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STUDIES OF FUNDAMENTAL FACTORS
CONTROLLING CATALYZATION
OF REACTIONS OF GASES
WITH CARBONACEOUS SOLIDS

August, 1981

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STUDIES OF FUNDAMENTAL FACTORS CONTROLLING CATALYZATION
OF REACTIONS OF GASES WITH CARBONACEOUS SOLIDS

FINAL REPORT

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Abstract

Studies of the effects of catalyst particle size and composition and of reaction temperature on the gasification of graphite in $H_2 + 2$ percent H_2O by dispersed metal catalysts have produced a fairly comprehensive understanding of the process. The experimental observations suggest that the role of catalysts is to effect dissociation of H_2O . The absorbed H and O adatoms then transfer, that is, "spill over," to the carbon surface and combine to form CO and CH_4 . Spill-over cannot occur if a thin insulating barrier is present between metal and graphite. Gasification is highly localized around each catalyst particle and results in the formation of surface channels and deep pits on single crystals of graphite due to anisotropy in carbon bonding. Similar, but extremely fine, terrace channeling occurs on the graphite microcrystalline aggregates compressed into planchets.

The rate of gasification by Fe over a wide range of particle size (~ 10 nm to 1 mm) is determined by the total surface area. Thus the simple relation that reaction rate $\propto \frac{\text{wt \% catalyst}}{\text{particle size}}$ provides a useful guide to the activity of a particular catalyst powder.

Transition metal alloys generally show a reduced level of catalytic activity. Ni-Cu alloys are of interest as they were found to produce a desirable increase in the CH_4/CO ratio of the product gas. Several readily available forms of highly dispersed iron powder could be used as expendable catalyst additives for coal gasification, particularly to enhance *in situ* (underground) methods.

Introduction

Heightened appreciation of the need to use the nation's abundant supplies of coal as a source of energy and chemical feedstocks has sparked increased interest in research into the basic mechanisms of the conversion of coal to liquids, gases, and metallurgical coke. The availability of new experimental techniques such as *in situ* electron microscopy, Auger spectroscopy, Mossbauer spectroscopy, and other instrumental techniques has also prompted a re-examination of earlier work concerned with mechanisms of gasification, that is, oxidation or hydrogenation of various forms of carbon. The very pronounced influence of catalysts on these reactions has been examined previously by a number of investigators who generally used bulk samples of graphite impregnated with metal salts. In addition, some studies have been conducted by electron microscopy. This work clearly revealed that small metal particles can catalyze the gasification of single crystals of graphite and produce narrow reaction channels that are directly related to the crystallography of the graphite surface.

The primary objectives of the research program summarized in this report were to re-examine the fundamental factors controlling the catalyzation of reactions of gases with carbonaceous solids. The specific experimental approach was to determine the effects of the size, number, and composition of catalyst particles on the overall reaction kinetics, and the nature of the gases

produced by heating in wet hydrogen in the temperature range 750 to 1100°C.

The technological goal of the program was to explore the feasibility of developing low-cost, expendable catalysts that could be used as additives in large-scale gasification plants. A significant increase in reaction rate (that is, the through-put of the gasifier) and a higher CO and CH₄ concentration (higher caloric value of the product gas) due to the use of a catalyst would have an important impact on the economics of coal gasification. Iron-containing materials with potential value as additives were identified. The results of the research are also relevant to other gas-phase reactions with carbon, including combustion, coking, and the consumption of graphite electrodes in electric-furnace steelmaking.

Experimental Methods and Materials

The experimental methods and materials used in this research are described in detail in the appended manuscripts. The general approach was to expose small pieces of natural or synthetic (pyrolitic) graphite single crystals, about 1 cm² section of 2 mm polycrystalline graphite planchets, or about 0.5 g samples of coal char to flowing H₂ + H₂O at atmospheric pressures at temperatures from 750 to 1100°C in a specially constructed reaction cell. A gas-mixing system was employed to permit control of the gas flow rate and moisture content. An oxygen sensor was used to determine

the O_2 partial pressure, and the CO , CO_2 , and CH_4 contents of the effluent gas were also determined. The size and composition of the catalyst particle were determined by electron microscopy, and the structure of the reacted regions on the graphite surface was examined in detail.

Major Results and Conclusions

The significant findings of the research program are discussed in detail in the various manuscripts and summaries appended to this report. The most important points are summarized below.

1. Metal particles catalyze highly localized gasification.

The form of the reaction zone depends on the type of graphite and the size of the catalyst particles. In the case of single crystals of graphite, very small particles of iron or other transition metals or alloys generate narrow channels, mostly aligned along $\langle 11\bar{2}0 \rangle$ directions; the depth of these channels is determined by the ledges present on the crystal surface. Broad wavy channels result if the metal particles are larger in diameter than the ledge height. In the case of synthetic graphite crystals, deep reaction pits develop in the graphite at the sites of grown-in lattice defects.

In the case of polycrystalline graphite planchets, the small vapor-deposited metal particles, about 30 nm in diameter, catalyze numerous very fine channels to give the appearance of a rather uniform gasification of the coated area. Large metal particles (8 μm diameter powder or 1 mm spheres) catalyze highly localized

pits around each particle and, if the reaction is continued, produce holes right through the graphite disk.

2. The rate of catalytic gasification is determined by the surface area of the catalyst. When compared on the basis of an equal mass of metal, particles 30 nm in diameter will cause a weight loss of graphite and corresponding CO and CH₄ production as much as 104 times greater than those produced by a single 1-mm Fe sphere.

3. Dissociation of H₂O molecules on the metal surface is the rate-controlling step. Adsorbed oxygen and hydrogen atoms presumably migrate over the catalyst surface, transfer to the graphite, and continue until they encounter labile carbon atoms to form CO or CH₄ molecules which evaporate from the surface. If the metal catalyst particle does not make good electrical contact with the surface, that is, if it is isolated with an insulating layer, the "spill-over" of hydrogen and oxygen from the metal to the graphite surface cannot occur and the reaction stops.

4. Composition of alloy catalysts has only a secondary effect on reaction rate. A series of alloys was investigated, and as expected, alloys close to pure iron in composition showed a higher reaction rate to form CO, whereas alloys close to nickel in composition exhibited the highest reaction rate to form methane. Nickel-copper alloys containing about 10 percent Cu exhibited a surprising result in that the CH₄-CO ratio was as much as 100 times

higher with this alloy as a catalyst than with pure nickel alone. The reason for this is that the addition of Cu suppresses the rate of formation of CO considerably but has a relatively very small effect on the methane formation rate. Thus, although the overall reaction rate is somewhat lower (would require more catalyst) a desirable high CH_4 -CO ratio can be produced.

5. Pronounced cyclic oscillations in reaction rate were noted. A bistable condition of either all CO or all O_2 adsorption on the catalyst surface depending on CO concentration results in an abrupt transition between high and low reaction rates.

6. Peripheral observations of miscellaneous discoveries pertaining to the breakup of evaporated films to form fine particles, effect of carbon in greatly reducing the surface energy of iron at high temperatures, disintegration of iron in wet hydrogen atmosphere (a new form of hydrogen erosion), and the possible existence of a coupled vacancy-carbon flux in iron were noted. These are all important subjects for further research.

Recommendations for Further Research

The present understanding of catalytic gasification of carbon is still far from complete. However, a number of new observations made during the course of this program provide new approaches to experimental and theoretical analyses. The main points for further basic research are summarized below.

1. Efforts to develop a theoretical model for the rate of

channel formation in the case of very small catalyst particles on graphite single crystals should be encouraged. Although the increase in channel length per unit time can be measured reasonably well from *in situ* observations (results reported have not been particularly consistent), a satisfactory theoretical model for the process does not exist.

2. The attractive CH_4 -CO ratio that can be achieved at high reaction temperatures ($\sim 1000^\circ\text{C}$) with Ni-Cu alloy catalysts should be explored much more extensively. A major complication is that methods to determine the surface composition of alloy catalysts for conditions that occur during gasification must be developed. During cooling, segregation of elements to the surface will probably occur, so that room-temperature measurements will not be particularly useful. On the other hand, heating in vacuum to the reaction temperature will not yield the surface composition that occurs in the gasification atmosphere. This is a very difficult problem because the analytical techniques available for surface analysis are not applicable at even moderate gas pressures.

3. The various peripheral observations summarized in Appendix I should be studied in more detail.

Recommendations for Applied Research

The results generated by this research demonstrate that the catalytic gasification of graphite can be enhanced tremendously by the addition of a suitable catalyst of extremely fine particle

size. Although most of the experiments were conducted by using evaporated metals to generate a layer of particles typically in the range 20 to a few hundred Å in diameter, other experiments employed finely divided metallic iron powder, ground iron-ore concentrate (primarily iron oxide), or metal-intercalated graphites. These latter materials are all very active catalysts and could be effective additives in large-scale gasification plants. The "graphimets" were found to be extremely effective catalysts because of the large number of extremely small "islands" of iron present on the exfoliated graphite surfaces. Although this material is expensive to purchase from a laboratory supply house, the method of preparation is extremely simple and it should not be expensive to produce in large quantities.

Some experiments were also conducted with ferrocene (a metal-organic liquid) to impregnate the graphite. Evaporation of the solvent leaves extremely fine metal complexes which decompose to form metallic iron particles very readily during heating. This material also exhibited extremely high catalytic activity (per unit weight of iron) and might prove to be an economically feasible additive to a gasification process.

The major limitations to direct carryover of these findings to large-scale gasification processes include the following:

1. This research was conducted at atmospheric pressure, whereas gasification processes normally operate as high as 20 atm.

pressure to enhance the yield.

2. The apparatus used was not suitable for gasification of coal because of the coal tars and other heavy components formed during low-temperature heating. Thus, the applicability of the measured effects of the catalysts on the reactivity of coal is unknown. However, results of experiments conducted with coal char, which had been heated separately to drive off the volatile constituents, fitted in well with the data obtained on polycrystalline graphite.

3. The action of the catalyst to dissociate water molecules to hydrogen and oxygen requires that it be maintained in the metallic state. Some modification of the present steam-gasification atmosphere will be required. Empirical study of these very practical aspects of gasification should be encouraged.

In Situ (Underground) Gasification

For economic and environmental reasons, *in situ* underground gasification of unmineable coal seams is receiving considerable attention despite the relatively abundant supplies of natural gas available at this time. The introduction of fine catalyst particles with the steam-gas mixture might enhance the reaction rate and upgrade the syngas product significantly, thus improving the economics of the process.

Preliminary enquiries have been submitted to the Gas Research Institute to conduct modeling and laboratory measurements of *in situ*

gasification based on the results and concepts generated by this Department of Energy contract research.

Acknowledgments

A number of present or former members of the Research Laboratory made important contributions to this research program. Dr. C. Glenn Shirley, now with Motorola, Inc., Phoenix, Arizona, participated in the early stages of the work, along with Drs. F. C. Schwerer, G. P. Huffman and J. V. Mahoney, of this Laboratory. In a subsequent phase, Dr. Udaya Rao, now with the Department of Energy, Basic Energy Technology Center, Pittsburgh, Pennsylvania, participated in another phase of the work as indicated by the list of publications. Excellent technical assistance was provided by C. C. Fisher and J. W. Conroy.

APPENDIX I

Summary of Incidental Observations

Several unusual microstructural features noted during this investigation suggested the influence of several unknown or not easily recognized phenomena. In some cases, the experiment was repeated or modified to confirm the validity of the observations, with the intention of exploring the implication further at a later date. The nature of the most interesting effects is summarized below.

Microstructure of Metal-Intercalated "Graphimets"

The catalytic activity of commercially available graphite powders intercalated with various metals for gasifying carbon in wet hydrogen was found to be more than 100 times greater on a weight basis than that of very fine ($\sim 8 \mu\text{m}$ diameter) iron powder. These materials, distributed by Ventron Corporation under tradenames, such as Graphimet Fe-10 (10% Fe), are prepared by intercalation with metal chloride followed by low-temperature reduction to remove the chlorine. According to the Ventron catalog, this process results in a uniform distribution of metal atoms on basal planes throughout the graphite. However, high-resolution electron microscopy revealed that the metal is present in the form of "islands" ranging from 1 to 10 nm in diameter on the surfaces of graphite flakes that have partially split into multiple layers. High-

resolution lattice imaging and electron energy loss spectroscopy indicated that the islands were metallic for Ni and Pt graphimets, whereas the Fe, Cu, and Co oxidized when these graphimets were exposed to air after vacuum drying. A paper coauthored with colleagues at the Cavendish Laboratory on the structure of graphimets will appear in the Journal of Catalysis.

Surface Energy of Fe-C Alloys

The appearance of graphite samples coated with Fe particles and heated to 1100°C (higher than the usual range for the gasification experiments) suggested a very low surface energy for the iron phase. The iron particles, which remained as spheres and produced narrow channels during gasification at lower temperatures, spread out as very thin ribbons along the vertical edges of the channels, which formed into very broad terraces. It appeared that the iron would continue to extend into an ever thinner film as the terraces expanded. In the case of polycrystalline graphite, the iron also spread out to form very thin "soap-bubble-like" films across the reaction pits that developed during gasification. These observations were described and illustrated during university seminars on catalytic gasification. Preliminary discussions were held with several university colleagues who expressed interest in a collaborative effort to determine the surface energy of iron under conditions of high carbon activity.

Spheroidization of Evaporated Thin Films

Very fine particles of iron and other catalyst metal were dispersed on the surface of single and polycrystalline graphite by vacuum evaporation followed by annealing in dry hydrogen at 750°C. It was noted that the mean size and number per unit area of the metal particles appeared to depend on the initial film thickness. A series of measurements revealed that this was indeed the case, as illustrated in the data plotted below. The $t^{2/3}$ size-thickness dependence does not appear to depend on the substrate but this was not investigated extensively. This relationship was mentioned in various talks on catalytic gasification and discussed with a number of people but no one has come up with an explanation that is compatible with the observations. Evaporated films are now known to consist of 3- to 5-nm-diameter columns of crystalline material separated by grain boundaries and vacancies, which result in ~2 percent shrinkage during recrystallization. Examination of the early stage of spheroidization revealed that the films first break up into irregular patches of approximately the same size, which then draw up in spheres during prolonged heating. The appearance of the patches is reminiscent of the craze pattern that often forms when mud or clay dries in the hot sun. A description of these observations will be prepared for publication in Thin Solid Films.

Dependence of particle size and distribution after spheroidization on the thickness of evaporated thin films.

Layer Structure of Pyrolytic Graphite

Catalytic gasification of single crystals of pyrolytic graphite in wet hydrogen with Fe powder resulted in the formation of terraced pits containing a single catalyst particle or a sintered cluster. The gasification reactions in effect etched the graphite crystal to reveal a distinctive layered structure. The spacing between layers was about 3 to 8 μm in the poorer grade of crystals (misorientation $\sim 4^\circ$) and was considerably larger in the high quality crystal ($\sim 1^\circ$ misorientation). A short note to Carbon on these direct observations of substructure in single crystals of pyrolytic graphite will be prepared.

Suggestion of a Coupled Carbon-Vacancy Flux

Some graphite gasification experiments were conducted by using thin (50 to 100 μm) iron foils under conditions where carburization occurred on one surface and decarburization on the other. The appearance of unusual pits and hillocks on the carbon entrance and exit surfaces, respectively, suggested the possible occurrence of a coupled carbon-vacancy flux although the effect was not totally reproducible. Experiments specifically designed to test the hypothesis of a carbon-vacancy flux have been planned with Dr. K. H. Westmacott of the Lawrence Berkeley Laboratories, University of California. This investigation will be conducted during 1981-1982.

Fretting of Iron in Wet Hydrogen

Some experiments were conducted to determine the effect of relatively large iron particles (20 μm - 1 mm dia.) in catalyzing gasification of graphite in $\text{H}_2 + 2\% \text{H}_2\text{O}$ at 700 to 1000°C. Close examination of the relatively coarse pits produced revealed that numerous very small iron particles were present on the graphite and were generating reaction channels on the terrace and ledges within the pit. The source of these particles was found to be hydrogen-induced fretting of the iron surface. This form of hydrogen corrosion, which occurs at atmospheric pressure and in the absence of stress, has not been observed before. A brief note will be prepared for AIME Transactions describing this phenomenon.

APPENDIX II

PRESENTATIONS AND PUBLICATIONS

Fundamental Factors in Catalyzed Carbon-Gas Reactions.

J. V. Mahoney, C. G. Shirley and R. M. Fisher, ERDA, Heterogeneous Catalysis Research Meeting, Germantown, Md., November 22-23, 1976.

Electron Microscope Studies of Iron-Catalyzed Gasification of Graphite.

R. M. Fisher, C. G. Shirley, A. Szirmae and J. V. Mahoney, Scientific Problems of Coal Utilization, DOE Symposium Series No. 46, Morgantown, W. VA., May 23-25, 1977.

Electron Optical Studies of Catalyzed Gasification of Graphite.

A. Szirmae, C. G. Shirley and R. M. Fisher, 35th Annual EMSA Meeting, Boston, MA., August 22-26, 1977.

Electron Microscope Observations of Iron-Catalyzed Gasification of Graphite.

A. Szirmae, V.U.S. Rao and R. M. Fisher, 9th Int. Congress on Electron Microscopy, Toronto, Vol. 1, August 1-9, 1978.

Catalytic Gasification of Graphite and Coal Char by Metals, Alloys and Compounds.

R. M. Fisher, Cavendish Lab. Solid State Physics Seminars, Cambridge, UK, November 1, 1978.

Catalytic Conversion of Graphite to Methane by Group VIII Catalysts.

R. M. Fisher, V.U.S. Rao and A. Szirmae, Symposia on Catalytic Materials, The Materials Research Society, Boston, MA., November 30, 1978.

Fundamental Factors in Catalyzed Carbon-Gas Reactions.

A. Szirmae and R. M. Fisher, DOE/OER Heterogeneous Catalysis Research Meeting, Germantown, MD., December 14, 1978.

Characterization of Catalysts for Coal Liquefaction by Physical Methods.

V.U.S. Rao, Bulletin, APS, Vol. 24, No. 3, March 1979, p. 260.

Catalytic Gasification of Graphite and Coal Char by Metals, Alloys and Compounds.

R. M. Fisher, Seminar, Oxford University, Oxford, UK, May 7, 1979.

Catalytic Activity of Minerals in Coal Char.

R. M. Fisher and A. Szirmae, 14th Biennial Conference on Carbon, Pennsylvania State University, June 25-29, 1979, p. 151.

A-II-2

Catalytic Gasification of Graphite.

R. M. Fisher, Mechanical Engineering Seminars, University of Maryland, October 5, 1979.

Studies of Auger Electron Spectroscopy and Characteristic Energy-Loss Spectra of Alloy Catalysts for the Gasification of Graphite in Water Vapor and Hydrogen.

V.U.S. Rao, A. Szirmae and R. M. Fisher, J. of Catalysis 62, 1980, pp. 44-58 (Academic Press).

Catalytic Gasification of Graphite.

R. M. Fisher, Materials & Molecular Research Division Seminars, Lawrence Berkeley Lab., University of California, April 2, 1980.

Catalytic Gasification of Char and Graphite by Coal Ash.

R. M. Fisher and A. Szirmae, Carbon, in press (1981).

Catalytic Conversion of Graphite to Methane by Fe, Co, Ni and Cu Alloys.

R. M. Fisher, V.U.S. Rao and A. Szirmae, Fuel, in press (1981).

Reaction Rate Oscillation During Nickel-Catalyzed Gasification of Graphite in Wet Helium.

R. M. Fisher and A. Szirmae, prepared for publication in the Journal of Catalysis.

Effects of Metal Particle Size, Number and Composition on the Catalytic Gasification of Graphite in Wet Hydrogen.

R. M. Fisher and A. Szirmae, prepared for publication in Carbon.

PRESENTATIONS AND PUBLICATIONS
PROMPTED BY CONTRACT STUDIES*

Electron Energy-Loss Spectroscopy of Iron Oxide Films and Particles.
R. M. Fisher, P. E. Batson, S. J. Pennycook and L. M. Brown,
Proc. EMSA, San Antonio, 1979, 516-17.

Electron Optical Characterization of "Graphimets".
R. M. Fisher, D. J. Smith, L. A. Freeman, S. J. Pennycook and
A. Howie, Proc. 14th CARBON Conf., 1979, 318-19.

Electron Microscopy of Metal-Intercalated Graphite.
L. A. Freeman, David J. Smith and R. M. Fisher, Inst. of Phys.
Conf. Series (London) #52, 1980, p. 439.

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S. J. Pennycook, P. E. Batson and R. M. Fisher, Developments in
Electron Microscopy and Analysis, Inst. of Phys. Conf. Series #52,
1980, p. 337.

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D. J. Smith, R. M. Fisher and L. A. Freeman, J. of Catalysis,
in press (1981).

Electron Microscopy of Catalyst in Characterization of Catalysts.
A. Howie and J. Thomas, J. Wiley & Sons, 1981**

*Based on research carried out at the Cavendish Labs. while
R. M. Fisher was our Overseas Fellow of Churchill College,
University of Cambridge.

**Our micrograph of catalytic gasification pit appears
on the dust jacket.

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