catalytic and non-catalytic reduction of NO_x by NH₃ in stack gas treatment. Sulfur oxides are derived from sulfur in the fuel. Sulfur must be removed at some point, since sulfur is objectionable in air in any form. Two approaches have been used to control emissions: pre-combustion fuel cleaning or post-combustion stack gas cleaning.

Increasingly stringent environmental regulations have prompted a fundamental change in the approach to pollution control. Specifically, this represents a change from catalytic remediation of pollutants, produced in the present technology, to the devising of a new catalytic process that prevents or minimizes pollutant formation. Research objectives for catalytic research relating to electricity generation include the provision of new and improved technology:

- ▶ To achieve pollution abatement not only by removal of pollutants but also by catalytic processes that prevent pollution formation.
- ▶ To achieve higher energy efficiency in electricity generation.
- ▶ To achieve more economic generation (lower plant operating and particularly plant investment costs).
- ▶ To make available economical processes for use of the abundant national fuel resources - coal, gas, biomass.

7.2 PRODUCTION OF CLEAN FUELS

7.2.1 Clean Gaseous Fuels

7.2.1.1 IGCC - Integrated Gasification Combined Cycle

There is growing interest in manufacturing a clean fuel gas from solid fuels to be used for generating electricity in an Integral Gasification Combined Cycle system (Figure 1). In IGCC,

Figure 1. Integrated Coal Gasification Combined Cycle. (Alpert, 1991)

BFW = boiler feed water

gasification consists of reacting coal, biomass, or petroleum coke with steam and oxygen or air at a high temperature to form a fuel gas, consisting mostly of CO and H₂. The gas is cooled and purified. In the combined cycle plant section, the highly purified gas is burned and the hot combustion gas is routed through a gas turbine to generate electricity. Then, the residual heat in the exhaust is recovered in a steam boiler for use in a conventional steam turbine generator to produce additional electricity. A promising alternative is the use of the purified gas to generate electricity, employing a catalytic fuel cell, a technology not included in this study because it is the subject of a separate forthcoming Research Needs Assessment by the Office of Program Analysis.

IGCC has important environmental and energy efficiency advantages.

- The H₂S and NH₃ in fuel gas can be removed to a greater extent than is practical for removal of SO₂ and NO_x from combustion gases which, because of the addition of nitrogen introduced in combustion air, are much larger in volume. In IGCC operations, sulfur removal levels of over 99% have been demonstrated on a plant

scale. Emissions are well below the existing NSPS emission standards of 90% removal for new plants.

- ▶ Interest in IGCC is heightened by increasingly stringent environmental restrictions, particularly those regulating sulfur emissions.
- ▶ The clean gas is highly suitable for use in high-efficiency gas turbines. Electricity is produced with greater energy efficiency than in pulverized coal-fired plants. Hence, CO₂ emissions are reduced.
- ▶ Essentially any solid carbonaceous feedstock can be used in modern gasification plants.
- ▶ Combined-cycle plants can be composed of standardized modules, sized for large and small utilities.
- ▶ Studies have shown the possibility of capturing and sequestering CO₂ from IGCC by adding shift and sequestering stages to process flow sheets. New imaginative approaches are needed.
- ▶ Opportunities exist to develop catalytic technologies to co-produce electricity and fuels/chemicals and improve gas purification processes.

Of particular importance in advancing technology to commercialization is the development of several improved gasifiers that have been demonstrated in the IGCC operation. These are summarized in Table 1.

What will be the world's largest IGCC plant (Commission of European Communities, 1992) in Puertollano, Spain, is scheduled to begin operations in 1996. It will produce 305 MWe at 45% efficiency with emissions of SO₂ of < 10mg/Nm³ and of NO_x of < 60 mg/Nm³.

Table 1.
Integrated Gasification Combined Cycle Demonstration Plants

Name	Demonstration Location	Tons of Coal per Day	MW Electricity
Texaco	California	1200	135
Dow	Louisiana	1700	160
British Gas/Lurgi	Scotland	500	
Royal Dutch/Shell*	Netherlands	2000	250

* Construction completed July 1993, Fall start-up. (Salzman et al., 1992)

Additional IGCC variations will be demonstrated under the DOE Clean Coal program, funded jointly by industry and DOE (Table 2). Of further interest is the IGCC plant planned for Delaware. This facility will charge about 2400 tons per day of high-sulfur petroleum coke to a Texaco gasifier and generate 125 MWe electricity. It has also been announced that a 260 MW_e IGCC plant based on coal will be built in Florida. In addition, an agreement has been signed to install the IGT U-Gas process in China.

It is fair to say that IGCC is a combination of modern technology process units, well engineered to meet new needs. There are opportunities to provide further improvements using the advanced catalytic processes discussed below. Opportunities also exist to improve processes for catalytic conversion/removal of H₂S and NH₃ from syngas.

7.2.1.2 Co-Production of Electricity and Chemicals/Fuels

In an IGCC plant in which a purified mixture of CO + H₂ is manufactured, it may be advantageous to use part of this gas to generate electricity and part to manufacture chemicals/fuels such as methanol, ammonia, or hydrogen, according to recent proposals. Such a facility has been termed a *powerplex*, EPRI, 1992. Coal gasification is required to produce a mixture of CO and H₂, known as synthesis gas (syngas). Synthesis of chemicals and fuels from syngas has had a long industrial history. At present, this includes production of methanol and the large-scale production of hydrocarbon transportation fuels by SASOL in South Africa. Various technological suggestions have been advanced for the co-production of chemicals/fuels and electricity, designed to take advantage of the IGCC situation. Coal-based power plants are capital intensive. An advantage for IGCC co-production plants would accrue from operating the gasifier at capacity all the time and, when electricity needs are low, manufacturing methanol with part of the syngas. This methanol can be marketed or used for "peak shaving" generation of electricity.

Economic evaluation studies, carried out for EPRI, have led to the design of a plant that is integrated to both electricity and methanol production (Fluor, 1982; EPRI, 1987; Chem Systems, 1990; Houston LP, 1992). Included is base load to cycling operation, that is, full electricity to full methanol production. The potential economic advantage of co-production of electricity and methanol is significant. It is projected that the cost of electricity would be lowered by 10% (Kern *et al.*, 1991; Bauman *et al.*, 1991). In other studies, the co-production of electricity and ammonia and urea is being explored, with an emphasis on environmental benefits (Bradshaw and Wetherington, 1991). Interest in IGCC is heightened by the recognition that the price of gas could increase greatly, whereas coal prices are expected to be relatively stable.

A recent study (Houston L&P, 1992) concluded that co-production of chemicals such as methanol or urea can result in significant reduction in the cost of electricity, if the selling price of chemicals escalates at a rate greater than inflation. The price of methanol and urea are tied closely to the price of natural gas. It is also reported that a better knowledge of the integration of gasification plants with combined cycle power generation holds the potential for further improvements and capital cost savings, making IGCC and co-production more competitive in the future. A highly integrated plant in which the combustion turbine compressor supplies one-

half the air required for the oxygen plant has been estimated to produce electricity at 40-45 mills/kwh (EPRI, 1993). Opportunities for new catalytic technology to improve integration of catalytic synthesis of fuels/chemicals into IGCC operations are discussed below.

Table 2.
DOE Clean Coal Technology IGCC Projects
(Various stages of development, 1993)

Project	Technology
Wabash River Coal Gasification Repowering Project West Terre Haute, Indiana	Destec, slurry feed, oxygen-blown, two stage entrained flow (entrained flow, slagging first stage and non-slagging second stage) gasifier (265MW)
TAMCO Power Partners Toms Creek IGCC Demonstration Project Coeburn, Virginia	IGT/Tampella U-Gas, air-blown, fluidized bed with zinc titanite and ceramic candle filter hot gas clean up (107 MW/55 MW net coal based)
Sierra Pacific Power Piñon Pine IGCC Power Project Reno, Nevada	MW Kellogg, air-blown fluidized-bed gasifier with limestone injection and zinc ferrite and ceramic candle filter hot gas clean up (80 MW)
Air Products Commercial Scale Demonstration of Liquid-Phase Methanol (LPMEOH) Process Daggett, California, or other site	Texaco, slurry feed, oxygen-blown, single state entrained flow gasifier providing synthesis gas to the LPMEOH system (150 tons/day)
Combustion Engineering IGCC Repowering Project Springfield, Illinois	ABB CE dry feed, air-blown, entrained bed, gasifier with limestone injector and moving-bed zinc ferrite hot gas clean up (65 MW)
Tampa Electric Company IGCC Demonstration Project Lakeland, Florida	Texaco, oxygen-blown, entrained-flow gasification system with moving-bed solid sorbent hot gas clean up (260 MW)
Camden Clean Energy Project IGCC Demonstration Project Camden, N. J.	British Gas/Lurgi Fixed Bed Oxygen-blown Gasifier High Sulfur W. Virginia Coal (480 MW)

7.2.1.2.1 Slurry-Catalyst Synthesis

Methanol synthesis is highly exothermic. In order to prevent harmful temperature increases, low conversion per pass is accepted, necessitating costly recycling of unreacted gas. The use of catalysts slurried in inert liquid provides a concept of heat management, which has been

extensively tested in a 10 year, \$25 million program. During this time some 7000 hours of operation were carried out in a 10 ton-per-day plant in La Porte, TX (Brown *et al.*, 1990). An advantage of about 10% has been estimated for liquid phase methanol synthesis; LPMEOH, using syngas from coal, over conventional vapor-phase technology.

Once-Through Synthesis

In this process, all or part of the syngas is passed through a bed of methanol synthesis catalyst on a once-through basis, that is, without recycling unreacted CO and H₂. The unreacted syngas then goes to the combustor. In this way, methanol synthesis avoids the cost of recycling (EPRI, 1987). A once-through operation, using a slurry-catalyst reactor at the IGCC plant at Cool Water, CA, has been proposed. The process is shown in the flow diagram in Figure 2 (Brown *et al.*, 1990).

Co-Production of Methanol and Dimethyl Ether

Much interest has been aroused by novel technology (Brown *et al.*, 1991; Hansen *et al.*, 1991; Lee, 1992; Lewnard *et al.*, 1993) being developed for the conversion of syngas to a mixture of methanol and dimethyl ether in a single reactor in which the following reaction sequence occurs:

IGCC/METHANOL CO-PRODUCTION POWER PLANT WITH LOAD FOLLOWING CAPABILITY

Figure 2. IGCC/LPMEOH Methanol Production Flow Diagram. (Brown *et al.*, 1990)

A combination of two types of catalysts makes this reaction sequence possible. The water gas shift, WGS, reaction

can also be carried out simultaneously, using a water gas shift catalyst. Then the overall net reaction is

Co-production of methanol and dimethyl ether offers an opportunity for increased syngas conversion per pass. The effect of the combination of these reactions is essentially to avoid unfavorable thermodynamic limitations for methanol synthesis. Methanol, a product of the first reaction step, is consumed in the second reaction, forming dimethyl ether and water. The water is used in the third reaction, generating carbon dioxide and hydrogen, the latter being used for methanol synthesis. Thus, the product of each step is a reactant for another, creating a strong driving force for the overall reaction (Hansen and Joensen, 1991; Brown *et al.*, 1990; Lee, 1992). The slurry catalyst reactor system has been tested for conducting the simultaneous synthesis of MeOH, DME and WGS. Process development has focussed on the use of coal-derived syngas that is rich in CO (Brown *et al.*, 1990).

Improved Synthesis Catalysts

Intensive research has resulted in a wide variety of improvements in catalysts and process systems for synthesis of methanol and related chemicals/fuels (Mills, 1993). It is expected that improved catalyst systems can be incorporated in the co-production of electricity and chemical manufacturing.

7.2.1.3 Catalytic Gasification

Manufacturing synthesis gas from methane is a highly developed catalytic process, used internationally for the large-scale production of chemicals. Syngas production by gasification of coal has been used extensively. Tennessee Eastman currently uses the process to manufacture methanol, and it is also used at Great Plains, North Dakota, to produce methane. Coal gasification, the partial combustion of coal in the presence of steam, is a non-catalytic process carried out at temperatures which range from about 1000 ° to 1500 ° C. Various attempts have been made to devise a practical process that could operate at lower temperatures.

It has long been known that alkali hastens the critical slow reaction

The chemistry of base-catalyzed carbon-steam reactions involves the formation of hydrogen and a phenoxide whose structure has been determined (Mims and Pabst, 1982). The phenoxide can be decomposed at low temperatures, using a transition metal oxide as catalyst (Heinemann and Somorjai, 1992; Pereira *et al.*, 1990). Mixtures of alkali and transition metal oxides can serve as catalysts for continuous steam gasification of coal or chars at temperatures below 600°C. Mixtures of alkali and alkali earth oxides are almost as effective as the alkali transition metal oxides, and they are not easily sulfur poisoned. Electron microscope studies show that alkali compounds attack carbon in the presence of water in a solid edge recession. Alkali transition metal oxides form a low melting eutectic, resulting in a liquid film that hastens the gasification by edge recession.

Catalyst mobility can be important for reactions involving a solid reactant. Providing catalyst mobility for effective catalyst performance is a new concept. Extensive laboratory and pilot plant studies demonstrated that, by the addition of potassium salts, gasification could be carried out at commercially useful rates at temperatures some 100°C lower than previously required (Penner and Wiesenhahn, 1987; Exxon, 1981). Recovery of most of the potassium entrapped in the ash from minerals in the coal was a key consideration. The development of improved catalytic gasification could provide an important step forward in developing a process for integral gasification/fuel synthesis.

7.2.1.4 IG/S Integral Gasification/Synthesis

Integral Gasification/Synthesis is the concept of carrying out simultaneous gasification of coal or biomass and synthesis to desired hydrocarbons or oxygenates. The gasification temperature, pressure, and other conditions must be such that the synthesis product is thermodynamically possible. A synthesis catalyst is present during gasification. In practical terms, for integral gasification/synthesis to function, it is required that gasification be carried out at considerably lower temperatures than usual. It should be pointed out that the reaction $C + H_2O \rightarrow CO_2 + CH_4$ is almost thermally neutral and is thermodynamically favorable. Therefore, it should be possible to trade C for CH₄ at no energy cost! It is encouraging to note that in coal gasification it has been demonstrated that methane synthesis can occur to a certain extent. *There is a challenge to synthesize methanol, less thermodynamically stable than methane, under IG/S conditions.*

7.2.1.5 Utilization of Methanol

A novel concept for improving efficiency in methanol fuel use involves the catalytic decomposition of methanol to produce a fuel gas. The reaction is highly endothermic. The heating value of the syngas is greater than that of the methanol from which it was derived. If waste heat is utilized to supply the needed energy, there is an expected gain of 20% in energy efficiency (Yoon *et al.*, 1985). The use of catalysts *to enhance fuel-use efficiency* presents opportunities of considerable potential. This is a research area which has been relatively neglected.

7.2.2 Liquid Fuels from Coal

By 1970, new concern for environmental protection had focused attention on air pollutants away from combustion of coal used for generating electricity. New regulations that were imposed made many U.S. coal deposits unsuitable for use in many existing plants because of their high sulfur content. Sponsored by industry and government, intensive research and development programs were carried out to develop technology for the manufacture of a clean liquid fuel from coal, suitable for use in generating electricity. Several direct hydroliquefaction processes were developed and tested on a tons-per-day scale. These included processes known as Solvent Refined Coal, Donor Solvent, H-Coal, Two-Stage Liquefaction, and a German process at Bottrop (Elliott, 1981; Meyers, 1984).

Sulfur in coal is present in both inorganic sulfides, mainly as pyrite, and in organic compounds, mainly as thiophenes. A significant factor in producing a low sulfur liquid from coal is that, while the pyrites are fairly readily removed, removal of the organically bound sulfur is more difficult. Moreover, as desulfurization proceeds, removal becomes increasingly more difficult so that it is not practical to go to very low sulfur levels without subsequent product refining.

By 1976, it was becoming apparent that advanced coal hydroliquefaction technology was economically unattractive compared to flue gas desulfurization, FGD. It is possible to remove 95-98% of SO_2 with flue gas desulfurization technology.

Flue gas desulfurization processes have been installed extensively. At present, the technology used to manufacture liquid fuels for electricity generation is not deemed attractive, although it may have merit in certain circumstances (Commission of European Communities, 1992). Instead, research interest in coal hydroliquefaction has been directed to the production of transportation fuels. Considerable technical and scientific progress in this area has been made, as noted in Chapter 9. However, interest in production of a coal-derived fuel gas for generating electricity has greatly increased.

7.2.3 Chemically Recuperated Gas Turbine (CRGT)

A new method for generating electricity from natural gas has been proposed by the California Energy Commission (Janes, 1990). The process allows for the recovery of high-temperature heat from the exhaust of an advanced gas turbine. Heat transfer is accomplished by utilizing the endothermic catalytic methane-steam reforming reaction. The recovery of heat is accomplished more efficiently by chemical means than by using heat transfer in a steam boiler. The chemically recuperated gas turbine (CRGT) consists of three major components (Figure 3):

- ▶ Advanced gas generator equipped with an intercooler
- ▶ Steam cooled power turbine equipped with a reheat combustor

► **A partial methane steam reformer**

Desulfurized natural gas reacts with steam over a nickel-based catalyst at about 815°C, producing a fuel gas containing hydrogen and carbon monoxide. The normal exhaust temperature from a gas turbine is about 540°C. The most effective way to elevate the exhaust temperature is to reheat before the power turbine. Some of the high-temperature heat is used to partially convert natural gas to hydrogen and carbon monoxide. The natural gas/H₂+CO mixture leaves the reformer as a hydrogen-rich, low-Btu fuel gas mixture. Combustion can be expected to result in low NO_x when fueling the gas generator combustor. Manufacturers of reforming catalysts have evaluated operating conditions and concluded that a combination of catalysts currently in use can be expected to perform according to CRGT design. However, a more active catalyst is needed for reforming below 680°C, which would be advantageous. Detailed process engineering and cost calculations have been performed by the CA Energy Commission and checked by engineering and equipment manufacturers.

Figure 3. Chemically Recuperated Gas Turbine with Intercooler and Reheat.
(Janes, 1990)

In the current combined cycle system for generation of electricity, the exhaust heat from the gas turbine is removed to drive a conventional steam turbine. The combined gas and steam turbines are able to convert 51% of the energy in natural gas to electricity. Average utility efficiency is about 33% for conventional gas and oil-fired boilers in operation. A projected thermal efficiency of the chemically recuperated gas turbine, CRGT, has been estimated to be 60%, about 10% higher than for the gas-fired turbine alone. The substantial increase in projected energy efficiency, employment of near-standard equipment, favorable cost estimates, and expectations of low NO_x emissions make CRGT an attractive technology. A combination

of present industrial catalysts is deemed capable of functioning adequately, but there is a need for a steam reforming catalyst capable of functioning at lower temperatures than conventional.

Since the price of natural gas is expected to rise to its former level, in the long term, synthetic natural gas, SNG, from mine-mouth coal may be a wiser investment than natural gas. Improved processes for manufacturing methane from coal have been developed and offer this long-range option. It should be added that, while manufacturing syngas from methane is a highly developed commercial catalytic process, recent results of a different approach, direct partial oxidation of methane, offer considerable promise for improvement (Hickman and Schmidt, 1993).

7.3 POLLUTION REMEDIATION

7.3.1 CO₂ Emissions

Increased absorption of the sun's rays by increased concentrations of light-absorbing molecules in the atmosphere surrounding planet earth and the consequent rise in temperature has been termed the Greenhouse Effect. Global warming could melt present ice caps, raising sea levels and significantly decreasing land area in the U.S. and elsewhere. There is concern that increasing the presence of CO₂ in the atmosphere generated by increased combustion of fossil fuels will increase the Greenhouse effect.

The technology and economics of capture, utilization, and disposal of carbon dioxide from fossil fuel-fired power plants has been critically examined recently (M.I.T./DOE - 1993). This study finds that direct capture and disposal would likely increase the cost of electricity by about a factor of two or more for the case of retrofit of current coal-fired power plants and by 50% or more for the case of successful development of advanced, high efficiency power plants (such as IGCC or fuel cells) that are specifically configured to integrate CO₂ capture.

If a requirement for full or near-full cessation of CO₂ emissions from power plants is envisioned, certain research discussed here by Spencer, 1991 and in the M.I.T./DOE report is believed warranted. Opportunities for CO₂ utilization include enhanced oil recovery, plastics manufacture, production of biomass fuel (utilizing sunlight to convert CO₂ and H₂O photosynthetically by microalgae) and chemical conversion of CO₂ to fuels.

Chemical conversion of CO₂ to fuels, for example, by the reaction

would require a significant energy source for hydrogen production that could be used several fold more efficiently by directly serving power plant end-markets. The fundamental question is the source of hydrogen. Hydrogen can be generated by electrolysis of water which requires 312 kJ/mol of H₂. To avoid generation of more CO₂ in the hydrogen production process, a non-fossil energy source is needed. The most likely solution is to produce the H₂ from solar or nuclear sources of energy. However, if solar or nuclear energy sources are available, they could

be used directly to displace fossil fuel and reduce the amount of CO₂ produced in the first place. However, there are additional considerations in the production of transportation fuels. Specifically, due to our current infrastructure, liquid transportation fuels are more desirable than electricity or hydrogen because of fuel storage and transportation considerations. However, as pointed out in the M.I.T./DOE report, the efficiency loss is probably too large a price to pay using present technology. This provides an opportunity for catalytic research for more economical and energy efficient conversion of CO₂ to fuels.

7.4 RESEARCH RECOMMENDATIONS

Technology objectives for catalytic research relating to the generation of electricity:

- ▶ to achieve pollution abatement, not only by removing pollutants but also by devising catalytic processes which prevent pollution formation
- ▶ to achieve higher energy efficiency in electricity generation
- ▶ to achieve more economical generation (lower plant operating and particularly plant investment costs)
- ▶ to make available economical processes for use of abundant national fuel resources — coal, gas, and biomass.

Improved Manufacture of Electricity (* indicates highest rating)

* IGCC. Research is proposed to provide synthesis catalysts for advanced processes which combine Integrated Gasification Combined Cycle generation of electricity and fuels/chemicals manufacture. Synthesis catalysts are needed, specifically designed for load-following; for a "once-through" synthesis operation; for slurry-catalyst systems. Synthesis catalysts of interest include those for manufacture of methanol, of methanol/dimethyl ether mixtures, of ammonia, and of hydrogen. Particular consideration should be given to hydrogen co-production because of its growing critical requirements.

* IGCC Coal + Biomass. Processes using a combination of these two fuel substances can provide special opportunities to prevent or lessen CO₂ emissions. Various process flow sheets have been proposed. Catalysts are needed to meet the conditions of projected applications.

Research is needed to improve energy utilization efficiency for methanol and/or dimethyl ether synthesis by developing systems for their catalytic conversion to a *fuel gas* of increased fuel content, using waste heat. Manufacturing synthesis gas by direct selective catalytic oxidation appears to be a promising new target. Research is recommended.

Research is recommended for integral gasification/fuel synthesis, utilizing opportunities presented by recent advances in catalytic gasification.

CRGT (Chemical Recuperated Gas Turbine).

It has been concluded that a combination of existing catalysts could function under the proposed conditions of temperature, pressure, and contact times. However, it is believed that research could provide specifically designed catalyst modifications which would improve the process.

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Chapter 8

CATALYSTS FOR CONTROL OF EXHAUST EMISSIONS

Kenzi Tamaru and G. Alexander Mills

8.1 INTRODUCTION

The application of catalysts to control emissions of CO, NO_x, and reactive hydrocarbons from automobiles began in the U.S. in 1975. Catalytic control of NO_x from electricity generating power plants started in Japan and West Germany at about the same time. As a measure of the present importance of catalysts for emissions control, it is noted that of the \$1900 million annual sales of catalysts in the U.S., sales of catalysts used for emissions control are larger than either catalysts used for petroleum refining or for chemicals manufacturing.

Environmental problems are becoming of increasing importance. Nonpolluting production and use of energy fuels is now considered to be one of the most serious challenges faced by mankind. Environmental protection is an integral component of every energy technology. To be successful, a new process must be both economically and environmentally superior. Energy-related environmental problems involve several topics: acid rain, global warming and the deleterious effects on crops and human health caused by ground-level ozone. Chemicals of concern as atmospheric pollutants are SO_x, NO_x, CO, CO₂, O₃ (ozone), and volatile hydrocarbons. The interactive chemistry of these atmospheric pollutants is complex, particularly since ozone is a product of secondary reactions. In summary, ozone is formed as the result of a sequence of photochemical and radical reactions between O₂ and CO, or O₂ and hydrocarbons in which NO_x is critically involved in intermediate reaction steps (Seinfeld, 1991).

The application of catalysts for prevention and abatement of NO_x is now discussed, particularly in the utility industry. Then catalytic control emissions in the transportation sector is addressed.

8.2 CATALYTIC PREVENTION AND ABATEMENT OF NO_x POLLUTION

Among the developing efforts for effective NO_x control technologies, the most notable are: combustion modifications; selective catalytic reduction systems; catalytic decomposition of nitrogen oxides; and three-way automotive catalysts.

8.2.1 Catalytic Combustion to Prevent NO_x Formation

In a conventional flame operated at high temperature with air, NO_x is formed to an appreciable extent since the equilibrium concentration of NO_x from nitrogen and oxygen increases at higher temperatures, particularly above 1500°C (Figure 1). Combustion of natural gas for application in a high temperature turbine can raise temperatures to 1600°C, resulting in unwanted NO_x.

levels. Catalytic fuel combustion, which can operate effectively at lower temperature than thermal combustion, is being tested as a means of *preventing* NO_x formation. Turbine temperatures are limited to about 1300°C due to limitations in construction materials. In present operation, air is added to the combustion gases to bring the turbine inlet gas temperature to this level. Addition of this amount of air before combustion would lower temperatures and result in unacceptably slow combustion. The concept is to speed up combustion to acceptable rates by the use of a catalyst, while keeping the temperature at 1300°C . One example of such a system is illustrated in Figure 2 (Garten, 1992).

The effect of various combustion systems on NO_x and CO concentrations is illustrated in Figure 3. If we think of the results of using a conventional flame combustor, which gives somewhere between 400 and 2,500 ppm NO_x in the flue gas, it is easily recognized that the catalytic combustion system gives markedly lower values than the flame combustor. Also, the catalytic combustor gives lower concentrations of CO, which leads to a slower ozone formation rate.

Thus, the use of a catalytic combustion can provide many advantages. The temperature in the catalytic combustion systems can be maintained at lower temperatures where the equilibrium NO_x is negligible. Also, the ignition temperature to start combustion can be lower and combustion can proceed in a stable manner.

Catalytic combustion is, accordingly, one of the promising technologies to be developed in the future. However, there are many problems to be solved. These include providing catalysts which are thermally stable and provision of materials and design combinations to achieve sustained performance at high temperatures.

Figure 1. NO_x Formed in Premixed Homogeneous Combustion. (Cusumano, 1992)

Figure 2. Gas Turbine Options. (Garten, 1992)

Figure 3. The Abatement of NO_x Production by Means of Catalytic Combustor.

8.2.2. NO_x Remediation by Selective Catalytic Reduction, SRC

8.2.2.1 Catalytic Reduction of NO_x by Ammonia

Stationary sources of NO_x far outweigh cars and trucks as major sources of generation of NO_x. At present, control of NO_x emissions from electric utility plants is carried out commercially by selective catalytic reduction by ammonia. Commercial installations are widespread in Japan and Western Europe (Austria, Germany, Holland, Scandinavia, and Switzerland) where technology was developed (Bosch and Janssen, 1987). Ammonia is added to combustion gases to achieve 90-95% NO_x removal by the reaction

A vanadia/titania catalyst is used in a parallel flow-through honeycomb catalytic structure. In some instances, silica is included in the catalyst formation. WO₃ or MO₃ may replace part of the V₂O₅. A key to the success of the V/Ti catalyst is that it is not poisoned by SO₂ under operating conditions as are platinum catalysts which were developed earlier. Design by computer modelling has been used to achieve a 50% improvement in catalytic volumetric activity to optimum pore structure control. (Beekman and Hegedus, 1991).

However, there is need for catalyst improvements. Sulfur oxides contained in the flue gas cause problems. SO₂ is converted to SO₃ which react to form sulfates which plug catalyst pores and cause erosion and corrosion. Further as the catalyst deteriorates, the activity at a fixed NH₃/NO_x ratio decreases and the slippage of NH₃ increases, with resultant discharge of NH₃ into the atmosphere. Increasing the NH₃/NO_x ratio increases activity but further increases slippage. Research is needed to understand better the fundamental nature of active sites and reaction pathways in order to make improvements in this developed technology.

8.2.2.2 Catalytic Reduction of NO_x by Hydrocarbons in the Presence of Oxygen

Reduction of NO_x by hydrocarbons has recently attracted much attention internationally as a possible new denitrification process for exhaust gases from utility plants and from diesel and lean-burn gasoline engines. Catalysts comprised of copper ion-exchanged on zeolite ZSM-5 were the first discovered to be active and selective for reduction of NO_x under oxidative conditions. (Held *et al.*, 1990; Iwamoto *et al.*, 1990). Intensive research at numerous laboratories has been reported at recent symposia, (Tokyo, 1990 and San Diego, 1994). Research has focused both on fundamental catalytic chemistry and on the applications testing of a variety of catalysts.

Much debate has ensued on the role of hydrocarbons in the selective reduction of NO_x under oxidizing conditions. Various schemes have been proposed, namely; a) a redox mechanism involving Cu(I), generated through reduction by hydrocarbon, b) oxygenated hydrocarbons as reaction intermediates, and c) deposition of catalytically active carbonaceous materials which

react further with NO. Isocyanate species, -NCO, have been postulated as intermediates in NO-C₃H₆-O₂ dynamic behavior. The reaction between nitro compounds and NO₂ has been proposed as the main route of N₂ formation for NO-C₃H₆-O₂ on Ce-ZSM-5 catalysts.

A wide variety of catalyst compositions has been tested under practical conditions for NO_x reduction by hydrocarbons. Performance capabilities have been established for catalysts fabricated by ion-exchanging zeolites with Cu, Co, Ni, Ce, Rh, Ga, and In (for example, Li and Armour, 1993; Jen *et al.*, 1994).

It has been shown that Ce/Sr-ZSM-5 has high activity under a wide range of conditions due to the efficient utilization of hydrocarbons. Gallium-containing catalysts have a high activity under a wide range of reaction temperatures (Yogo *et al.*, 1993).

NO_x reduction depends a great deal on the hydrocarbon used. The performance of olefins, methane, propane isobutane, have been reported (Gopalakrishnan *et al.*, 1993; San Diego, 1994). Hydrocarbon emissions from a gas-cogeneration system, such as an electric power plant, are comprised mainly of CH₄. Therefore, it would be advantageous to develop a catalyst which is active for reduction of NO_x by CH₄ in oxygen-rich atmospheres (Armor and Li, 1994; Zhang *et al.*, 1994).

Catalyst support components other than zeolites of the ZSM-5 type have also been investigated. Metals ion-exchanged on ferrierites are very active catalysts for the reduction of NO_x in the presence of oxygen (Li and Armor, 1993).

Platinum-group metals catalysts are also regarded as promising. Supported on gamma alumina, they displayed high NO_x conversion activities when tested in real diesel exhaust gases, especially at relatively low temperature between 200° and 350°C. It is claimed that they have higher activity and durability than Cu-ZSM-5 catalysts under real diesel exhaust conditions (Obuchi *et al.*, 1993).

At present, while scientific and technological progress is very promising, no commercial process has been developed for catalytic reduction of NO_x under oxidative conditions. This is regarded as a high priority research topic.

A prime motivation to develop such technology, as discussed in the next section, is that lean-burn engines, which operate at high air/fuel ratios, have the ability to provide higher fuel efficiencies. Three-way automotive catalysts have been successful in controlling exhaust emissions from conventional automotive engines which operate under stoichiometric air-fuel conditions. However, the exhaust from lean-burn gasoline and diesel engines contain over 5% oxygen. Under these not-oxidizing conditions the 3-way catalysts are no longer effective for NO_x control. There is a real research need for alternative catalyst systems for lean-burn gasoline and diesel engines.

8.2.3 Catalytic NO_x Decomposition

The decomposition of NO_x to harmless nitrogen and oxygen is one of the most challenging topics in removing NO_x from exhaust gases. As discussed above, thermodynamics informs us that at lower temperatures NO_x should be decomposed to its constituent elements, which are nitrogen and oxygen. Accordingly, the catalytic decomposition of NO_x could become the simplest and cheapest method for removal of NO_x from combustion exhaust gases.

Since Jellinek first studied catalytic decomposition of NO in 1906, many materials have been examined for NO decomposition. The following systems have been found to be the most active: supported noble metals such as platinum; the silver-cobalt oxide system; perovskite systems; and metal-exchanged zeolites such as Cu-ZSM-5. Of all the known NO decomposition systems studied so far, copper-exchanged ZSM-5 is the most active.

However, present catalysts are not active enough at commercial conditions (Catalytica, 1993). Furthermore, the Cu-ZSM-5 catalyst is inactivated for NO decomposition by the presence of sulfur dioxide, although it remains active for catalytic reduction of NO (Iwamoto *et al.*, 1991).

New approaches are needed. For example, a novel solution to NO_x reduction has been tested using a corona discharge applied to electrodes with catalytic coatings that promote the favorable $2\text{NO} \rightarrow \text{N}_2 + \text{O}_2$. NO_x decomposition was achieved. Currently higher energy efficiency is being sought, necessary for commercialization (Suhr *et al.*, 1990.)

8.3 CATALYSIS FOR CONTROL OF AUTOMOBILE AND TRUCK EMISSIONS

8.3.1 Controlling Automobile Emissions

Automobile exhaust emissions are determined by fuel composition, engine design and operation and by catalytic converters located in the exhaust system. Exhaust gases from spark-ignition automobiles contain harmful CO, NO_x, and hydrocarbons (incompletely and partially combusted fuel constituents). As discussed in Seinfeld (1991), NO_x reacts photochemically with reactive hydrocarbons to form ground-level ozone and also contributes to acid rain formation. SO_x also appears in auto exhaust gases to the extent that the fuel contains sulfur.

Automotive converters using oxidation catalysts were introduced in the U.S. in 1975, converting CO and unreacted hydrocarbons to CO₂ and H₂O. Three-way automotive converters catalyze these oxidation reactions and also simultaneously reduce nitrogen oxides. They have been widely adopted to meet federal NO_x standards, beginning in 1981.

Catalysts for automotive emissions control are now well developed and, in general, are capable of meeting presently mandated U.S. standards for CO, NO_x, and HC emissions from auto exhaust pollutants compared with those built 25 years ago, before emissions control (Taylor, 1990). However, the 1990 CAAA requires significantly greater future reduction than is now mandated. Required is reduction of NMHC (non-methane hydrocarbons) to a maximum of

0.125 gm-per-mile (down from 0.41 in 1991), CO to 1.7 gm-per-mile (down from 3.4 in 1991), and NO_x to 0.2 gm-per-mile (down from 1.0 in 1991). Further, auto catalytic converters must remain effective for 100,000 miles, up from 50,000 miles.

California has set in place a program of future emissions standards much more stringent than the 1990 CAAA including requirement that 10% of new cars have "zero" emissions. This is tantamount to requiring electric cars.

Thus, the U.S. has set in motion the necessary legislation to remove autos as a serious source of air pollution in the 21st century and beyond. This legislation is research-forcing since technology is not now available which is considered to be economically and technically satisfactory.

In seeking to reach acceptable air quality and to determine where emphasis should be placed, it has been recognized that the diminution of pollution from autos is less than anticipated from control regulations. From a study of emissions inventory, the less-than-expected results (about half as well as expected) have been largely attributed to certain autos with high emissions rates (Calvert *et al.*, 1993). Most of the mobile source emissions are by a small percentage of vehicles. Half the CO and HC emissions come from 10% of the vehicles. Some are older vehicles. However, unexpectedly, high emission rates are detected from a few modern autos due to tampering or other reasons. It has been noted that motor vehicles are now responsible for less than half urban NO_x emissions into the atmosphere. Hence, major reduction in NO_x from stationary source emissions should also be considered.

Automobile pollution control necessarily interrelates fuels composition, engine combustion performance and catalytic converter remediation systems (Armor, 1992). As far as engines are concerned, it is clear from Figure 4 (Acres, 1991) that NO_x formation is linked to CO and HC control. Figure 5 (Acres, 1991) describes the effectiveness of NO_x, CO, and HC control by the Pt/Rh catalyst as a function of the optimal stoichiometric air/fuel ratio (equivalence ratio, λ). In addition, fuel economy and maximum power vary considerably with air-fuel ratio. Major steps have been taken by auto manufacturers to accommodate to the requirements for efficient operation of converter catalysts (Taylor, 1993).

Modern 3-way converter catalysts control CO and HCs by oxidation. Simultaneously NO_x is removed by reduction according to the equations:

The generic converter catalyst structure was invented in the early 1950s (Houdry, 1952). Catalytic materials in automobile converters are generally supported on a ceramic honeycomb monolith. The honeycomb, made of cordierite (2MgO·2Al₂O₃·5SiO₂), contains 200-400 square channels per square inch and is coated with an activated alumina layer called the wash coat.

Catalytic Pt, Pd, and Rh are highly dispersed on the high area wash coat. Rh metal displays high activity for the removal of CO, HCs, and NO_x and is particularly important for reduction

Figure 4. The effect of air/fuel ratio on engine operations. (Acres, 1991).

Figure 5. The effect of exhaust gas stoichiometry on the conversion efficiency of a rhodium/platinum catalyst. (Acres, 1991).

of NO_x . Fresh Pd is more active than Pt in most cases for these three pollutants but is more susceptible to poisons such as lead and sulfur and sinters rather easily in a reducing atmosphere. Ceria may be added at a loading of 2-30 wt.% to the washcoat of three-way catalysts to store oxygen to promote the water-gas-shift reaction, and to stabilize the noble metals against thermal damage (Taylor, 1990). Nickel can be added to scavenge H_2S .

Although it is estimated that 96% of the exhaust HC and CO and 76% of the NO_x can be eliminated by the use of catalytic converters, there are needs and opportunities for improvements, discussed by Farrauto *et al.* (1992) and other authors referenced in this section. Three-way catalysts operate near the stoichiometric air-fuel combustion ratio and exhaust temperatures are normally 400-600°C. However, today's catalytic converters do not reach minimum operating temperatures until about 100 seconds after cold start of an automobile. During this warm-up period, more than 50% of NHHc and CO emissions pass unreacted. The problem of cold-start pollution has been addressed by seeking to provide special procedures and catalytic apparatus.

- ▶ Electrical preheating the catalyst, which requires the honeycomb monolith that supports it to be made not of ceramic but of a metal that can withstand temperatures up to 1000°C.
- ▶ Moving the catalyst nearer the engine manifold, where temperature is higher, would also heat the converter faster. This move would expose the catalyst to higher temperature during use.
- ▶ Use of a starter catalyst placed near the exhaust manifold, which can be coupled with the primary catalytic converter in the conventional location.
- ▶ Use of a hydrocarbon storage device, a unit upstream from the converter which prevents hydrocarbons from passing unreacted through the converter by adsorbing them when the catalyst is cold and releasing them to the catalyst when it has reached operating temperature.

Catalyst reformulations offer several opportunities for improvements.

- ▶ There is a need for increased catalyst longevity - specifically resistance to sintering at high temperature and resistance to poisons (P, Zn, S).
- ▶ There is a desire to use precious metal more efficiently, particularly rhodium which is expensive and in limited supply.
- ▶ Effective catalytic decomposition of NO_x remains a key need.

Fuel composition is an integral factor in emissions control.

- ▶ It has been recently demonstrated that even low levels of sulfur in gasoline can be critical to converter efficiency. The sulfur emissions lowers the catalytic activity of the converter.
- ▶ Lowering fuel vapor pressure would assist in lessening HC emissions.
- ▶ Alternative fuels, including oxygenates, can be attractive since they are potentially less polluting.
- ▶ It has been pointed out by Bertolacini (1992), that a 'perfect' converter catalyst would make a choice of fuels not limited by inefficiencies of the converter. Thus, from a combustion viewpoint there would be no need to limit fuel aromatics which have useful octane enhancement properties and certain manufacturing advantages.

There is an important opportunity to improve *fuel efficiency* by raising the air-to-fuel ratios from current stoichiometric ratio of about 14.6 to between 18 and 21. Unfortunately, current three-way catalysts cannot reduce NO_x to N_2 in the more highly oxidizing environment. What is needed is an effective 'lean' NO_x reduction catalyst. The lean nitrogen oxides reduction system must be closely integrated with the engine so that the exhaust stream will have the type and amount of hydrocarbons needed to reduce these oxides. Promising research has identified CuZSM 5 catalyst combinations but they are not yet sufficiently active and stable (Armor and Li, 1994).

If catalytic technology can be developed that removes NO_x effectively when gasoline-fueled spark-ignition engine are operated lean (that is with high air-fuel ratio), significant *fuel efficiency gains* could be made. Research is recommended to explore the *application of catalysts in engines* capable of removing NO_x under lean-burn conditions with the objective of increasing fuel efficiency and environmental protection.

8.3.2 Controlling Truck Emissions.

Exhaust gases from diesel engines contain particulates - primarily soot, liquid hydrocarbons, and sulfates - in addition to CO , NO_x , and volatile HCs. Liquid hydrocarbons consist of unburned fuel and lubricating oil. Sulfur oxides are formed from sulfur contained in the fuel. Even though sulfur in diesel fuel will drop to 0.05% in 1994 from current 0.15-0.13%, significant amounts of sulfur oxides will still be present in the exhaust. It is expected that exhaust aftertreatment will be needed for soot, liquid organics, and for sulfur abatement. Research has been focussed on filters to remove soot, and on oxidation catalysts to remove liquid organics and on preventing sulfate formation (Farrauto *et al.*, 1992).

In the region in diesel engines where plenty of oxygen is present, thermal NO_x is formed, whereas in the oxygen-deficient region, carbon-containing particles or soot are formed in a

heterogeneous manner. One of the ways of abating NO_x is to modify the engine to lower the temperature of the oxygen-excess region by slowing the rate of fuel supply, which may on the other hand, result in an increase in soot formation and may decrease fuel efficiency. Diesel converter catalysis technology complements diesel-engine technology. The focus is on reducing NO_x formation in the engine with the expectation that carbonaceous material can be dealt with via catalytic aftertreatment.

The lean-burn type engine, to which the diesel belongs, works under excess air conditions and exhibit high energy efficiency, but on the other hand emit considerable amounts of NO_x in the exhaust gases in the presence of excess air. One of the ways to alleviate NO_x emissions would be direct catalytic decomposition of NO_x to its constituent elements, N_2 and O_2 , but in most cases the decomposition is inhibited by the presence of excess oxygen since it is more strongly adsorbed on the catalyst surface than NO_x . On the other hand, the catalytic reduction of NO_x by hydrocarbons is accelerated by the presence of oxygen (Held, 1990; Iwamoto *et al.*, 1991; Obuchi *et al.*, 1993) and accordingly may become a good method for abating in the presence of excess oxygen. It is an important task to selectively reduce NO_x and also to improve the thermal stability and life of catalysts, in particular, susceptibility to coexisting gases and vapors such as steam and sulfur compounds.

It should be noted that alternative fuels could reduce particulates and other pollutants for diesel engines. Compressed natural gas and methanol are beginning to be used in city buses in several cities. Even though these fuels are cleaner burning, catalysts are still needed to lower CO, NO_x , and HC emissions.

The discussion of environmental protection by catalysis, the subject of this chapter, is augmented by the presentation of the research status and opportunities in applications chapters.

8.4 RESEARCH NEEDS

- ▶ Pursue an understanding of the chemistry of pollutant formation and remediation.
- ▶ Develop technology to abate ozone pollution by:
 - Catalytic removal of ozone at sites where its formation is high.
 - Decreasing introduction of NO_x into the air.
- ▶ Develop catalysts to:
 - Achieve combustion at lower temperatures where formation of NO_x does not occur.
 - Catalytic decomposition of NO_x to nitrogen and oxygen at practical rates.
 - Improve selective reduction of NO_x .
- ▶ Explore the application of catalysis for removing NO_x under lean-burn engine conditions with the objective of increasing fuel efficiency and environmental protection.

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Chapter 9

CATALYSTS FOR LIQUID TRANSPORTATION FUELS FROM PETROLEUM, COAL, RESIDUAL OIL, AND BIOMASS

Russell R. Chianelli, James E. Lyons, G. Alexander Mills

9.1 INTRODUCTION

Heterogeneous catalysis has played a major role in production of our liquid fuels supply. This role has increased dramatically since the ordinary distillation processes, first used to produce liquid fuels, were not adequate for producing the quantity and quality of liquid fuels necessary for the "hydrocarbon economy". In fact, catalytic cracking, reforming, and hydrotreating processes were largely responsible both for the availability of large quantities of motor fuels and for the growth of the large research effort in heterogeneous catalysis which occurred after W.W. II. It is the purpose of this section to outline future challenges in liquid fuels production. Economic scenarios have been described (Longwell, 1990). We will also describe opportunities in heterogeneous catalysis research which will enable us to meet these challenges. We should also recognize that heterogeneous catalysis plays a major role in the development of better catalytic converters which have had and will continue to have a major impact on emissions from liquid fuel burning engines. This topic has been covered in a previous chapter.

9.2 FUELS FROM PETROLEUM FEED STOCKS

In the past thirty years efficiency and environmental factors have been the drivers in the refining of petroleum to liquid transportation fuels. Generally, there has been a trend to use more of the petroleum barrel for liquid transportation fuels. This involves catalytic cracking, using zeolite catalysts for breaking down larger molecules to motor fuels boiling range, naphtha reforming, using noble metal catalysts to reform smaller molecules into this range and hydrotreating, using sulfide catalysts to remove sulfur and nitrogen. The past has seen remarkable progress in the science and technology. However, there is still room for improvement, and progress is needed to meet the environmental demands placed on the catalysts. In most cases fundamentals of catalyst structure/function are still needed.

9.2.1 Environmental Drivers

Generally, the impact of the 1990 Amendments to the Clean Air Act on catalysts and catalytic processes will be to demand more from existing processes in the short run, and new catalysts and catalytic processes in the long run. Catalysts will be required that produce molecules in the proper motor fuels boiling range more efficiently with less aromatics and more branched paraffins. Catalytic cracking processes are currently at 70% efficiency and further improvements could lead to dramatic results. A 1% improvement leads to a 22Mbbbl/year

savings (Longwell, 1990). Catalysts will also be required which saturate aromatics and remove sulfur more effectively. Since oxygen addition is now mandated, better catalysts will be required to produce oxygenates like MTBE, particularly the isobutylene needed for MTBE manufacture.

9.2.2 Improvements to Existing Catalysts

The following sections list studies in understanding and performance which will be necessary for the current generation of catalysts to meet demands for further improvements in efficiency and environmental performance. Three major classes of existing catalysts are considered: zeolites, sulfides, and noble metals.

9.2.2.1 Zeolites

Zeolites are an example of a class of catalytic materials where structure/function relationships have a firm foundation because of detailed knowledge of the structure and its effect on reaction activity and selectivity. It is also a class of catalytic materials which has proved remarkably successful and important in petroleum refining technology.

Zeolites also continue to present the promise of new and important innovations. We have not yet reached the limit of the potential of this class of catalytic materials. New structures are being discovered regularly and the catalytic potential of the zeolitic structures, such as VOPO and others, are still being investigated. Still, more work needs to be done to understand the complex structural relations which can exist among zeolitic phases and how they effect catalyst preparation and function. Preparative methods for controlling phases and particle sizes are still needed. New zeolites are constantly demanded for new applications, such as producing more olefins as precursors for oxygenate production. Following is a list of research needs in this area:

- ▶ Structure/catalytic function relations for existing zeolites and environmentally important fuels reactions. Particularly important is to build on the understanding of acidity in these catalysts.
- ▶ A better understanding of zeolite structure and phase relationships as provided by advanced probes and theory.
- ▶ A better understanding and control of zeolite synthesis and catalyst preparation.
- ▶ The discovery of new zeolitic materials and their relation to catalytic reactions of interest.
- ▶ Development of zeolitic materials for reactions specific to environmental fuels issues. For example, zeolites for producing isomerized olefins as precursors for MTBE.

9.2.2.2 Sulfide Catalysts

Sulfide catalysts are probably the oldest class of catalytic materials used in the production of liquid transportation fuels. Developed after W.W.I for the hydrogenation of coal tar liquids, the sulfide catalysts are currently used in virtually every refinery in the world. They are used to remove sulfur, nitrogen, and to hydrogenate feeds. They may be used before another catalytic process, such as reforming or catalytic cracking, to hydrogenate and to remove sulfur which may poison the noble metal or zeolitic catalyst. Catalytic cracking feedstock hydrotreating is an example. Or they may be used after catalytic treatment to finish the product and meet final product specification. When used in this form they are called hydrotreating catalysts.

Modern sulfide catalysts are usually alumina supported Mo or W based catalysts which are promoted with Co, Ni, or both. This promotional effect is one of the most interesting and useful of catalytic phenomena. It has also been the subject of intense investigation. However, though some progress has been made, it still remains something of a mystery, especially regarding the structural details of the effect. The electronic nature of the promotional effect has been established on theoretical grounds (Harris, 1988). It is thought that a special phase exists which contains the promoted sites, and this has been termed the CoMoS phase (Candia, 1982). Also, recently the relation of the layered MoS₂ structure to hydrogenation activity and desulfurization activity has been demonstrated (Daage, 1993). Work in establishing the basis for activity and selectivity in these materials has been hindered because the working catalytic materials are highly disordered, and reliable characterization techniques for disordered materials are lacking.

The current generation of sulfide catalysts has proven remarkably successful in meeting past sulfur removal goals. Because these goals have been met in the past, these catalysts have not received as much attention as other catalysts. However, it is clear that the current generation of catalysts is not sufficient to meet the environmental demands placed on sulfur removal, nitrogen removal, and hydrogenation of aromatics. Improved catalysts are required which are based on a firm understanding of catalytic structure/function relations. Following is a list of research needs in this area:

- ▶ A continued effort to apply theoretical techniques to understanding the fundamental origins of catalytic phenomena in the transition metal sulfide catalytic materials.
- ▶ A continued development of an understanding of the promoted system with an ability to optimize activity or extrapolation to new catalytic systems.
- ▶ A continued development of structure/function relations in these systems with an emphasis on larger molecules which represent the most important barriers to new levels of sulfur removal. Thiophene studies should be de-emphasized.
- ▶ Development of an understanding and optimization of the sulfide's ability to catalyze aromatic hydrogenation in the presence of sulfur.

- ▶ Development of characterization techniques which can reliably characterize disordered sulfides. For example, further work must be done with the EXAFS technique to demonstrate its usefulness on disordered materials.
- ▶ Development of new catalytic processes which take advantage of the sulfide's ability to both desulfurize and saturate aromatics simultaneously.

9.2.2.3 Noble Metal Catalysts

Noble metal catalysts instituted a revolution in reforming technology when the Pt/alumina catalyst was first introduced by UOP in the early fifties (Haensel, 1991). This was a major innovation for catalytic sciences because many thought that a noble metal catalyst could not be economically introduced in refining technology. The original Pt/alumina catalysts were followed by improvements in selectivity and activity provided by the Pt/Ir/alumina and the Pt/Re/alumina catalysts in the seventies. These catalysts are in use today, and there is still room for further improvements.

The noble metal catalysts provided some of the best examples of basic and applied catalyst research in the recent past. The basic periodic trends for ethane hydrogenolysis and other reactions led the way toward an understanding of the role of noble metals in catalysis (Sinfelt, 1978). Detailed spectroscopic analyses of noble metal catalysts have given remarkable insight into their basic properties.

However, many problems remain to be understood and catalyst improvements need to be made. Following is a list of research areas in this field:

- ▶ An understanding of the basic structural chemistry of small noble metal clusters needs to be developed. Bimetallic clusters and the interfaces of noble metal particles in their catalytic state need to be advanced.
- ▶ Theoretical and structural probes need to be advanced which relate to the noble metal catalysts in their highly dispersed states.
- ▶ Structure/function relations need to be developed which are related to small particles of noble metal catalysts for reactions of environmental importance.
- ▶ New noble metal catalysts need to be developed based on the fundamental principles outlined above. This may include an understanding of the role of 4 and 5d electrons and how noble metals may be replaced by cheaper metals.
- ▶ The role of carbonaceous overlayers needs to be elucidated and the learnings applied to develop new catalysts.

9.2.3 The Need for New Catalytic Materials

Most of the new catalytic materials required for liquid transportation fuels will be covered in sections below when alternate fuels processing will be discussed. This is because improvements to current hydrocarbon-based liquid fuels will be done with existing processing equipment, requiring a drop-in catalyst, whereas alternate fuels production will require new processes and equipment, making the application of new catalytic materials more favorable. However, there are some examples of new catalytic materials which can impact on the current hydrocarbon fuels picture.

9.2.3.1 Solid Acids

There is a need to replace current alkylation and isomerization processes which involve HF or H₂SO₄ with processes which are environmentally more acceptable. This may be done through the discovery of solid acids which have the appropriate acidity. The strongest superacids would be expected to be too strong for this application but acids with intermediate strengths may be discovered which effectively perform this reaction (Hsu, 1992). Research should be supported for theoretical understanding and development of new strong acid catalytic materials

9.2.3.2 Carbides

Transition metal carbide catalytic materials have been reported to mimic noble metals in activity. Their development has been hindered by the ability to synthesize carbides, as well characterized materials, with high surface area. Research should be performed which is directed to developing synthetic methods to achieve this and to demonstrate catalytic structure/function relationships. The work of Brewer-Engel (1968) in describing the thermodynamics of compound formation between early and late transition metals of the periodic table may be particularly useful here.

9.3 CONVERSION OF SYNTHESIS GAS TO LIQUID FUELS

9.3.1 Overview

The manufacture of liquid energy fuels from syngas (a mixture of H₂ and CO, usually containing CO₂) is of growing importance and of enormous potential (Haag *et al.*, 1987; Mills, 1993) because:

- ▶ Abundant U.S. supplies of coal, gas, and biomass can be used to provide the needed syngas.
- ▶ The liquid fuels produced, oxygenates or hydrocarbons, can help lessen environmental pollution. Indeed, oxygenates are required to a significant extent by the Clean Air Act Amendment of 1990.

- ▶ Such liquid synfuels make possible high engine efficiencies since they have high octane or cetane ratings.
- ▶ There is new, significantly improved technology for conversion of syngas to liquid fuels and there are promising opportunities for further improvements.

Much of the improved technology for selective synthesis of desired fuels from syngas has resulted from advances in catalytic chemistry. However, novel process engineering has been particularly important recently, utilizing known catalysts in new configurations, to create new catalytic processes.

The manufacture of liquid synfuels is capital intensive. Thus, in evaluating advances in fuels technology, focus is on potential for improved economics, particularly on lowering plant investment costs. A second important criteria is the potential for environmental benefits.

Improved technology and special needs, some political and some environmental, have led to a variety of recent commercial installations of liquid hydrocarbon fuels from syngas. The novel MTG (methanol-to-gasoline) process began operation in New Zealand in 1985 (Tabak and Yurchak, 1990; Mills, 1993). A new type of Fischer-Tropsch unit, a fixed fluid bed unit, was installed by SASOL in South Africa in 1989 (Dry, 1990). The largest synfuels plant is being started up in Mossel Bay, South Africa, using SASOL synthesis technology. Also in 1993, the SMDS (Shell Middle Distillate Synthesis) plant will begin operation in Malaysia. A small plant near Denver is in start-up operation producing diesel fuel based on slurry-phase catalytic conversion of syngas made from landfill gas.

Insofar as oxygenate fuels from syngas are concerned, gasoline blends containing mixed alcohols manufactured from syngas were marketed in Italy for a period of time in the 1980s. In the U.S., the Tennessee-Eastman plant has been recently expanded, manufacturing products which include methanol, using syngas made from coal. Blends of gasoline and low levels of methanol have been tested extensively. Higher molecular weight alcohols are usually included in the blend to help prevent phase separation which can occur when small amounts of water are inadvertently present. At present, blends containing low levels of methanol are not well regarded as commercially desirable by the public and industry.

In contrast, fuel M85, 85% methanol and 15% gasoline, provides excellent performance in vehicles designed for this fuel. M85 is being marketed in California and other U.S. locations. In addition, flexible fuel vehicles, FFVs, are being manufactured which can use gasoline or methanol or blends of any intermediate composition.

Methyl tertiary butyl ether, MTBE, was first introduced in gasoline blends in Italy in 1973. Its growth has been phenomenal (Haigwood, 1991), reaching 6 million gallons per day in the U.S. (gasoline is 300 mgpd). It is synthesized by the reaction

MTBE is partly derived from syngas; 36% by weight of MTBE is provided by methanol. Plants to manufacture tertiary-amyl methyl ether, TAME, are also being installed.

One interesting technical innovation in ether synthesis is the use of "catalytic distillation" to carry out the above reaction with the advantage that the reaction is driven almost 100% to the ether.

There has been concern about insufficient isobutene for MTBE needs. However, the need is being met by dehydrogenation of isobutane and by new cracking catalysts which produce higher than usual amounts of isobutene. Isobutanol can be produced from syngas and dehydrated to isobutene.

The use of oxygenates in fuels is greatly influenced by the Clean Air Act Amendment (CAAA) of 1990. In 44 cities it is required that gasoline contain 2.7% oxygen (equivalent to 15 vol.% MTBE) in the winter months, beginning in 1992. In these cities, the carbon monoxide in the air exceeds the amount deemed allowable for health reasons. Further, in 1995 gasoline in 9 cities not in compliance with air standards are to contain 2% oxygen year-round. There are other later requirements for clean fuel fleets. It should be noted that gasoline reformulation has been voluntarily instituted to a large degree by the petroleum industry. Reformulated gasoline contains some oxygenates.

Our discussion will be concerned with two types of hydrocarbon fuels and three types of oxygenate fuels which can be synthesized from syngas. Seven alternative reaction pathways are shown in Figure 1.

9.3.2 Chemistry of Syngas Catalysis

The development of improved catalysts and processes has, to a great degree, been made possible by advances in understanding the chemistry of syngas catalysis reactions (Herman, 1991).

Particularly important have been advanced instrumental characterization of catalyst surface structures, as well as reaction mechanism studies using isotopic labeling and kinetic research. It is now clearly established, perhaps unexpectedly, that over Cu-ZnO/Al₂O₃ catalysts and under industrial conditions for methanol synthesis, hydrogenation of CO₂ predominates over CO hydrogenation and that copper metal is the active catalytic component (Waugh, 1992). CO is converted to CO₂ by the water gas shift reaction. The reaction steps of the WGS reaction are independent of those in methanol synthesis. It is believed that methanol formation proceeds through reaction of CO₂ to formate and methoxy intermediates. It has been established that higher alcohol formation over alkali-containing catalysts is a kinetically controlled chain growth mechanism superimposed on a thermodynamic background. Experimental and theoretical calculations support the mechanism in which chain growth in oxygenate synthesis is *via* aldol addition with oxygen retention reversal (Klier *et al.*, 1992).

For hydrocarbon synthesis, a quantitative understanding has been developed of product carbon distribution numbers in Fischer-Tropsch synthesis over both iron- and cobalt-based catalysts

Figure 1. Pathways for Syntheses of Liquid Fuels from Syngas.

(Bartholomew, 1991). This knowledge, coupled with kinetic data, has been vital in the development of new processes for diesel and gasoline manufacture. Likewise, research on heat and mass transport are being used in critical development of greatly improved slurry phase catalytic processes.

Exploratory research on innovative catalytic concepts is a powerful tool for making major improvements. Exciting advances have been made in novel catalysts from metal alloys, alkoxide activation of CO and supported rhodium catalysts, and concepts of expert systems (artificial intelligence) for catalyst design.

9.3.3 Process Economics

9.3.3.1 General

Many detailed economic estimates have been made by experienced engineers for the manufacture of synfuels. The cost of production of synthetic fuels is much more dependent on plant investment costs than on raw materials costs. Considerable variations in estimates occur partly because costs of plant construction and of raw materials are quite site-specific. However, it is clear that, under usual industrial conditions, synfuel manufacturing costs are greater than costs for gasoline made from petroleum at present petroleum prices.

It is now rapidly being recognized that the value of a fuel can be strongly dependent on environmental criteria. These alter fuel economics. Higher environmental performance justifies higher prices. Thus, while the current price of gasoline at the refinery is 65 cents per gallon, MTBE (with an 87 % rate of heat combustion) sells at 100 cents per gallon. It can be considered that fuel prices are determined by the following values: 1) heat of combustion, 2) octane or diesel rating, 3) environmental properties.

The main barrier to synfuels from syngas is their cost relative to gasoline made from petroleum at present day prices. As described in this report, there is the potential to lower the cost of liquid synfuels from syngas by new and improved catalytic synthesis technology which can:

- ▶ Lower the cost of manufacture by lowering plant investment costs
- ▶ Justify higher-than-gasoline price by providing improved engine performance
- ▶ Justify higher-than-gasoline price by providing environmental benefits (MTBE is an example) (Another example is zero sulfur, zero aromatics diesel fuel from syngas).
- ▶ Improve economics of synfuel manufacture by providing for high price coproducts: chemicals or electricity.
- ▶ Provide for liquid synfuels from biomass which are not subject to future tax on CO₂ emissions.

9.3.3.2 Economic Impact of Expected Improvements

It is reasonable to expect that the proposed research can provide technology which will improve economics of clean fuels manufacture by 10 to 30 %. Realistic engineering studies have assessed possible improvements to be in this range. The use of a fixed fluid instead of a circulating fluid catalyst bed for manufacture of gasoline to decrease overall plant investment by 18 % has been published by SASOL. This is illustrated in Table 1. Investment costs are the major contributors to synfuels manufacturing costs.

Use of a slurry catalyst reactor has been estimated to cut the cost of methanol manufacture by 10 %. A further example of cost reduction is the estimate for combined use of a slurry catalyst reactor and an improved gasifier to manufacture gasoline and diesel fuel. The fuel cost improvement is about 30 %.

Additionally, studies by Bechtel (Fox, 1993) confirm improvements of 30 % possible in synthetic fuels manufacture by proposed new technology, cf. Table 2.

Table 1.
Capital Cost Comparison, Sasol Circulating, and Fixed-Fluid
Bed Synthesis Units (*Jager et al.*, 1991)

Type	No. of Reactors	Pressure	Relative Capital Cost		
			Reactors	Gasloop	Total Plant
CFB BASE	3	normal	1.00	1.00	1.00
FFB	2	normal	0.46	0.78	0.87
FFB	2	high	0.49	0.71	0.82

Table 2.
Improvement in Indirect Coal Liquefaction (*Gray et al.*, 1992)

Configuration	Lurgi Gasifier + Synthol F-T	Shell Gasifier + Synthol F-T	Shell Gasifier + Slurry F-T
Efficiency %	44	55	59
Gasoline/Diesel Selling Price \$ /Barrel	59	51	43

9.4 THE CATALYTIC PRODUCTION OF FUTURE FUELS

9.4.1 The Change From Conventional To Reformulated and Alternative Fuels

9.4.1.1 Driving Forces For Change

- a. **Reformulated Gasoline:** Environmental concerns are requiring changes in the nature of the liquid transportation fuels that will be acceptable in the future. Vapor pressure restrictions limit butanes and other light alkanes to levels far lower than were acceptable in the past. Aromatics, in particular benzene, are undergoing restrictions as well. Both butanes and benzene are compatible with conventional fuel materials and provide high-octane and good drivability characteristics. Branched alkanes of five carbon atoms or more are deemed to be more environmentally friendly and can be used to enhance octane without violating vapor pressure restrictions or using aromatics. At the same time, oxygenates are mandated to meet standards of the Clean Air Act Amendment. Oxygenates, such as alcohols and ethers, have long been used as high-octane fuel components, so their introduction into future fuels will have the dual benefits of both a

clean-burning and a high-octane product. Sulfur restrictions as well as removal of low level toxics will also be mandated. Thus, light hydrocarbons including butanes, benzene, sulfur, olefins, and low level toxics will be removed from the gasoline of the future. In their place will be greater levels of branched alkanes and alcohol or ether oxygenates.

- (i) **Oxygenates** — Oxygenates will be a major source of clean-burning, high-octane liquid fuel materials in the future. Alcohols and the ethers that can be made from them are the oxygenates that are used to replace aromatics, reduce toxicity, and reduce ozone and carbon monoxide in the reformulated gasolines of the 1990s. As we will show, new catalytic chemistry for the direct air-oxidation of light alkanes to produce alcohol-rich oxidates could be developed to produce components of reformulated gasoline or liquid fuel alternatives to gasoline in areas where there is nonattainment of CO limits set forward by the Clean Air Act Amendment. In this way, light alkanes which are cheap, available from natural gas or refinery streams, and are rejected from the gasoline pool, might be converted into environmentally acceptable, high-octane quality fuels. Alcohols of the type that can be formed directly from natural gas or light refinery stream components are methanol, ethanol, isopropyl alcohol, and *tert*-butyl alcohol; they are not only useful as liquid fuel components themselves, but are used in the manufacture of ether oxygenates such as MTBE, TAME, and ETBE as well. Table 3 shows some of the fuel-related properties of the C₁ - C₄ alcohols and the ethers that can be made from them. It can be seen that these materials have desirable fuel properties in addition to meeting the fuel oxygen-content requirements of the Clean Air Act.

Table 3.
Properties of Ethers and Alcohols

Property	MTBE	TAME	ETBE	TAEF	DIPE	ETOH	GTBA	IBA	IPA	MeOH
Oxygen, Wt%	18.2	15.7	15.7	13.0	15.7	34	21.6	21.6	26.6	49.9
Sp. Gravity	0.74	0.77	0.74	0.764	0.73	0.79	0.791	0.81	0.789	0.796
Boiling Pt., °F	131	187	163	215	155	172	181	226	180	149
RVP (lbs/in ²)	7.8	1.5	2.5	1	4.9	2.3	1.8	0.6	1.8	4.6
Blending RVP	9	2	5	2	5	23	12	5	14	75
RON BV	100-112	111	117-121	106-112	—	122	103	-	113-119	126
MON BV	98-102	98	100-105	88-94	—	96	91	-	95-101	104
R+M/2BV	103-111	104	110	100	105	109	97	102	104-110	115
M Btu/Gal	93.5	100.6	96.9	—	100	76	94.1	95.1	87.4	56.8

MTBE = methyl tertiary-butyl ether
TAME = tertiary-amyl methyl ether
TAEF = tertiary-amyl ethyl ether
DIPE = diisopropyl ether
ETOH = ethanol
IPA = isopropyl alcohol
IBA = isobutyl alcohol

ETBE = ethyl tertiary-butyl ether
RVP = Reid Vapor Pressure
RON BV = research octane blending value
MON BV = motor octane blending value
GTBA = gasoline grade tertiary-butyl alcohol
MeOH = methanol
M Btu/Gal = thousands of Btu per gallon

As desirable as it is to convert light alkanes directly to alcohols, doing this in an efficient manner using existing technology is a major problem. The light alkanes, *e.g.*, methane, ethane, propane, and the butanes are among the most abundant and inexpensive raw materials. They are found not only in natural gas but also in light petroleum fractions and are being generated in ever greater quantities in petroleum refineries due to the increasing severity of catalytic cracking of heavier crudes. There exist few commercial processes for the efficient upgrading of these substrates to high-value products and no direct catalytic functionalization of these substrates with air or oxygen to produce chemical or fuel alcohols. New catalytic processes for accomplishing this are needed, and work in this area should be encouraged.

- (ii) **Branched Alkanes** — Gasoline and its crude precursor contains substantial quantities of normal alkanes. These hydrocarbons have very poor octane blending values ($R+M/2 < 50$). Addition of aromatics, oxygenates, and other high-octane additives offset the poor performance attributes of linear alkanes. Isomerization of *n*-alkanes increases octane by 30-40 numbers. A problem with current acid catalysts for isomerization is that activity is relatively low, and under isomerization conditions considerable cracking may occur. In addition, the milder the temperature, the more favorable is the branched/normal ratio. Thus, research which could provide a new generation of solid superacid catalysts for low temperature selective isomerization of normal to branched alkanes is of great interest.

As we have mentioned, large quantities of butanes are being removed from the gasoline pool. Isobutane is the main candidate for olefin alkylation reactions. Alkylation provides a generally highly branched hydrocarbon mixture having good fuel properties for blending into reformulated motor fuel. Current alkylation catalysts, H_2SO_4 and HF, are corrosive and environmentally hazardous. Again, an active solid acid catalyst for the efficient heterogeneous catalytic alkylation of olefins is needed. High acidity is also desired to make possible alkylation of the less reactive olefins like propylene.

We have discussed the need for olefins both as alkylation feedstocks and as fuel and chemical precursor materials. Dehydrogenation is an endothermic, high temperature catalytic technology, and improvements are needed. We will discuss the merits of oxidative dehydrogenation and suggest that catalytic research is needed in this area as well. In short, we must become more skillful at activating aliphatic C-H bonds, not only to oxidize or functionalize alkanes, but to rearrange or couple them, to give viable future fuel products.

- b. **Alternative Fuels** — In addition to the reformulated motor fuels discussed above, more and more emphasis is being placed on whole fuel replacement/alternative motor fuels. Methanol is being used in fleets in areas of low attainment of air quality. Natural gas and propane have been used, as well as other unconventional fuel materials. Research support which fosters conversion of our plentiful coal reserves into fuel and chemical products is

critical. Among the driving forces for alternative fuels is the desire for energy independence and the interest in utilizing cheap or available nonpetroleum raw materials. Research which enables us to broaden the available raw material base in an economic manner to make environmentally acceptable fuel materials will be of great benefit to the nation and to industry as well. New catalytic reaction chemistry has the greatest probability of helping to achieve this goal.

As we mentioned above, raw material availability is a major driver of alternative fuels. As petroleum reserves dwindle, all hydrocarbon raw materials which could be converted to liquid fuels become more dear. Often the search for oil yields extensive gas reservoirs. Gas availability on a worldwide scale rivals that of crude oil but problems of transportation and differences in end use application often limit its utility. Most natural gas is found in areas remote from its ultimate use. Currently, much of this remote gas is associated with petroleum production. Because it cannot be used at the location where it is produced, it is often flared on a large scale, representing not only a wasted energy resource but also contributing to global warming as a result of carbon dioxide production. Because of its low energy density, methane is relatively costly to transport. Figure 2 shows the relative differences between the costs of transporting various liquid and gaseous fuels (Parkyns, 1990). It is readily seen that the conversion of methane to a liquid fuel such as methanol or a hydrocarbon liquid would both drastically cut the cost of transport over long distances and provide an alternative fuel liquid from an abundant, under-utilized resource.

Figure 2. Transportation Costs of Liquid Fuels.

Catalytic alkane conversion science is maturing to the point that one can envision the economically attractive conversion of natural gas to liquid fuels on a commercial scale by the turn of the century. This situation has many international and national implications. Remote accumulations of low value gas such as exist on the North Slope of Alaska and various offshore sites could be exploited. Value could be maximized for domestic gas reserves in high value-added products. The national interests would be well served if the U.S. held the technological lead in gas conversion technology and could influence the course of gas conversion abroad. One of the most costly steps in the current technology for converting natural gas to liquid fuels is the energy-intensive steam reforming step. The products of steam reforming are catalytically converted to methanol which has value as an alternative liquid fuel product or which could be converted to gasoline *via* existing technology (Chang, 1977; Lee *et al.*, 1980; Walker, 1986). A new catalytic approach that permits the direct production of a methanol-rich oxidate from natural gas and completely avoids costly steam reforming is highly desirable. We will discuss research approaches aimed at such a goal in subsequent sections.

9.4.1.2 Roles of Catalysis in Providing Future Fuels

Table 4 indicates many of the ways in which energy-efficient catalytic processing can make major impacts on the way we produce fuel materials. Research must continue to produce more active catalysts, catalytic processes which are more selective, catalysts which provide new routes to fuel products from available alternative feedstocks, and finally process simplicity and efficiency. Inspection of Table 4 shows that catalysis is far from a mature field. Much must be learned if we are to use catalytic process technology to its full potential.

Consider, for example, the way we currently obtain both oxygenates and alkylate for fuel use. Unreactive alkanes are converted *via* energy-intensive endothermic processes to unsaturated intermediates; syngas or olefins (Table 4), prior to further reaction to produce alcohols or alkylate. If we were able to better catalyze the direct activation of the carbon-hydrogen bonds of alkanes, we might be able to directly convert them to alcohols or branched higher alkanes in a single exothermic energy-producing step. Such routes are considered in greater detail in other sections of this report.

Table 4.
Energy-Efficient Catalytic Processing for Fuels and Chemicals

High Catalytic Activity

- ▶ Permits less severe operating conditions (T&P)
- ▶ Greater throughput, smaller reactor size
- ▶ Lower capital and operating costs
- ▶ Milder conditions may allow higher selectivity
- ▶ Activation of available, low cost, unreactive feedstocks

High Reaction Selectivity

- ▶ Minimizes energy-intensive separations
- ▶ Reduces by-products and toxic emissions

- ▶ Less reactant required to provide a unit of product
- ▶ Eliminates high costs of environmental remediation

Alternative Feedstocks

- ▶ Feedstocks are often 60-70% of manufacturing costs
- ▶ Natural gas, coal, and biomass are among potential alternatives

Process Simplicity And Efficiency

- ▶ Fewer process steps
- ▶ Integration of steps
- ▶ Energy utilization, process heat, cogeneration

9.4.2 Catalytic Production Of Oxygenates For Alternative/Reformulated Fuels

We have considered the need for oxygenates in future fuels from several standpoints. Of those oxygenates that can meet future fuel requirements, alcohols and ethers stand out as the most important. Each fuel alcohol or ether, however, has its own set of properties which dictate both the nature and level of its usage as well as the kind of catalysis which is currently used or might ultimately be used to produce it. For this reason, we will discuss each major fuel oxygenate in the context of technology currently employed in its manufacture, the current catalytic research on new routes which is ongoing and should continue, and some long-range challenges for catalytic conversions which would require new science and technology.

9.4.2.1 Alcohols

a. Catalytic Production of Methanol

(i) Conventional Technology

Methanol is currently produced largely by the steam reforming of natural gas to synthesis gas, followed by the efficient catalytic conversion of syngas to methanol (Rostrup-Nielsen, 1975). Gasification of coal to produce syngas is another method also used but is at the present time less economically attractive (Khan *et al.*, 1993).

(ii) Improvements to Existing Technology

- ▶ **Catalytic Conversion of Methane to Syngas** — Catalysts are now being developed for the direct production of synthesis gas having a hydrogen to CO ratio of nearly the desirable 2/1 ratio for generating methane. These heterogeneous catalysts promote the reaction of methane with oxygen to give synthesis gas that would not require shifting (Schmidt, 1993). Work of this nature helps us to understand processes which already have commercial potential.

- ▶ **Catalytic Conversion of Syngas to Methanol —** Technology that will permit a higher conversion per pass of syngas will improve the economics of methanol manufacture. In current methods of manufacture, conversion per pass is limited by thermodynamics to 25% and in practice is about 10%. Expensive recycle is required. Several encouraging concepts for higher conversions per pass are being investigated.
- ▶ **More Effective Heat Removal —** If heat could be removed more effectively from the reactor, temperature increases that create hot spots, decrease methanol conversion levels, and shorten catalyst life could be prevented. A slurry catalyst system, LPMEOH, has been developed and operational parameters have been established in the laboratory and in a 10-ton-per-day pilot unit (Brown et al., 1991). Demonstrations on a larger scale are being proposed. Utilization of a fluid bed catalytic reactor for heat removal has been explored with some success.
- ▶ **Methanol Removal from Reactor to Achieve Higher Conversion —** Conversion of syngas to methanol is limited by thermodynamic considerations under present industrial conditions. However, the following schemes are proposed for removal of methanol from the reactor which would increase conversion and decrease or eliminate the need for expensive recycle (Mills, 1993):
 - Gas solid trickle flow reactor
 - Reactor system with interstage product removal
 - Condensing methanol principle
- ▶ **Novel Catalysts for Methanol Synthesis —** These novel catalysts can be used at 150-180°C instead of the usual 250-300°C. They would permit higher conversion of syngas because of more favorable thermodynamic limitations at lower temperatures. Also, operation at lower pressure in less expensive equipment would be possible. Additionally, the possibility is offered that the expensive oxygen plant would not be required. Syngas made in an air-blown gasifier would be used and the nitrogen separated more easily from liquid methanol product rather than from gaseous oxygen. Unusually high activity catalysts have been discovered. These are based on metal alloys, KOCH_3 (methyl formate route), and supported platinum group metals (Pd, Rh). Although these catalysts have promise, each has practical problems. It is here that fundamental research can provide critical information and ideas.

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(iii) New Catalytic Approaches

- ▶ **Direct Conversion of Methane to Methanol** — Considerable research is underway in an attempt to convert methane to methanol directly and bypass the costly steam reforming step. Although well integrated processes have been developed (Rostrup-Nielsen, 1987) for conventional technology through syngas, there is no escaping the fact that it is first necessary to conduct an energy intensive endothermic steam reforming step followed by a subsequent catalytic conversion step which has equilibrium limitations. It stands to reason that if one could directly convert natural gas in a single exothermic oxidation step in high yield, this would be more attractive than current routes. One would, in effect, supplant a two-step route having a costly endothermic first step with a direct one-step route which is highly exothermic and could cogenerate energy.
- ▶ **Thermal Oxidation of Methane to Methanol** — Over the past decade there has been a resurgence of work on the direct autoxidative conversion of methane to methanol. Research in the 1980s (Yarlagadda *et al*, 1988) suggested that rather high yields of methanol might be achieved from direct non-catalytic methane oxidation. Subsequent results have shown that yields are much lower than had at first been hoped for, and calculations from gas phase kinetic studies indicate that obtaining methanol in higher than 5% yield from gas phase radical processes is unlikely (Labinger, 1988). Laboratory studies fall far short of even this limited result. Catalysts have been developed (Durante, 1989) which initiate the formation of radicals which are largely expelled into the gas phase. Under some conditions, methanol yields approaching 5% methanol (70% selectivity at 7% conversion) have been observed but these are far short of commercial viability under most future scenarios. More work is needed to fully understand this important catalytic reaction area.
- ▶ **Suprabiotic Catalyst Systems — Beyond Chemzymes** — It is well known that methanol is produced from methane under mild conditions by enzymatic catalyst systems such as methane monooxygenase. The enzymatic systems have practical limitations because of the need for low temperature oxidation and for stoichiometric coreductants, among others. Synthetic biomimetic catalysts, dubbed chemzymes, can mimic enzymatic catalysis but suffer from the same two drawbacks. Recent studies indicate that it may be possible to mimic some of the characteristics of the biological systems while catalyzing alkane oxidations using only

oxygen and no coreductant with catalysts which are robust enough to survive industrial process conditions. Although limited success has been achieved to date with methane, more easily oxidized hydrocarbons can be converted to their respective alcohols using this approach (Ellis and Lyons, 1990). What is now needed is further work both to enhance catalytic activity and to introduce hydrophobicity to expel product rapidly from the catalyst and increase alcohol selectivity.

- ▶ Electrophilic Metal Catalysts — Catalytic materials containing palladium, thallium or mercury centers in a molecular environment which enhances their electrophilicity have been shown to be capable of cleaving the C-H bond of methane. When this is done in the presence of a strongly oxidizing oxygen-atom donor such as sulfuric acid at elevated temperatures, methyl bisulfate is the resulting product. The formation of methyl bisulfate from methane occurs catalytically in the presence of palladium, thallium, or mercury containing catalysts (Periana, *et al.*, 1993). Hydrolysis of this intermediate produces methanol. In this way methanol has been produced from methane in 40% yield — a great improvement over the <5% yields generated in free radical gas phase processes. Further work is needed to develop systems which might be able to use molecular oxygen directly and which might work in less corrosive environments.

(iv) Coproduction of Methanol and Dimethyl Ether

- ▶ Higher syngas conversion per pass can be achieved by providing a catalytic system which produces a mixture of methanol and dimethyl ether, DME, in a single reactor (Brown *et al.*, 1991; Hansen and Joensen, 1991). This is a chemical method of removal of methanol from the reaction system. DME is synthesized by the sequential reaction:

Depending on the catalyst and conditions, CO₂ may be produced instead of H₂O. A combination of a methanol synthesis and a methanol dehydration catalyst is employed. DME has a number of applications for fuels and manufacture of fuels and chemicals. The development of mixed MeOH and DME manufacture is regarded as important new technology.

(v) Increased Energy Efficiency in Methanol Use

- ▶ If waste heat from an engine exhaust is used to provide the energy to convert methanol back to syngas, an endothermic reaction, the heating value of the syngas is larger than that of the methanol from which it is derived (Yoon *et al.*, 1985). A gain in energy efficiency of as much as 20% is possible.

b. Catalytic Production of Ethanol

(i) Conventional Technology

- ▶ Fermentation ethyl alcohol can be manufactured from sugar, starch, or cellulosic raw materials, utilizing yeasts. In the U.S., corn is currently the principal feedstock. The fermentation process yields a low alcohol content beer which is distilled to the azeotrope, 95% alcohol. Synthetic ethanol is produced by the direct process in which ethylene is hydrated over a phosphoric acid catalyst at about 400 C and 1000 psi. Overall yield of ethanol is greater than 97%. In the U.S., there is currently nearly 400MM gal/yr of synthetic ethanol capacity. Total ethanol capacity exceeds 1.4 billion gallons per year.

(ii) New Catalytic Approaches

- ▶ Homologation of Methanol — A significant amount of research has been carried out over the past twenty years on the reaction of methanol with synthesis gas to give ethanol and water. Homogeneous and heterogeneous catalysts have been used. An attractive aspect of this reaction is the cost of starting materials. Improvements in catalytic activity and reaction selectivity are still needed. Relatively little has been done on this reaction. Non-catalytic autoxidation of ethane gives ethanol in up to 50% selectivity (Gesser *et al.*, 1991) at low conversion (<10%). No high yield catalytic conversion has been reported. This reaction, if it could be developed, would have a major raw-material advantage over the commercial synthetic route from ethylene. Both the suprabiotic approach and catalysis by electrophilic metal centers, reviewed above, may have potential here (Lyons and Ellis, 1991; Sen *et al.*, 1992) as well.

c. Propanol and Isopropyl Alcohol

(i) Conventional Technology

- ▶ Isopropyl alcohol is a chemical for which there is nearly two billion pounds of annual capacity in the U.S. It is not currently widely used as a fuel additive and its chemical usage is in decline. It has fine fuel alcohol properties, being a clean-burning, high octane additive with good water tolerance. Its current method of manufacture *via* hydration of propylene, however, provides a product which is rather costly for fuel use. Recent work (Mobil) has demonstrated that condensation of IPA with propylene gives diisopropyl ether, DIPE, which has good fuel oxygenate properties as well.
- ▶ Propanol, n-propyl alcohol is produced in much smaller volumes than isopropyl alcohol. All propanol manufacturing in the U.S. uses the oxo process in which ethylene is catalytically hydroformylated to propionaldehyde in the liquid phase using synthesis gas. The aldehyde is then stripped off and hydrogenated to the alcohol in a second process step. Because of the lower volume and greater complexity of the manufacturing process, propanol is much more costly than isopropyl alcohol. Thus, even though it has interesting fuel oxygenate properties, cheaper methods of manufacture would be needed for its usage in fuels to be significant.

(ii) New Catalytic Approaches

Olefin hydration and hydroformylation are mature technologies which have undergone decades of refinement and are practiced at a very high level of efficiency. Propylene, however, is rather costly and this results in a relatively high priced product. Thus, new approaches to the production of three-carbon alcohols could best benefit from a cheaper raw material. Direct oxidation of propane to either alcohol would provide an economical process for fuel production if the catalytic technology were efficient enough. However, no catalyst currently exists for accomplishing this reaction well at the present time.

- ▶ Suprabiotic catalysts have been shown to slowly convert propane to isopropyl alcohol, but yields are still too low to be practical (Ellis and Lyons, 1989). Novel electron deficient macrocyclic metal complexes of iron are active enough to homolyze the C-H bond, and developments in this field suggest that significant improvements are yet to come. Electron withdrawal from the macrocycle dramatically enhances the iron III/II reduction potential, increasing the activity of the complex for C-H bond homolysis. Incentive exists for implanting systems of this type into appropriate surface environments both for thermal and

oxidative stability at high temperatures and to achieve the practical benefits of oxidations in the vapor phase. It is conceivable that suprabiotic systems could be developed that would prefer primary over secondary C-H bonds. Cytochrome P-450, an enzymatic *in vivo* catalyst, converts C-H bonds to C-OH moieties in the liver (Ortiz de Montilano, 1986). *In vitro* experiments on long-chain alkanes indicate a preference for terminal over internal C-H bonds and biomimetic catalysts in several surface environments possessing structural features which promote terminal attack (Herron and Tolman, 1987). Though quite long-range, work in this area may in time allow the direct functionalization of alkanes at the primary carbon atom in preference to secondary C-H bond activation leading to catalytic processes which could indeed produce propanol from propane.

- Electrophilic metal catalysts might also be expected to give preference to terminal over internal attack on a substrate such as propane. The stabilities of the intermediate metal alkyls, M-R, would be expected to increase as R goes from tertiary to secondary to primary. Thus, catalysts which operate by heterolytic cleavage of C-H bonds to generate M-R and a proton might favor terminal attack over internal attack and might give propanol from propane as the major product. Much work remains to be done in this area and the potential for catalysis is great. These systems seem well suited for heterogeneous catalysis although early versions are largely homogeneous. Because of the relative stability of primary and secondary metal alkyls, these systems are purported to be capable of higher selectivity in oxidative functionalization reactions since product is less susceptible to oxidation than is starting material (Labinger, 1988). Thus heterogeneous catalysts possessing tailored electrophilic transition metal sites have the potential for promoting interesting regioselective alkane oxidations with high selectivity.

d) Four-Carbon Alcohols (BA, TBA, SBA, IBA)

(i) Conventional Technology

A variety of catalytic processes produce four-carbon alcohols for use as fuel additives, additive precursors, and chemicals. Butanol is manufactured in over a billion pounds per year. The dominant technology is hydroformylation of propylene to produce butanol which is used exclusively for chemicals production. *Tert*-butyl alcohol, TBA, is a by-product of propylene oxide manufacture and is dehydrated to isobutylene which is converted to MTBE for use

as an oxygenate in reformulated gasoline. TBA has been used as a high octane clean-burning fuel additive both in the U.S. and abroad. The other isomeric four-carbon alcohols, isobutyl alcohol, and *sec*-butyl alcohol are not made on a large scale. Isobutyl alcohol, IBA, has been proposed as a blending agent such as TBA and MTBE and can be dehydrated to isobutylene for MTBE manufacture as well (Mills, 1993).

(ii) New Catalytic Approaches

- ▶ Direct Catalytic Oxidation of Isobutane — A new series of suprabiotic catalysts, having iron in a perhalogenated macrocycle, have been shown to efficiently catalyze the conversion of isobutane to TBA with unprecedented rates and reaction selectivity (Ellis *et al.*, 1990; Lyons and Ellis, 1991). Since these catalysts homolyze C-H bonds, it is relatively straightforward to attack the tertiary C-H bond in preference to the primary C-H bonds in the parent alkane. If further developed, this new catalytic technology has the potential of decoupling TBA manufacture from propylene oxide production and producing a fuel oxygenate directly without a chemical coproduct. New catalytic technology of this type may be able to displace the costly dehydrogenation of isobutane to isobutylene for ultimate production of both alkylate and MTBE — prime components of reformulated gasoline to meet Clean Air Act standards. More research in this area is clearly warranted.
- ▶ Direct Catalytic Oxidation of Butane — Just as was discussed in the oxidation of propane, suprabiotic catalysts might be used to oxidize butane to either *sec*-butyl alcohol or butanol if they were sufficiently developed to have the regioselectivity of the biological systems. Heterogeneous catalysts having electrophilic metal centers might be made which could regiospecifically oxidize butane to butanol.
- ▶ Isobutyl Alcohol From Syngas — Isobutyl alcohol can be directly produced in catalytic reactions but the overall selectivity over known catalysts is not high (Mills, 1993). It has been found that recycle of methanol in mixed alcohol synthesis increases higher alcohol formation by homologation of lower alcohols. In syngas conversion the thermodynamically allowable isobutanol concentration is very high. Thus, it is becoming possible to modify catalysts and reaction conditions in such a way as to promote the direct production of IBA from syngas (Air Products). If successful, this approach could result in an alternative route both to fuel alcohols, isobutylene, and MTBE from syngas as a starting material.

e) Mixed Alcohols

(i) Conventional Technology

There was much enthusiasm during the 1980s for the production of mixed alcohols for use as octane enhancing components in gasoline blends. The following special catalysts were developed: 1) alkali modified copper methanol synthesis catalysts, 2) Co or Ni modified copper methanol synthesis catalysts, 3) MoS_x-based catalysts, and 4) supported platinum-group metals (Pd, Rh). A comprehensive technology base was developed and trial commercial production initiated in Italy. An extensive series of pilot unit tests were conducted in Japan using French/Japanese technology (Courty *et al.*, 1990). Processes are available for license. However at present, mixed alcohols are not regarded as promising commercially since they cost more to manufacture than methanol, and most importantly, the need for an octane-enhancing blending agent is being filled with MTBE, which is regarded as having better all-round properties.

(ii) New Catalytic Approaches

- ▶ Catalytic Oxidation of Mixed Alkanes — A number of alkane mixtures such as natural gas, LNG, NGL could conceivably be directly oxidized to a mixture of alcohols using catalysts such as those discussed above. Since these mixtures have light alkanes ranging from methane to the butanes and higher, it may be difficult for catalysts to operate selectively on a group of hydrocarbons having such a wide range of reactivity. On the other hand, co-oxidation of methane with ethane or propane seems to enhance methane autoxidation. Perhaps it is more realistic and practical to imagine operating on single gas components such as methane, ethane, propane, and the like. Direct conversion of natural gas to a liquid oxygenate in an efficient manner will require much new catalytic research and development.

9.4.2.2 Ethers

a) MTBE and ETBE

(i) Conventional Technology

- ▶ Methyl *tert*-butyl ether, MTBE, and ethyl *tert*-butyl ether, ETBE, are manufactured by reacting either methanol or ethanol with isobutylene. The isobutylene used for this reaction is either recovered from refinery processes or manufactured from isobutane

by dehydrogenation or by oxidation processes, as described previously. We have already discussed new oxidation processes to produce isobutylene *via* TBA. Better and cheaper catalytic dehydrogenation systems for isobutylene production are also needed. Because of its use in providing fuel oxygenate to meet Clean Air Act standards for reformulated gasoline, MTBE is currently one of the largest and fastest growing chemicals in the U.S. and ETBE is beginning to be produced as well.

(ii) New Catalytic Approaches

- ▶ Direct reaction of TBA with methanol — Research is currently underway to develop a process for the direct production of MTBE *via* the acid catalyzed reaction of TBA with methanol in one step (Knifton, 1989). Current technology requires that TBA be first dehydrated to produce isobutylene which would then be reacted with methanol or ethanol to give MTBE or ETBE. Although it is not a difficult step, removal of the hydration reaction would provide process simplicity and reduce costs. Devising process conditions which will remove water of dehydration in order to shift the equilibrium toward ether will be of great benefit. Acid catalysts which operate efficiently in this process are being developed.
- ▶ Catalytic Dehydrogenation and Oxidative Dehydrogenation — Isobutylene is needed as a feedstock for conventional MTBE plants. It can be obtained from refinery processing or *via* dehydrogenation of isobutane. Catalytic or thermal dehydrogenation is the currently practiced technology for converting the lower alkanes to olefins. This technology, however, is faced with many challenges. Light alkanes are quite unreactive. Dehydrogenation is highly endothermic and large amounts of heat must be added to a reactor at very high temperatures. Equilibrium conversions are not high and very elevated temperatures are needed. This presents problems in achieving high reaction selectivity and affects catalyst life and activity as well as coking. Oxidative catalytic dehydrogenation does not have the thermodynamic limitation that catalytic dehydrogenation has, since the reaction is driven to completion by oxygen as a hydrogen acceptor. Oxidative dehydrogenation is exothermic and therefore the problem of adding large amounts of heat to the reactor at high temperatures is avoided. Heat released can reduce catalyst coking. Although alkyl aromatics can be efficiently oxidatively dehydrogenated, (ARCO, Phillips, UOP) and ethane will react with oxygen to give ethylene and water,

much more catalyst development and process work must be done in the area of oxidative dehydrogenation before it can be applied broadly to light alkanes. Active selective oxidative dehydrogenation catalysts which can operate under industrially attractive conditions could provide breakthrough opportunities in isobutylene manufacture.

- Superior Isomerization Catalysts — Linear butenes from refinery processes and n-butane from natural gas are more abundant than isobutane. It has been found that butenes can be catalytically isomerized (Lyondell, 1992) to give isobutylene. Superacids have recently been developed which allow the rapid, selective low temperature isomerization of butane to isobutane which could be used as an MTBE feedstock, regardless of whether MTBE were made *via* dehydrogenation or oxidation routes. These superacids are based on activated iron substituted sulfonated zirconias and are the most acidic and active solid superacids known to date (Hsu *et al.*, 1992). More research and development on these fascinating solid superacids may be important not only for isomerization but for other catalytic applications as well.

b) TAME and TAEE

Tertiary methyl ether, TAME, and tertiary ethyl ether, TAEE, are high quality fuel oxygenates produced *via* acid catalyzed reaction of isoamylene with either methanol or ethanol, respectively. Isoamylene is a product of fluid catalytic cracking and is available in modest quantities in refinery streams. The driving force for converting isopentane to isoamylene either by dehydrogenation or oxidation to isoamyl alcohol followed by dehydration may not be as high as the analogous routes on isobutane. The reason is that isopentane is a high-octane, clean-burning branched alkane which has value as an integral part of the reformulated gasoline pool already. Nonetheless, catalysts which can selectively oxidize or dehydrogenate isopentane could give the olefinic precursor to TAME.

c) DIPE

Diisopropyl ether is a high-octane product having good properties as a fuel oxygenate. It is made by acid catalyzed condensation of propylene and IPA. A direct one-step acid catalyzed condensation of two moles of IPA would be a less costly alternative to this technology, if the IPA could be formed directly from propane by catalytic air oxidation, as previously discussed.

9.4.3 Alkylate And Branched Alkanes To Replace Benzene

a) Alkylation

(i) Conventional Technology

- ▶ Alkylation of olefins is conventionally carried out in refinery operations using either sulfuric acid or hydrofluoric acid as a catalyst. This catalytic reaction usually is used to alkylate mixed butenes with isobutane to produce a relatively high-octane hydrocarbon ($R+M/2 \approx 90$) to add to the gasoline pool. Branched alkanes are an effective way to add octane to reformulated transportation fuels in which aromatics, and in particular benzene, are backed out in order to meet environmental standards.

(ii) Current Research

- ▶ Solid Alkylation Catalysts — Solid alkylation catalysts have been under development in a number of laboratories for quite some time. Progress has been made with several novel systems, including MELS (King *et al.*, 1991), solid sulfonated zirconias (Hsu *et al.*, 1992; Hino and Arata, 1979), and others. A solid superacid which could smoothly alkylate an olefin with an alkane to produce a high octane nonaromatic transportation fuel material would be highly desirable from both an energy and an environmental standpoint. A superacid might increase the feed flexibility to allow alkylation of lower olefins and even allow the use of normal alkanes as alkylating feedstocks. A solid superacid which does not have the potential for HF release to the environment or the corrosivity of sulfuric acid systems would be an environmental boon. Advances in understanding and exploiting these new superacids are increasing and must be encouraged. More research on solid superacids in general and sulfonated zirconia, titania, and related oxidic systems should be undertaken for these reasons.
- ▶ Oxidative Dimerization of Light Alkanes — An enormous amount of research has been conducted over the past decade on the oxidative dimerization of light alkanes with most of the effort focused on converting methane to ethylene (Keller *et al.*, 1982; Jones *et al.*, 1987; Driscoll *et al.*, 1987; Taylor *et al.*, 1988; Hutchins *et al.*, 1988). A variety of reducible metal oxides have been studied in both the presence and the absence of oxygen in a large number of reactor types. The driving force for this work

was to convert natural gas to a liquid fuel material that could be easily transported and would be acceptable in the current transportation fuel system. Conversion of methane to ethylene, followed by subsequent production of liquid fuel from ethylene was a technology investigated by many groups. Much progress was made in understanding this reaction and yields of ethylene from methane exceeded 30%. Though not yet commercial and suffering from process limitations that may require a catalytic breakthrough, this work has come fairly close to developing practical technology. Work should proceed at some level in this area to continue to investigate applications to methane coupling but also coupling of other light hydrocarbons $C_2 - C_4$ into the gasoline range.

Other similar approaches were developed in which methane was oxychlorinated to methyl chloride (Mitchell *et al.*, 1992) followed by conversion of the alkyl halide to gasoline (IIT, PETC). Oxybromination chemistry has also been employed (SoCal) in the laboratory. Even higher yields could be obtained using this chemistry but problems associated with corrosion and halide contamination of products and the need for separations and new reactor technology are still among the things limiting this application. Again, the advances gained in being able to functionalize light alkanes in ways that were not possible at the inception of this work should encourage us to continue to pursue these and related catalytic reactions with the ultimate goal of being able to convert light alkanes either from natural gas or light refinery streams into higher value fuel and chemical products.

Another development which has occurred during the past decade is the ability to catalytically dehydrocyclize light alkanes, such as propane, to aromatic hydrocarbons. This kind of conversion is carried out over gallosilicate catalysts, most notably catalysts having framework substituted gallium in ZSM-5. Much research has been carried out (BP, Exxon) in an attempt to understand and apply this reaction chemistry. A small commercial unit capable of processing about 1000 bpsd of LPG has been built in Grangemouth, Scotland. As in the areas mentioned above, this work greatly extends our ability to manipulate aliphatic hydrocarbons; advances in the area will have impact on our energy future.

b) Isomerization of Linear to Branched Alkanes

Isomerization of C_4 - C_6 paraffins is an important technology practiced to convert streams with high normal paraffin content to branched alkanes and in so doing increase blending value octane numbers by as much as 20-30 points (UCC, BP, UOP, 1986). Isomerization is one of the least costly ways of producing octane barrels and is of importance as reformulated gasolines introduce octane *via* branched alkanes rather than benzene. A number of processes exist which use either platinum on amorphous supports or use zeolitic versions (UOP, IFP). The technology is in place around the world and is at a relatively high level of development. Superior catalysts which will allow low temperature operation, where equilibrium favors the branched relative to the normal alkanes, will be of value. In a subsequent section we have reviewed the recently patented superacid catalysts (Hsu, 1992) which are the most highly acidic known to date and are capable of rapid low temperature isomerization of butane. Furthermore, these catalysts are able to isomerize higher alkanes with little cracking. Continued improvements in solid superacid chemistry are of importance in replacing corrosive and toxic analogs from the environment. Many refinery operations currently use acid catalysis, and much of this technology is mature. Some of these processes would benefit from superacidity. Major advances in solid superacid chemistry could have an extremely beneficial effect on refinery processes of the future.

9.4.4 Hydrocarbon Fuels from Syngas

9.4.4.1 Fixed Fluid Bed Fischer-Tropsch Synthesis Reactor

The Fischer-Tropsch process has long been employed for production of gasoline from syngas, notably in Germany in WW II and in South Africa (SASOL), beginning in 1954. Recently, important new and improved technology has emerged, unexpectedly perhaps, since FT is such a long and well researched process.

SASOL announced in 1989 that a fixed fluid bed catalytic synthesis reactor had been installed (Dry, 1990). It is reported that this cuts the cost of the synthesis plant section in half, relative to the previous entrained fluid bed reactors. Improved plant operability is also reported. SASOL has also indicated that a slurry phase reactor system will be operated in 1993.

9.4.4.2 Synthesis To Wax, Hydrocrack To Diesel And Gasoline

Royal Dutch/Shell, Amsterdam, is constructing a 14,000 bpd plant in Malaysia at a cost of \$660 million. A novel combination of catalytic processes is employed in the Shell Middle Distillate Synthesis (SMDS) process (Sie *et al.*, 1991). Syngas from natural gas is converted to high molecular weight waxy hydrocarbons. It appears certain that a cobalt catalyst will be used, operated under conditions that provide for conversion to high molecular weight hydrocarbons (high alpha value; Anderson-Shulz-Flory constant) in the synthesis process. A key feature is the avoidance of production of low molecular weight hydrocarbons, particularly methane. The waxy product is selectively hydrocracked, using modern hydrocracking catalysts, to produce high quality diesel fuel, valuable waxes, and gasoline.

The Exxon Corporation has been active in developing a new process for synthesis of hydrocarbon fuels from syngas. Almost nothing has appeared in technical literature. However,

Exxon has said to stockholders that its divisions are "collaborating on advanced proprietary technology for on-site conversion of natural gas to liquid products". They have named it AGC-21 — Advanced Gas Conversion for the 21st Century (Eisenberg *et al.*, 1993). A demonstration unit is now in operation "obtaining critical data for scale-up to commercial size". An investment of over \$100 million has been made over a ten-year period and more than 100 patents have been obtained. It appears that this is also a variation in the FT-type process. It is reported that a new fluid bed gas reforming process has been developed. Exxon has said that the syngas is converted to an intermediate product. This may consist of C_5+ hydrocarbons which are isomerized and/or hydrocracked to produce a gasoline having suitable octane rating, and other products, such as diesel fuel (Eisenberg *et al.*, 1993).

9.4.4.3 Slurry Phase Fischer-Tropsch (FT)

One of the most exciting developments in FT technology is the slurry phase conversion of syngas to hydrocarbon fuels. Originally investigated in Germany by Koelbel following WW II, recent engineering and economic evaluations have given great impetus to the possible advantages of slurry phase FT. A major improvement is the capability to carry conversion-per-pass nearly to completion and so avoid major recycle costs. It has been recognized that information obtained on a larger-scale unit is needed. An important test was carried out in August 1992 in the La Porte, TX, unit, sponsored by DOE and a number of national and international industrial partners. Slurry phase FT operation is being conducted on a very small scale in a plant operated by the Fuel Resources Development Company near Denver. An iron-based catalyst is used and the diesel fuel product has been reported to have excellent properties.

9.4.4.4 Methanol-to-Gasoline and Related Processes

The Mobil MTG process (methanol-to-gasoline), developed cooperatively with DOE, has been in successful operation in New Zealand for six years. Improvements in the MTG process have been made since its installation in fixed bed form. The H. Topsøe Company has developed the Topsøe Integrated Gasoline Synthesis (TIGAS) process by operating all these steps of the MTG process — syngas production, methanol synthesis, and conversion — at the same pressure and the last two steps in a single synthesis loop (Rostrup-Nielsen, 1987). Also, with support from DOE, a fluid bed version of MTG has been demonstrated on a semi-commercial scale in Weseling, Germany. Furthermore, the related MTO (methanol-to-olefins) and MOGD (Mobil olefins to gasoline and distillates) processes have been developed.

9.4.5 Synthetic Fuels from Coal, Petroleum Residuals, Heavy Tars, and Biomass

Even though the analysis contained in this section concludes that the hydrocarbon feedstocks discussed have lower priority in the current 10 to 20 year projects, research that promises significant advances in the application of heterogeneous catalysis to their conversion to liquid transportation fuels should continue. That research should focus on fundamental aspects and those of catalytic process engineering which could substantially alter the economic or environmental debits associated with these feedstocks. We divide this group into two categories. The first group contains coal, residual oil, and heavy tar sources. This group, while

representing a considerable strategically secure resource, suffers from high environmental and economic constraints on production, transportation, and conversion to liquid transportation fuels. At this time, shale oil is excluded because the environmental and economic constraints seem even more severe. The second group contains biomass as the source for liquid transportation fuels which has the potential advantage of being CO₂ neutral.

9.4.5.1 Synthetic Fuels from Coal, Residual Fuel Oil, and Heavy Tars

Of this group, residual oils are currently available for conversion as a by-product of petroleum refining and could be converted without further production costs, providing that appropriate catalytic removal of sulfur and other pollutants occurs. Currently, these oils are burned for fuel and are limited in quantity because lighter crudes with small residual components are used in the refinery. Should a process be developed for conversion to liquid fuels, larger quantities could be obtained by using heavier crudes in the refinery. Processes exist for conversion of these feedstocks to liquid fuels, but they require large amounts of hydrogen for conversion. This is characteristic of this group. More efficient use of hydrogen and cheaper sources of hydrogen are required. Currently, hydrogen is obtained in the refinery as a by-product of reforming reactions. Large-scale conversion of feedstocks in this group will require additional sources of hydrogen. Research to discover alternate catalytic routes to hydrogen should be a high priority.

Hydrogen distribution among the molecular fragments produced thermally remains a fundamental issue in converting these feedstocks. It is known that small amounts of added catalysts can greatly increase the amount of liquid products which result from a hydroconversion process. This effect is poorly understood, and recycle of the catalyst particles is still an issue in order for these processes to be economical. Research should be supported at a fundamental level to understand the role of small amounts of catalyst in hydroconversion processes.

Coal and heavy tars differ from residual oil conversion only in the fact that they contain smaller amounts of inherent hydrogen, with coal being the most hydrogen-poor feedstock. All these feedstocks contain large amounts of sulfur and nitrogen which makes the resulting liquids difficult to hydroprocess. They also contain large amounts of aromatic compounds. Coal in particular yields a highly aromatic product, requiring intensive further hydrogenation of the resulting liquids. Research in this area should focus on novel catalysts which remove sulfur and nitrogen during liquefaction. This requires catalysts that are robust, inexpensive, and recyclable.

Residual oil and heavy tars often contain organically bound metals which make catalytic processing extremely difficult. The metals include typically V and Ni which, in addition to clogging catalysts, represent a disposal problem after conversion. Catalytic conversion of these feedstocks will require novel approaches to handling these metals as well.

Production of Liquid Fuels from Coal

Direct liquefaction of coal is proven technology which can be used if the price of petroleum exceeds 30\$/bbl and if environmental limitations can be addressed. The current best technology can yield more than 50% distillable liquids from coal on a m.a.f. basis, or 70% if the required

hydrogen is made from methane, with the process operating at better than 2000 lbs. of H₂ pressure. The liquids obtained from direct liquefaction require further upgrading for removal of sulfur and nitrogen. Coal liquids are also highly aromatic and will require extensive hydrogenation to meet environmental regulations. These two tasks require the same catalysts as described above for sulfur removal and aromatics saturation.

Increasing the liquid yield at lower hydrogen pressure will further improve the process. This will require better catalysts. Direct liquefaction catalysts are needed to more effectively shuttle hydrogen to thermally produced free radicals which otherwise may polymerize to produce non-liquid or heavy products.

The catalyst may be added to the liquefaction reactor in small quantities to modify the hydrogen pathway. Transition metals have been used for this purpose but are quickly converted to sulfides, which are the active catalysts.

A major cost of liquefying coal is the hydrogen required. Measures which utilize the hydrogen more efficiently, such as described in the previous paragraph, are advantageous. Catalytic ways of producing cheaper hydrogen would be of great benefit. Processes which combine methane and coal would also enhance the liquefaction of coal. This would require a catalyst which activates methane in the presence of coal. In summary, improved direct liquefaction processes require the following catalyst improvements:

- ▶ Improved hydrodesulfurization, hydrodenitrogenation, and aromatics saturation catalysts
- ▶ Improved hydrogen transfer and radical healing catalysts
- ▶ New catalytic processes for producing hydrogen and utilizing inexpensive sources of hydrogen in direct liquefaction. The BP-UOP Cyclar process may be a good place to start the search for an improved process.

9.4.5.2 Synthetic Fuels from Biomass

The concept of manufacturing liquid fuels from biomass is appealing because it would shift part of U.S. energy consumption from petroleum to feedstocks that are either renewable resources or the inevitable waste products of modern society. Currently, ethanol derived from corn or sugar cane is used to a limited extent in transportation fuels in the U.S. and Brazil.

An attractive scenario for fuel production from biomass can be based on organic wastes such as corn cobs, bagasse, wood chips, garbage, and sewage sludge. These materials ordinarily require disposal at some cost to a business or community. If these wastes can be transformed from liabilities to assets as feedstocks for fuels, the economics and societal impacts can be highly positive.

The most generally applicable approaches to converting biomass to fuels involve multiple steps, some of which are not catalytic. Some liquefaction processes have converted some of the

heterogeneous solid wastes to gases that can be purified before conversion to useful fuels, such as gasoline or diesel oil. Fortunately, there is a solid base of experience in conversion of organic wastes to methane-rich gases at several municipal waste facilities in the U.S. These gases, which contain methane, carbon dioxide, and inerts, can be feedstocks for several fuel production processes, described elsewhere in this chapter. The most immediate application is reforming landfill gas to synthesis gas that can be converted to fuels by the technologies described above. In fact, a small plant near Denver has begun production of diesel fuel from landfill-derived synthesis gas, using a slurry catalyst (Mills, 1993). In the long term, direct oxidation of the methane to methanol or oxidative coupling to form higher hydrocarbons may be more economical approaches. In either approach, the catalytic technologies are simply those being developed for natural gas conversion. The catalyst research outlined above is directly applicable to the utilization of biomass-derived methane.

A second major approach to using biomass as a fuel feedstock involves direct reforming to give synthesis gas which, in turn, can be converted to liquid fuels by the catalytic processes discussed above. The direct transformation of solid organic waste to synthesis gas is likely to involve reforming technologies like those used in the gasification of lignite, a technology that has received extensive study. The purified synthesis gas can be converted to methanol, mixed alcohols, or hydrocarbons by the catalytic processes described above. The research needs for this kind of catalyst development have been previously explained.

The production of synthetic fuels from biomass by either of the approaches mentioned above is likely to be less economical than production from natural gas or coal, because biofeedstocks have inherently lower energy contents. In addition, because the concentration of the biofeedstock in any one location is low (apart from municipal wastes in major metropolitan areas such as New York City), transportation costs for the feedstocks may be significant. The inherent economic disadvantages, however, are offset to some extent by reducing the disposal costs for biological materials that are regarded as wastes. The high costs for incineration or landfilling of municipal wastes may be adequate incentive to use them as feedstocks for fuels. For any specific biowaste, it is necessary to evaluate the costs of direct energy extraction by incineration with heat recovery vs. the value of the organic waste as a feedstock for fuel production. Similarly, methane-rich gases collected from a landfill can be used as a fuel directly, rather than being converted to a liquid fuel for sale.

Overall, the catalytic research needs for the most promising options to produce liquid transportation fuels from biomass are those required to produce synthetic fuels from natural gas or coal. Other options based on crops such as canola (rapeseed) are specific to the individual crop. Production of such fuels generally incur most for their costs (both in dollars and energy input) in the growth, harvesting and physical processing of the biomass. The catalytic treatment of the resulting oils is usually simple hydrogenation, a technology well developed for the production of cooking oils.

9.5 FUNDAMENTAL ISSUES IN LIQUID FUELS HETEROGENEOUS CATALYSIS

Research areas addressing questions of interest to specific classes of catalytic materials were outlined above. In this section, we list some fundamental questions which are general research questions underlying the phenomenon of catalysis by solids. Progress in answering these questions can lead to a new fundamental underpinning for the field of heterogeneous catalysis. Evidence suggests that, with the current generation of catalytic materials, we have only accessed part of the activity and selectivity inherent in catalysis by solids. Further improvement in the basic understanding of catalysis by solids can lead to a new generation of catalytic materials and catalysts with greater activity, selectivity, and stability. In order to achieve this however, a deeper probing of the catalytic phenomenon must occur and some deeply held ideas regarding catalytic behavior must be challenged.

9.5.1 The Role of Crystalline Active Catalytic Phases

It has been shown that on a per site basis the activity of unsupported MoS_2 is greater than that of supported MoS_2 and that the per site activity of well crystallized MoS_2 is greater still. Crystalline zeolitic materials exhibit stronger acidity than amorphous solids of similar composition. Yet commercial catalysts are often found in disordered states due to the desire to produce small particles of high surface area. Supports are usually included to increase the dispersion of metal and sulfide catalysts and to lower their cost. But evidence suggests that in most cases the support reduces the intrinsic activity of the active phase. This leads to several basic areas of research:

- ▶ The effect of crystalline order versus disorder in active catalytic phases.
- ▶ The effect of support interactions on the per site activity of the active phases.
- ▶ Methods of stabilizing small crystalline particles of active materials and forming them into useful catalytic particles.

9.5.2 The Role of Delocalized Electrons in Small Catalytic Crystallites

The active site has been the "Holy Grail" of catalytic science. Yet it is known that it is incorrect to view the catalytic solid as an array of single organometallic clusters. Catalytic solids often exhibit different and sometimes superior properties than related organometallic compounds with a small number of metals. In addition, organometallic compounds cannot usually be stabilized under conditions necessary for the catalytic processes described in this chapter.

Recent developments in the field of nanophase materials demonstrate clearly that crystallites in nanoscale range (1-10nm) have different and more useful properties than macrocrystalline or amorphous versions of the same material. Closer examination reveals that many familiar catalyst systems such as ammonia synthesis and sulfide catalysts are nanophase materials in their most active form.

The above suggests that delocalized electrons play an important role in the catalytic activity of metallic and semiconducting active phases. Several research areas of general interest arise from this point of view:

- ▶ Investigation of active nanophase material in catalytic environments.
- ▶ The role of immiscible solid catalytic phases in forming interfaces of catalytic interest. Examples are promoted sulfide interfaces, noble metal bimetallic cluster interfaces, *etc.*
- ▶ Surface phases formed under catalytic conditions. An example is carbide surface phases on metals.
- ▶ The role of delocalized electrons at catalytic surfaces.
- ▶ The role of bulk electronic structure in determining surface electronic properties.

9.6 OTHER ENVIRONMENTAL ISSUES IN LIQUID TRANSPORTATION FUELS HETEROGENEOUS CATALYSIS

Several other issues arise which are related to the use of producing liquid transportation fuels efficiently and safely. The solution to these issues presents important obstacles which may determine which catalytic approaches will be successful and which will be hindered. The researcher should be aware of them and research should be undertaken to assist in their resolution.

9.6.1 Environmental Uncertainties Regarding Alternate Fuels

A complete picture of the potential use of alternative fuels requires consideration of the long-term environmental effects of introducing large amounts of new fuels into the environment. It probably could not have been anticipated that chlorinated hydrocarbons would so adversely affect the environment. In the same way, we do not know the full effect of introducing a new fuel, such as methanol, into the environment. Research will eventually answer the question as we get to know the alternate fuels as well as we know hydrocarbon fuels.

In the same manner, the entire environmental cost of producing a new fuel must be considered. In switching to a new fuel, do we lower fuel efficiency to such a point that the environmental benefits are lost? When considering the overall process efficiency, do we consider the net environmental benefit? For example, does the environmental cost of farming outweigh the benefits gained from producing a "renewable resource" such as ethanol. In-depth studies of these questions should be carried out.

9.6.2 Biodegradability of Alternate Fuels

Fuels are inevitably spilled or lost. It must be established that the fuels are safely biodegradable as they enter the environment. Some ethers are reported to be strongly resistant to biodegradation. The biodegradability of oxygenates, such as MTBE, must be firmly established. This will allow confidence in the product and provide simple cleanup methods like bioremediation to be used on eventual spills. Auxiliary research should be performed to establish the biodegradability of alternate fuels.

9.6.3 Catalyst Disposal

The problem of disposing of or recycling used catalysts is becoming critical. The refiner can no longer bury these catalysts in landfills or on refinery sites. New methods are needed to recover metals from spent catalysts. Research in chemical or biological methods should be encouraged in order to be able to do this.

9.7 CONCLUSIONS AND RECOMMENDATIONS

Recommendations are summarized in this section. They are divided into short-term, middle-term (5 to 15 years), and long-term (beyond 15 years). Short term recommendations are already being implemented in many cases by industry and proposed research should impact on the middle- and longer-term recommendations.

9.7.1 Short-Term Recommendations

- ▶ Improved catalysts and improvements to existing processes to reduce aromatics, sulfur, nitrogen, and other pollutants.
- ▶ Improvements to catalytic processes to reduce pollution in the refinery.
- ▶ Improved catalysts and catalytic processes to provide oxygenates such as MTBE.

9.7.2 Middle-Term Recommendations

In this period the trend will continue to demand cleaner liquid transportation fuels based on petroleum hydrocarbons. Oxygenated hydrocarbons will continue to become a larger fraction of the total liquid transportation fuel supply. Methane and natural gas will become alternate sources of the liquid transportation fuel supply. Environmental demands on the refining processes themselves will become greater. This will require:

Highest Priority — Necessary for Success

- ▶ New catalysts and processes for the cleaning and conversion of CH_4 and natural gases to fuels and chemicals.

Medium Priority — Will Enhance Success

- ▶ New catalysts and new processes to provide very clean hydrocarbon based liquid transportation fuels which contain the minimum aromatics, sulfur, nitrogen, and other pollutants.
- ▶ New catalysts and processes which provide increased levels of oxygenated fuel supplies.
- ▶ New catalytic processes which are highly efficient and have low emissions at the refinery.

9.7.3 Longer-Term Recommendations

In this period, alternate fuels will begin to make a major impact on the hydrocarbon liquid transportation fuel supply. High-cost petroleum supplies will make alternate fuels based on secure resources such as coal, shale, and residual oil, more attractive. Introduction of a global carbon tax may make biomass attractive as a CO₂ neutral alternate source for making liquid transportation fuels. This will require:

High Priority — Necessary for Success

- ▶ New catalysts and catalytic processes for utilization of CO₂.
- ▶ New catalysts and catalytic processes for the production of H₂.

This includes better utilization of hydrogen, non-fossil sources of hydrogen, and new catalytic routes to hydrogen which do not yield CO₂ as a product.

Medium Priority — Will Enhance Success

- ▶ New catalysts and processes for producing methanol, ethanol, and other oxygenated alternate fuels

Lower Priority — Not Likely to Impact within Horizon of this Study

- ▶ New processes for cleanly converting coal, shale oil, and residual oil.
- ▶ New catalysts and catalytic processes for converting existing biomass feedstocks (carbohydrates) to liquid transportation fuels.

9.7.4 Recommendations for Catalyst Research

In this section are listed some recommendations covering specific areas of catalytic materials research.

9.7.4.1 Zeolites

For zeolitic catalytic materials the following areas of research are considered to be of major importance:

- ▶ Structure/catalytic function relations for existing zeolites and environmentally important fuels reactions.
- ▶ A continually increasing understanding of acidity in zeolitic catalysts.
- ▶ A better understanding of zeolite structure and phase relationships as provided by advanced probes and theory.
- ▶ A better understanding and control of zeolite synthesis and catalyst preparation.
- ▶ The discovery of new zeolitic materials and their relation to catalytic reactions of interest.
- ▶ Development of zeolitic materials for reactions specific to environmental fuels issues.

9.7.4.2 Sulfides

For the transition metal sulfides to continue to improve in activity and selectivity the following research areas are required:

- ▶ A continued effort to apply theoretical techniques to understanding the fundamental origins of catalytic phenomena in the transition metal sulfide catalytic materials.
- ▶ A continued development of an understanding of the promoted system with an ability to optimize activity or extrapolation to new catalytic systems.
- ▶ A continued development of structure/function relations in this system with an emphasis on larger molecules which represent the most important barriers to new levels of sulfur removal.
- ▶ Development of an understanding and optimization of the sulfide ability to catalyze aromatic hydrogenation in the presence of sulfur.
- ▶ Development of characterization techniques which can reliably characterize disordered sulfides.
- ▶ Development of new catalytic processes which take advantage of the sulfide's ability to both desulfurize and saturate aromatics simultaneously.

9.7.4.3 Metal Catalysts

Research is recommended in the following areas of metal catalysts:

- ▶ Understanding of the basic structural chemistry of small noble metal clusters needs to be developed. Bimetallic clusters and the interfaces of noble metal particles in their catalytic state need to be advanced.
- ▶ Theoretical and structural probes which relate to the noble metal catalysts in their real highly dispersed states need to be advanced.
- ▶ Structure/function relations need to be developed which are related to small particles of noble metal catalysts for reactions of environmental importance.
- ▶ New noble metal catalysts need to be developed based on the fundamental principles outlined above. This may include an understanding of the role of 4 and 5d electrons and how noble metals may be replaced by cheaper metals.
- ▶ The role of carbonaceous overlayers needs to be elucidated and the learnings applied to develop new catalysts.

9.7.4.4 New Catalytic Materials

Research in new catalytic materials, such as oxides, carbides, and solid acids, should be pursued (see chapter 2). Research on these catalytic materials should focus on materials which are stable under catalytic conditions, occurring during production or refining of hydrocarbon based liquid transportation fuels. Research should also occur in areas related to the production of new catalytic materials such that useful materials can be made in large quantities at reasonable cost.

New Catalytic Materials for Novel Processes

Catalysts should be developed which operate in nonconventional reactor systems. These include:

- ▶ Slurry catalysts which operate effectively as small particles or crystallites in reactors producing oxygenates from syngas.
- ▶ Fluid bed catalysts which operate effectively in reactors producing oxygenates from syngas and removing heat effectively during reaction.
- ▶ Nanoscale catalysts for direct liquefaction of coal.

New Catalytic Materials for Oxygenates

In addition to the classes of materials outlined above, new catalytic materials and catalysts are needed for the production of oxygenates. Methanol catalysts are needed which reduce reaction temperature for more favorable thermodynamics.

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Appendix A

REVIEWERS: COMMENTS AND ISSUES

A wide spectrum of experts reviewed the second draft of this report. The executive summary and appropriate chapters have been revised to incorporate most of the suggestions from these peer reviewers. The knowledge and insight provided by the reviewers has contributed greatly to the quality and completeness of this final report.

Generally, the reviewers found the report to be authoritative and the panel well qualified to provide research recommendations on subject. There was agreement with most of the report but some expressed opinions that certain items could have been emphasized to a greater degree. Generally, concerns about recommendations were said to be more a matter of degree than a matter of disagreement.

Some of the comments could not readily be adequately incorporated into the report and, as mentioned, some difference in opinions have been expressed in proposed research emphasis. These issues and comments are summarized in this appendix.

Hydrogen

Several reviewers agreed with importance assigned to research for hydrogen manufacture but thought that more definite research should be proposed, particularly for processes which do not involve CO₂ production. The following comments concerning hydrogen were made:

I was surprised and disappointed to see very little emphasis on the production of H₂. It is clear that there are insufficient supplies of hydrogen in our refineries. What is needed is a simple way of producing hydrogen from water. I thought the report could have been more ambitious (such as primary alcohol synthesis, production of hydrogen, stronger academic/industry interfaces).

The discussion of hydrogen does not indicate the source of hydrogen. Pure hydrogen is CO₂ - neutral only if produced from solar or nuclear energy. The report should indicate what route is proposed.

A theme that appears in several places in the report is that ways are needed to make hydrogen more cheaply. However, other than industrial advances in steam reforming of natural gas, the pace of advances in this area is very slow and clues are not furnished as to how this is to be accomplished.

Environmental

The following comments regarding environmental aspects were made:

You adopt the premise that the petroleum area will be driven by environmental concerns, yet almost no recommendations for work on catalytic control of emissions and many pages of recommendations for R&D in fuels strikes me as a contradiction. The report recommends leaving to industry work on catalysts for emissions control and goes deep into industrial processing of fuels.

A recognition also needs to be made that there is still a controversy on the effectiveness of oxygenates to control auto emissions without contributing to the problem. Mention should be made of the development of a superior catalytic auto exhaust muffler capable of operating at high efficiency under cold start conditions with complete conversions of pollutants to carbon dioxide and water. Such devices are currently under development and a successful system would have drastic effect on the economics of reformulated gasoline. This would be a killer technology for much of the anticipated catalysis and process innovations needed to meet future auto emissions standards.

Another repeated theme is — do something to cut down on CO₂ emissions or find uses for CO₂. Yet many of the reactions advocated (water-gas shift, Fischer-Tropsch, etc.) form CO₂. As practiced with iron catalysts, the Fischer-Tropsch reaction releases one CO₂ molecule for each -CH₂- formed.

Direct/Indirect Coal Liquefaction.

The following comments concerning direct/indirect coal liquefaction were made:

One general concern is the report's emphasis on synthesis gas chemistry for the production of liquid fuels, with corresponding de-emphasis for direct coal liquefaction and heavy oil upgrading. We are less convinced than the authors about a trend toward or reliance on methane for liquid fuels. Gas prices have tended to follow petroleum prices, while coal prices have been flat. Moreover, coal supply is assured, while an inexpensive gas supply is less certain. Therefore, it is believed that greater opportunities exist than this report would suggest for improvement in direct liquids production from coal and heavy oils through catalysis research.

Surface Science

The following comments regarding surface science were made:

Personally, I believe that there is an over-emphasis on surface science and characterization of materials. Findings put too much emphasis on the rational design of catalysts. I believe computer modelling is being oversold nationwide!

The list of needs in science of catalysis is really surface science focused. We also need to establish new chemistry which will be possible with catalysis. There is too much analysis of

catalyst surfaces and not enough evaluation of their utility. Many publications discuss the characterization of a catalyst without offering comparative data for the use of that catalyst compared to current catalyst alternatives. We need to put more chemistry back into catalysis.

It is a big leap from the arduous empirical concoction of a fluid cracking catalyst to the design and synthesis of a complex catalytic material. It would be good to make an honest statement about this complexity and the magnitude of the challenge ahead, and to develop with concrete evidence the reality of catalyst synthesis as it now stands, even if it is only primitive, and from this to develop what catalysis synthesis can be. It is important to develop the case with evidence, rather than asserting it.

The chapter on chemicals focuses on selective oxidation and that is appropriate. What is absent is a more ambitious quest for new chemistry. For example we need to discover catalysts for adding O_2 or water to olefins to produce primary alcohols. We need better catalysts for higher yields of sulfuric acid from SO_2 . We need catalysts to produce phenol from benzene and O_2 , to produce H_2O_2 from H_2 and O_2 directly, and propylene oxide via O_2 and propylene.

Economics

The following comments concerning economics were made:

We believe that the main barrier to commercialization of technologies which process these feedstocks is processing costs, not environmental concerns. Catalyst development could have a significant effect on reducing processing costs. It is clear throughout this report that the authors recognize that improvements and trade-offs must be considered in economic terms, but the treatment of economics is qualitative and inconsistently applied. While we recognize the difficulties in doing a comprehensive analysis of such a broad topic, we recommend that more formal attention be paid to defining and addressing economic issues in setting research priorities.

The point is made that advanced U.S. technology is important to improve the national balance of trade. Assume that many millions of dollars are funded to tackle the objectives outlined in this report. Will the researchers publish, patent, or give industry the rights to obtain patents? The current system suggests that the results will likely be presented to the science community for all nations to develop and commercialize with no real opportunity for U.S.-based industry. There should be a recommendation on how the panel would like to see intellectual property, funded through this research, provided to U.S.-based companies who pay some of the taxes which fund this research.

There is a sense of by-passing reality in the report. Research in catalysis is governed by industrial needs and by political decisions. Certainly the report recognizes the constraints imposed by the Clean Air Act Amendments and other legalities. But it does seem, for instance, to advocate that ethanol be synthesized from ethylene with barely a hint that there is a federal tax benefit of fifty four cents per gallon of ethanol made by fermentation of starch and later, from cellulose.

Other Specific Topic Comments

The following comments were made on other topics:

The anchoring of homogeneous catalysts to make heterogeneous catalysts was briefly alluded to. Perhaps more emphasis should be placed on this concept. This may be the fastest approach to developing new heterogeneous catalysts for difficult reactions. New approaches need to be discovered to truly anchor organometallic compounds without losing their homogeneous activity and selectivity.

Throughout the different chapters, I found a concern for the sulfur problem, but it is not given sufficient weight in the summaries. We need to uncover new chemistry to treat this sulfur and/or convert it into acceptable byproducts.

Ab initio calculations are an area of potential increased collaboration between national laboratories, with massive computing power, and industrial and academic researchers. Mention should be made of more close collaboration between academia/industry/government as a potential for making more rapid progress in several areas of catalysis.

Appendix B

PROJECT OBJECTIVES AND METHODOLOGY

BACKGROUND

In response to a Notice Inviting Grant Applications (Notice 92-7 published in the Federal Register, Vol. 57, No. 13, Tuesday, January 21, 1992, Page 2272), Consultec Scientific, Inc., submitted a grant application and was subsequently awarded a Special Research Grant to organize and direct a panel of experts to conduct a Research Needs Assessment entitled, "Advanced Heterogeneous Catalysts for Energy Applications". The objectives of this project were to provide an assessment of the direction, content, and priority of research needs over the long term (5 to 20 years) that will provide the best chance for success in achieving enhanced utilization of advanced heterogeneous catalysts for energy related applications. Included are energy conservation through process improvement, uses in alternative fuel development or alternate feedstock utilization, and applications to alleviate pollution from energy processes. Specific examples are heterogeneous catalysts in coal liquefaction, coal gasification, biomass conversion to gaseous and liquid fuels, use of non-petroleum feedstocks in chemicals manufacturing and conversion of natural gas to liquid fuels. The study does not address electrochemical, photochemical, biochemical or homogeneous catalysts.

DISCUSSION OF THE PROBLEM

The need for new and improved technology to meet our energy needs has been articulated in the National Energy Strategy prepared by the DOE in 1991. It is clear that major needs are technology for economical manufacture of transportation fuels from abundant non petroleum sources, for pollution abatement in energy utilization, and technology which would lead to energy conservation. The application of catalysis is believed to have great promise to provide the basis for fulfilling such needs.

Fortunately, there are abundant resources of coal, biomass, and gas in the United States. It is known that these can be transformed to high quality fuels, however, at present such processes produce fuels which are about twice as expensive as petroleum at world prices.

Heterogeneous catalysis has revolutionized petroleum refining and petrochemical manufacture. It is believed that intensive, directed research can lead to appropriate technology applied to alternative feed materials. General guidance has been provided recently by the reports, "Catalysis Looks to the Future", National Research Council, 1992; Coal Liquefaction - A Research and Development Needs Assessment (DOE Panel 1989); and the earlier, "Opportunities for Chemistry", (Primentel Report) National Academy of Science, 1985. However, these only give general guidance. The present study is designed to provide specific up-to-date evaluative assessments and prioritized recommendations.

Great strides have been made in the transformation of catalysis from an art to a science. This assessment of research needs is based on examining a logical progression of catalytic technical areas summarized below:

Catalyst synthesis begins with the design concepts of physical structure and elemental composition, including oxidation states and coordinational and other interactions between catalyst components. The knowledge of and lack of knowledge of metals, ceramics, zeolites and special supports such as membranes was assessed as well as preparational techniques.

Catalyst characterization by the wide array of modern instrumental techniques offers critical insight into catalytic structures on an atomic scale. Some of the techniques that are presently available for characterization include:

Surface Science: LEED, UPS, XPS, AUGER, SIMS, RIS, SIRIS, XAFS, XANES, XRF, SERS, NMR, Mossbauer, FTIR

Imaging: SEM, TEM, STM, Scanning Auger

Classical: IR, UV, XRD, Raman

These and other characterization technologies were reviewed for applications in catalysis.

Catalysts performance testing strategies in diagnostic experiments and in practical fuel synthesis conditions is expected to be a major consideration. A knowledge of the status of catalytic mechanism determinations is believed to be fundamental to determining research needs and directions. Further, an assessment of an understanding of resistance to deactivation by poisoning or sintering is important since the practical value of a catalyst is often determined by its capability to remain active and selective.

Interpretation of experimental information is critical to catalytic advances. Therefore, this study included a major focus on the status of knowledge and future prospects for a better understanding of catalyst structure/performance relationships and particularly deduction of scientific factors which underlie catalyst activity and selectivity.

Engineering of catalytic processes is often the key to successful operation. This entails the utilization of kinetic and calorimetric information. Reaction modelling and computer reaction design is of growing importance. Successful catalyst application also depends on an appropriate knowledge of mass and heat transfer within catalyst pellets and in reactor systems. It is significant that innovative engineering has been responsible for several of the most important catalytic engineering advances, *e.g.* fluid bed processing.

Catalysts for pollution abatement represent a significant component of this assessment. This includes processes for catalytic conversion of stack-gas pollutants to a harmless form. A prominent example is conversion of NO_x directly to N_2 and O_2 . Environmental aspects of catalyst preparation and use can control catalyst acceptability.

Systems evaluations can provide important research guidance by revealing quantitative information on the value of utilizing a catalyst in a particular process. Evaluation of the economics of fuel manufacture and use, as well as the implications of alternative feedstock utilization, were part of this needs assessment.

The overall approach utilized to fulfill the objectives of this assessment, was to address generic catalytic operational elements — catalyst preparation, characterization, performance testing, etc. as discussed above. These elements provide the basis for mutual technologies which are applicable to specific issues, namely, coal and biomass conversion to liquids and gases, flue gas clean-up, use of nonpetroleum feedstocks in chemicals manufacture, and conversion of natural gas to liquid fuels. The panel members are foremost experts in the specific science and technology in these fields, and there are at the forefront in their expertise in state-of-the-art catalytic theory and practice. In catalyst synthesis, design follows function. Function, activity, and selectivity are determined by interactive reactant/catalyst chemistry.

Heterogeneous catalysts are recognized to be central to production and consumption of fuels, manufacture and processing of chemical feedstocks and plastics, pollution abatement, and energy conservation. Recent advances in catalytic science and technology have been profound. These give exciting promise for new and greatly improved catalytic technology in national energy applications. It is visualized that benefits can be:

1. Synthetic fuels manufacture which is much more economically attractive (lower plant investment and operating costs).
2. Use of alternative feedstocks available in the United States (gas, coal, biomass).
3. Energy conservation through improved processes which operate with better energy efficiency.
4. Abatement of pollution in fuels processing and use, including fuels which lower tail gas pollution. At present, the use of catalysts to remove pollutants has been stressed. However, we are moving into an era in which catalytic processes are being devised which avoid the formation of pollutants. Examples are use of non-liquid acids for alkylation and use of a combustion catalyst to carry out combustion at lower temperatures (*e.g.* for generation of electricity using turbines, being developed at Catalytica) and so avoid the formation of NO_x .
5. Significant scientific advancement applicable in catalysis and related fields.

Consideration of these factors and an educated estimation of the difficulty and likelihood of success formed the basis of our evaluative process and prioritization of recommendations.

It is believed that there are excellent opportunities for catalytic technology to make major improvements in the long range (5 - 20 years) to our national energy applications. As Antoine

de Saint Exupry said in his book, *Wind, Stars, Sea and Sand*, "When it comes to the future, our task is not to foresee it but to enable it to happen."

METHODOLOGY

The assessment was performed for the Department of Energy by an international panel of scientists representing a wide background of experience and expertise necessary to produce a comprehensive and authoritative assessment report.

Dr. Harvel Wright, President of Consultec Scientific, served as Project Manager. Dr. G. Alex Mills, Center for Catalytic Sciences, University of Delaware, served as the Principal Investigator. The remainder of the panel of experts included:

Dr. Russell Chianelli	Exxon Research and Engineering Co.
Dr. Heinz Heinemann	Lawrence Berkeley Laboratory
Professor Henry Foley	University of Delaware
Professor Gary Haller	Yale University
Dr. James E. Lyons	Sun Company
Dr. George Parshall	E. I. Dupont de Nemours & Co.
Dr. Jule Rabo	U.O.P., Inc.
Dr. Jens Rostrup-Nielsen	Haldor Topsoe A/S
Professor Wolfgang Max Hugo Sachtler	Northwestern University
Professor Kenzi Tamaru	Science University of Tokyo

This outstanding team of experts was carefully selected to meet the following criteria:

1. The team provides a broad coverage of the technical areas that are needed for the study. Figure 1 indicates the technical areas which are covered by the panel members.
2. The team contains representatives from both academia and industry.
3. The panel includes experts from Europe and Japan to insure international coverage from these areas.
4. The team is sufficiently broad and diverse that the possible bias of one or more members will not be sufficiently important to produce an undesirable bias in the final report.

Panel members had two responsibilities during this study. First, each panel member was to research a given area and prepare a section of the report. Second, the panel was to prepare and prioritize a list of research needs in the subject area. Twice during the study the full panel held two day long meetings with DOE personnel. The first meeting was concentrated on establishing the objectives and developing the plans for carrying out the study. The second meeting concentrated on the panelists presentation of their respective findings and on establishing and prioritizing the research needs.

A draft of the report of the study was prepared and submitted to a list of peer reviewers for their comments. The peer reviewer comments were then addressed and the final report prepared and

submitted for publication. The deliverable product from this assessment is this report representing the findings of the panel of experts. Based on the collective expertise of the experts who have contributed ideas and suggestions during this study, this report stresses recommendations which the panel feels will enable the DOE to focus its research directions and improve its research capabilities over the long term (5 to 20 years).

AREAS OF PANEL EXPERTISE AND EXPERIENCE

<u>CATALYSIS SCIENCE AND TECHNOLOGY</u>	Mills	Chianelli	Foley	Haller	Heinemann	Lyons	Parshall	Rabó	Rostrup-Nielsen	Sachtler	Tamaru
<u>Preparation:</u>											
Rational design - state of art	X	X	X		X	X	X			X	X
Rational design - computer graphics expert systems (A.I.)			X								
Materials science - ceramics, zeolites, other supports, membranes	X	X	X	X	X	X	X	X	X		X
Materials sci. - metals, complexes, compounds	X	X	X	X	X	X	X	X			X
Preparational techniques	X	X	X	X	X	X	X	X			X
<u>Characterizations:</u>											
Surface science: XDR, FTIR, NMR, ESCA, TEM, LEEDS, UPS, EXPS, SIMS, STM		X	X	X	X	X	X	X	X	X	X
Physi-, chemi- sorption areas, pore size distributions	X	X	X	X	X				X	X	X
<u>Performance Testing:</u>											
Methodology, technique, apparatus, Analytical: activity, selectivity	X			X	X	X	X	X	X		X
Mechanism determination, kinetics, isotopic tracers	X			X	X	X	X		X	X	X
Resistance to deactivation, poisons, sintering	X	X		X	X	X	X		X	X	X
<u>Interpretation:</u>											
Structure - support interactions	X	X		X	X	X	X	X	X	X	X
Structure - performance relationships, atomistic, electronic	X	X		X	X	X	X		X	X	X
<u>Engineering:</u>											
Heat, mass transfer issues					X				X		
Innovative reactor design			X		X		X	X	X		

	Mills	Chianelli	Foley	Haller	Heinemann	Lyons	Parshall	Rabó	Rostrup-Neilsen	Sachler	Tamaru
<u>Environmental Aspects:</u>											
Catalysts for abatement	X	X	X	X	X			X	X	X	X
Preparation and use			X	X			X				X
<u>Systems Evaluation:</u>											
Economic evaluation							X		X		
Supply (coal, gas, biomass) impact					X		X		X	X	
Environmental impact		X		X	X		X		X		X
Overall evaluation	X	X			X		X	X	X	X	
RESEARCH EXPERIENCE											
<u>Academic, Institutional</u>	X		X	X	X	X		X		X	X
<u>Industrial</u>	X	X	X		X	X	X	X	X	X	
APPLICATIONS EXPERIENCE											
<u>Transportation:</u>											
Fuel supply, fuel use	X	X	X		X	X		X	X	X	
<u>Industrial:</u>											
Petrochemicals	X	X	X		X	X	X	X	X	X	
<u>Pollution Abatement</u>		X		X	X				X	X	X

Appendix C

GLOSSARY

ACGIH	American Conference of Governmental Hygienists
AGC	Advanced Gas Conversion
AES	Auger Electron Spectroscopy
AFM	Atomic Force Microscope
ALE	Atomic Layer Epitaxy
CAAA	Clean Air Act Amendments
CFCS	Chloro Fluoro Carbons
CFDS	Computational Fluids Dynamics Services
CRGT	Chemically Recuperated Gas Turbine
EELS	Electron Energy Loss Spectroscopy
ESCA	Electron Spectroscopy for Chemical Analysis
ETM	Electron Tunneling Microscope
EXAFS	Extended X-ray Absorption Fine Structure
DIPE	Diisopropyl Ether
FCC	Fluid Catalytic Cracking
FFV	Flexible Fuel Vehicle
FGD	Flue Gas Desulfurization
FT	Fischer-Tropsch
FTIR	Fourier Transform Infra Red
GNP	Gross National Product
HCFCs	Hydrochlorofluorocarbons
HDM	Hydrodemetalization
HDS	Hydrodesulfurization
HFCs	Hydrofluorocarbons
HREEL	High Resolution Electron Energy Loss

IFP	Institute Française du Petrol
IGCC	Integrated Gasification Combined Cycle
IGT	Institute of Gas Technology
IIT	Illinois Institute of Technology
IM	Inspection and Maintenance
ISS	Ion Scattering Spectroscopy
LEED	Low-Energy Electron Diffraction
LNG	Liquid Natural Gas
LPCVD	Low Pressure Chemical Vapor Deposition
LPG	Liquefied Petroleum Gas
LPMEOH	Liquid-Phase Methanol
MAS	Mixed Alcohol Synthesis
MASI	Most Abundant Surface Intermediate
MBE	Molecular Beam Epitaxy
MELS^o	Tetravalent Metal Phosphonates
MOGD	Mobil Olefins to Gasoline and Distillates
MTBE	Methyl Tertiary Butyl Ethel
MTG	Methanol-To-Gasoline
MTO	Methanol-To-Olefins
NGL	Natural Gas Liquids
NMHC	Non-Methane Hydrocarbons
NMR	Nuclear Magnetic Resonance
NRC	National Research Council
PETC	Pittsburgh Energy Technology Center
RDS	Rate Determining Step
RITE	Research Institute of Innovative Technology for the Earth
SASOL	South African Coal, Oil, and Gas, Ltd.
SCR	Selective Catalytic Reduction
SMDS	Shell Middle Distillate Synthesis
SNG	Synthetic Natural Gas

SRC	Solvent Refined Coal
STM	Scanning Tunneling Microscope
TBHP	Tert-Butyl Hydroperoxide
TIGAS	Topsøe Integrated Gasoline Synthesis
TPD	Temperature Programmed Desorption
TPR	Temperature Programmed Reduction
TVA	Tennessee Valley Authority
VOCs	Volatile Organic Compounds
XANES	X-ray Absorption Near-Edge Structure
XPS	X-Ray Photoelectron Spectroscopy
ZSM	Zeolite Synthetic Mobil
Nanoscale	molecular scale. 1 nanometer = 10^{-9} meter = 10Å
Heuristic	rules assembled through experience (rather than theory)

DATE

FILMED

8/26/94

END