DOE/PC/91304--T14

FINAL REPORT

LOW SEVERITY UPGRADING OF F-T WAXES WITH SOLID SUPERACIDS

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Prepared for the Department of Energy
Grant No. DE-FG22-91PC91304
September 30, 1995

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PREFACE

This is the final report for a three year research program sponsored by the Department of Energy through the University Coal Research Program. The research was carried out by Dr. Wei Wang as part of the requirements for the PhD in Chemical Engineering in the Department of Chemical and Petroleum Engineering at the University of Pittsburgh. The work was supervised by Professors Irving Wender and John W. Tierney. Dr. Jianli Hu, a Research Associate in the Chemical and Petroleum Engineering Department also made substantial contributions. The material in this report is taken from Dr. Wang's PhD dissertation, which should be consulted for additional details on experimental methods and results.

In addition to this report, the following publications and presentations resulted from this work.

W. Wang, "Hydrocracking and Hydroisomerization of Long Chain Alkanes by Anion-modified Metal Oxides," PhD Dissertation, University of Pittsburgh, 1994.

R.A. Keogh, S. Lambert, D. Sparks, B.H. Davis, I. Wender, J.W. Tierney and W. Wang, "Hydroisomerization and Hydrocracking of n-Hexadecane over a Platinum Promoted Sulfated Zirconia Catalyst," *Energy & Fuels*, **8**, 755-762 (1994).

K.R. Venkatesh, J. Hu, J.W. Tierney and I. Wender, "Hydrocracking of n-Hexadecane: Activity and Stability of Metal-Promoted Solid Superacids in Relatively Severe Reducing Conditions," 33rd Pittsburgh-Cleveland Catalysis Society, Pittsburgh, May 1995.

J. Hu, W. Wang, J.W. Tierney and I. Wender, "Low Severity Upgrading of F-T Waxes with Solid Superacids," Poster, DOE Contractor Review Meeting, June 1994.

J. Hu, W. Wang, J.W. Tierney and I. Wender, "Upgrading of Long-Chain Paraffins with Sulfate-Modified ZrO_2 Catalysts," *Colloid and Surface Science Div., 206th Annual Meeting, American Chemical Society*, Washington DC, 1993.

J. Hu, W. Wang, J.W. Tierney and I. Wender, "Low Severity Upgrading of F-T Waxes with Solid Superacids," DOE Contractor Review Meeting, June 1993.

J. Hu, W. Wang, J.W. Tierney and I. Wender, "Upgrading of Long-Chain Paraffins with Sulfate-Modified ZrO_2 Catalysts," 13th North American Meeting, The Catalysis Society, Pittsburgh PA, May (1993).

ABSTRACT

The use of solid acids, especially $\text{Pt/ZrO}_2/\text{SO}_4$, to convert long chain alkanes and Fischer-Tropsch waxes to liquid fuels under mild reaction conditions was explored in this work. Anion and/or hydrogenation metal modified zirconium oxides were synthesized, characterized, and tested for hydrocracking and hydroisomerization of model compounds, chiefly with n-hexadecane. The relationship between catalytic activity and acidic character of the bifunctional $\text{Pt/ZrO}_2/\text{SO}_4$ catalyst was investigated.

Incorporation of small amounts of anionic groups, especially sulfate, enhances the surface acidic character of zirconium oxide. The catalytic activity of $\text{Pt/ZrO}_2/\text{SO}_4$ for acid-catalyzed reactions of long chain alkanes was strongly affected by the number and nature of its acid sites, and its acid strength.

The nature and amount of the hydrogenation metal has a great effect on the acidic properties and catalytic activity of ZrO_2/SO_4 . Pt doped ZrO_2/SO_4 exhibited high activity and selectivity to isoparaffins in hydrocracking and hydroisomerization of long chain alkanes including Fischer-Tropsch waxes at reaction temperatures between 433 and 443K, and 360 psig of hydrogen pressure. During the reaction, Pt not only prevented coke formation, but also dissociated hydrogen molecules into hydrogen atoms, which could spill over to Lewis acid sites, generating highly active protonic acid sites.

With an increase in hydrogen pressure or Pt loading, selectivity to cracked products increased with a concomitant decrease in selectivity to isomerized hydrocarbons. This catalyst was very active at hydrogen pressures between 300 and 1600 psig, with the highest activity occurring at 1600 psig of hydrogen pressure.

Externally added olefins affect the reactivity and product selectivity of hydrocracking and hydroisomerization of hydrocarbons catalyzed by $\text{Pt/ZrO}_2/\text{SO}_4$. Olefins with terminal double bonds interacted more strongly with acid sites than those with an internal double bond. Addition of a hydride transfer agent, such as adamantane or methylcyclopentane, not only enhanced the reactivity of $\text{Pt/ZrO}_2/\text{SO}_4$ but also increased selectivity to long chain isoparaffins.

Product distribution of hydrocracking and hydroisomerization of n-hexadecane catalyzed

by Pt/ZrO₂/SO₄ obtained from the batch reactor was similar to that obtained from a continuous fixed-bed reactor.

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NOMENCLATURE

f	Objective function to be minimized.
k_1	Apparent rate constant for isomerization of n-hexadecane, $(\text{gcat}\cdot\text{min})^{-1}$
k_2, k_3	Apparent rate constant for hydrocracking of n-hexadecane and isohexadecanes, $(\text{gcat})^{n-1}\cdot((\text{gPt})^n\cdot\text{atm}\cdot\text{min})^{-1}$
m	Reaction order with respect to hydrogen pressure.
n	Reaction order with respect to Pt.
n'	Consumed hydrogen, mole.
N	Number of experiments,
P_0	Initial hydrogen pressure, atm.
P_{H_2}	Hydrogen pressure during reaction, atm.
R	Gas constant, $0.082 \text{ atm}\cdot\text{K}^{-1}\cdot\text{mole}^{-1}$.
t	Time, min.
T	Temperature, K .
V	Gas volume, cm^3 .
$w_{\text{cat.}}$	Amount of catalyst, gm.
w_{Pt}	Weight percentage of Pt, gPt/gcat
w_n, w_i, w_c	Weighting factors for n-hexadecane, isohexadecanes and cracked products.
Y_1, Y_2, Y_3	Observed fraction of unreacted n-hexadecane, isohexadecanes and cracked products, mole.
$\hat{Y}_i$	Fraction of product i predicted by model

1.0 INTRODUCTION

Liquid fuels, mainly derived from petroleum, play a dominant role in the transport market, and this dominance is expected to continue⁽¹⁾. Forecasts indicate that there will be a rapid growth in the consumption of transportation fuels in the near future. However, oil reserves are predicted to near exhaustion within a few decades⁽²⁾. Production of liquid fuels from other abundant energy resources, such as coal and natural gas has gained much attention as a potential replacement for petroleum-based liquid fuels.

The Fischer-Tropsch (FT) reaction involves the conversion of coal or natural gas to synthesis gas ($\text{CO} + \text{H}_2$), which is then catalytically converted to hydrocarbons⁽²⁾. The FT process produces a broad spectrum of hydrocarbon products⁽³⁾; the chain length distribution ranges from C_1 to over C_{200} . The selectivity of products is related to the probability of chain growth (α)^(4,5). A large amount of undesirable gas products such as methane and ethane are produced at low values of α . However, at a high α , these gaseous products are minimized, and high molecular weight products are produced. The production of desirable liquid products in a specified carbon number range via the direct FT synthesis is relatively low. The liquid paraffinic hydrocarbons produced are highly linear and have a low octane number; this makes them less desirable as gasoline components. By directing the FT synthesis towards heavy paraffins, which are subsequently selectively cracked, suitable products (gasoline, diesel and jet fuels) can be obtained.

In 1980, research on a slurry phase FT process was carried out at the Mobil Research and Development Corporation⁽⁶⁾. Production of high-boiling waxes was maximized with small amounts of undesirable light gases in the first stage. Subsequently the waxes were cracked with a ZSM-5 catalyst in the second stage. In 1985, Shell developed the so-called Shell Middle Distillate Synthesis (SMDS) process^(7,8), which was a combination of an FT synthesis with subsequent cracking and hydrocracking of FT waxes, for production of kerosene and diesel oil. The SMDS process consisted of three stages: conversion of natural gas (methane) into synthesis gas (H_2/CO), an FT process referred to as the Heavy Paraffin Synthesis (HPS), and selective

hydrocracking referred to as the Heavy Paraffin Conversion (HPC). The world's first commercial SMDS plant came on stream in Malaysia in 1993. The catalysts used by Mobil and Shell in the cracking stage could successfully produce a high yield of diesel fuel, but their performance was poor for gasoline, and they could not provide high selectivity to isoparaffins, which are desirable products for high-octane gasoline as well as for jet fuels. On the other hand, commercial cracking processes are usually carried out under severe reaction conditions (temperature > 573 K, pressure > 500 psig), which are thermodynamically unfavorable for formation of isomerized branched alkanes. Development of an effective catalyst for hydrocracking and hydroisomerization of waxes obtained via an FT synthesis could be of benefit to the refining industry.

It has been reported⁽⁹⁾ that a solid acid catalyst, $\text{Pt/ZrO}_2/\text{SO}_4$, is effective for hydrocracking and hydroisomerization of n-hexadecane under relatively mild reaction conditions (temperature = $403 - 443$ K, pressure = 300 psig). No undesirable light products such as methane and ethane were found with a selectivity to hydrocracked isoparaffins greater than 90% . A ratio of multibranched to monobranched alkanes greater than two was achieved. This type of solid acid catalyst appeared to be promising for obtaining high quality liquid fuels from FT waxes.

The primary objective of this work is to explore the use of strong solid acid catalysts to convert straight chain long hydrocarbons and FT waxes into quality liquid fuels. The objectives include establishing preparation conditions for the catalysts used, their physical and acidic properties and catalytic activity relationship; investigating the effects of reaction conditions on catalytic and product selectivity; and endeavoring to gain insights into the mechanism of the acid-catalyzed hydrocracking and hydroisomerization of long chain hydrocarbons using the bifunctional $\text{Pt/ZrO}_2/\text{SO}_4$ and related catalysts.

2.0 SCIENTIFIC DISCUSSION

2.1 Hydrocarbon Conversion by Hydrocracking and Hydroisomerization

2.1.1 Hydrocracking

Hydrocracking is a major refining process carried out in the presence of hydrogen under pressure. It involves cleavage of carbon-carbon bonds followed by hydrogenation yielding saturated small hydrocarbons⁽¹⁰⁾. Since 1960, hydrocracking has achieved considerable importance in petroleum refineries for converting hydrocarbons of high boiling ranges into more valuable products such as gasoline, diesel, jet fuel and lubricants^(11,12). The advantages of this process lie in its flexibility, i.e, a wide variety of feedstocks ranging from light naphthas to residual oils can be hydrocracked to obtain lighter products. Hydrocracking also allows production of high octane gasoline at one time and middle distillates at another time⁽¹³⁾. Moreover, very heavy hydrocarbon deposits such as tar sands and shale oil can be upgraded by hydrocracking processes to obtain useful oils. Since a large amount of paraffin wax is available from the FT synthesis, production of middle distillates by selectively hydrocracking waxes has gained considerable interest. One of the areas undertaken at Shell Hydrocracking Research is focused on the development of catalysts and process technology which will enable heavier feedstocks to be processed. Currently, Shell employs a mild trickle-flow hydrocracking process to convert heavy paraffins into desired gas oil or kerosene products⁽⁷⁾. UOP has developed a moderate pressure hydrocracking process (MPHC) for upgrading FT waxes to increase selectivity to diesel⁽¹⁴⁾. Mobil has upgraded FT waxes via a MPHC process to obtain a high yield of kerosene and diesel⁽⁶⁾.

In hydrocracking, the high partial pressure of hydrogen prevents condensation of alkenes, reducing coke formation. The chain length of n-alkanes has a great influence on reactivities of hydrocracking⁽¹⁵⁾. Unlike thermal cracking, there is a small amount of gaseous products such as methane and ethane produced during catalytic cracking or hydrocracking, in which carbonium ion rather than free-radical mechanisms are involved⁽¹⁶⁾.

2.1.2 Hydroisomerization

Isomerization of a hydrocarbon changes its molecular structure with retention of its molecular weight⁽¹⁰⁾. In 1933, Nenitzescu and Dragan⁽¹⁷⁾ first reported an acid catalyzed isomerization of saturated hydrocarbons. They found that when n-hexane was refluxed with aluminum chloride, it was converted into its branched isomers. That finding was of considerable economic importance in the petrochemical industry. Development of new technologies for isomerization is driven by two major factors⁽¹⁸⁾. First, the development of high performance piston aircraft engines requires gasoline with octane numbers of 100 or higher; however, the straight-run light naphtha from petroleum, an important constituent of motor gasoline, consists mainly of straight chain C5-C8 hydrocarbons which have low octane numbers (45-70)⁽¹⁹⁾; considerable upgrading is needed to meet the requirements of today's internal combustion engines. The octane numbers of branched hydrocarbons are higher than those of their straight-chain counterparts. Government regulations in the USA as well as in Europe are becoming more stringent with regard to levels of lead additives used by refiners to enhance octane ratings in the gasoline pool^(21,22,23). Isomerization is a useful way for many refiners to upgrade light naphtha. Rreformulated gasoline legislation has increased interest in using oxygenated compounds for improving the combustion performance of gasoline, and a compound of interest as an additive in this application is methyl tert-butyl ether (MTBE). The process of butane isomerization is of particular importance to provide the isobutene for MTBE manufacture. These factors have led to a need to efficiently produce isoparaffins for motor fuel applications.

A recent product projection⁽¹⁸⁾ shows that there is a decreasing demand for gasoline and an increasing demand for middle distillates. The middle distillates, such as diesel, jet fuel and lubricating oils, only amount to about 10% of the total crude oils, but they are very desirable products because of their high selling price. A low pour point is an important characteristic quality of jet fuel, diesel fuel and lubricants, particularly in marketing areas where severe winter weather is encountered⁽²⁴⁾. Middle distillates obtained directly from petroleum are usually normal paraffins with high pour points. Unfortunately, highly branched long chain isoparaffins with

carbon numbers larger than seven are rare in nature. Direct hydroisomerization of n-paraffins in heavy petroleum fractions such as jet fuel or lubricants has attracted considerable attention for improvement of low-temperature properties^(24,25,26).

2.2 Catalysis in Hydrocracking and Hydroisomerization

2.2.1 Catalytic Hydrocracking

The development of a chemical process in oil refining usually requires the aid of highly efficient catalysts⁽¹¹⁾. Hydrocracking is largely dependent on the development of catalysts with improved activity and selectivity. Considering the expected increase in middle distillate demand, highly active catalysts with optimum middle distillate selectivity are of clear interest.

Most hydrocracking catalysts of commercial interest are bifunctional in nature, consisting of both a hydrogenation/dehydrogenation component and an acidic support, which serve for (a) cracking of high molecular weight hydrocarbons; and (b) hydrogenation of the unsaturates formed during the cracking step. The catalytic activity and product selectivity during hydrocracking are influenced by the combination of these two activities⁽²⁷⁾. In general, as the hydrogenation activity of the catalyst increases relative to its acidity, formation of high boiling products is favored while that of light hydrocarbon products is minimized. However, catalysts with low hydrogenation activity relative to acidity yield products with higher ratios of branched paraffins to normal paraffins and less saturation of aromatics. Dual functional catalysts can be tailored to meet specific refining objectives⁽²⁷⁾.

Pelleted tungsten sulfide was the most successful hydrocracking catalyst in the early days⁽²⁸⁾. This catalyst had a very good tolerance to high concentrations of impurities such as nitrogen, sulfur and oxygen, but it failed to produce high octane gasoline because of extensive hydrogenation. Later, conventional amorphous bifunctional catalysts were developed, such as sulfides of nickel or tungsten supported on Al_2O_3 or $\text{SiO}_2\text{-Al}_2\text{O}_3$, but they failed to isomerize long chain n-paraffins to a significant degree^(13,29). It was found that selectivities to isomerized long chain paraffins were improved considerably when a metal of high hydrogenation capability, such

as platinum, was used to balance the acidity of the supports^(24,25,30).

During the last two decades, extensive research on zeolite-based catalysts has resulted in substantial progress in hydrocracking and hydroisomerization of long chain paraffins. It has been shown that Pt-doped zeolites are superior over conventional amorphous catalysts with respect to acidity, selectivity to isoparaffins and resistance to poisoning^(26, 31-34) and they have been successfully commercialized as hydrocracking catalysts in the petrochemical industry. Reaction temperatures required by zeolite catalysts are usually high ($> 573\text{ K}$)⁽³⁵⁾ and, although zeolite catalysts increase selectivity to isoparaffins, monobranched long chain isoparaffins predominate in cracking products, because of pore structure limitations. The multibranched long chain isoparaffins preferred for high density jet fuel components and premium engine oils^(36,37) are only formed to a minor extent. Development of catalysts with high selectivity to multibranched isoparaffins would be valuable for industrial applications.

2.2.2 Catalytic Hydroisomerization

Hydroisomerization of light paraffins has been practiced extensively in the petroleum refinery industry. The objective is either to manufacture isobutane which is needed for alkylation with olefins, or to increase the octane number of the C5-C8 fraction in the gasoline. In recent years, with increasing demand for middle distillates of high quality, the hydroisomerization technology has been developed in the upgrading of heavier petroleum fractions to lower the pour point of jet fuel, diesel and lubricants⁽²⁵⁾. The major difficulty in hydroisomerization of alkanes with more than six carbon atoms is their pronounced tendency to cleave⁽²⁶⁾.

Conventionally, catalysts used in hydroisomerization of paraffins are dual functional in nature, consisting of both a hydrogenation-dehydrogenation component and an acidic support. The stability, activity and selectivity of the catalysts depend on the ratio of the number of acid sites to the number of hydrogenation sites. Acidic catalysts lacking a hydrogenation component, e.g. $\text{SiO}_2\text{-Al}_2\text{O}_3$ ⁽³⁸⁾ or ReHX zeolite⁽³⁹⁾, as well as bifunctional catalysts with a weak hydrogenation component, e.g. nickel sulfide⁽²⁹⁾ or $\text{WS}_2/\text{SiO}_2\text{-Al}_2\text{O}_3$ ⁽¹³⁾, fail to isomerize long chain alkanes to a significant extent. It was found that, by introducing a good hydrogenating metal, platinum, into

bifunctional catalysts, e.g. Pt/SiO₂-Al₂O₃⁽³⁰⁾ or Pt/CaY⁽³¹⁾, high selectivities for isomerization of long chain alkanes, e.g. n-decane, n-dodecane or n-hexadecane, in the presence of hydrogen, could be achieved without excessive cracking.

2.2.3 Thermodynamic Considerations for Isomerization

Skeletal isomerization of straight-chain paraffins has become increasingly important in the petroleum refining industry, to produce lead-free high octane gasoline⁽⁴⁰⁾ and to synthesize branched paraffins which are then allowed to react with olefins under mild conditions to obtain highly branched hydrocarbons⁽⁴¹⁾. Isomerization of normal paraffins is generally carried out under equilibrium controlled conditions⁽⁴²⁾. The equilibrium favors an increase in branched isomers at low reaction temperatures. Petro⁽⁴³⁾ gives data for the isomerization equilibrium of nonanes at 300 and 600 K. The total percentage of isononanes decreases only slightly (from 96.3% to 83.5%) when the temperature is increased from 300 to 600 K, but the percentage of each of the isononanes changes drastically. While the percentage of the monobranched isononanes increases from 21.2% to 54.4%, that of the multibranched isononanes decreases (dibranched and tribranched isononanes decrease from 47.8% to 27.7% and 27.3% to 1.4%, respectively, with an increase in temperature from 300 to 600 K). The isomeric alkanes are less thermodynamically favored as temperature increases. Operating at low temperatures, which favors formation of highly multibranched isoparaffins, is catalytically practicable. It was found that certain catalysts of high acid strength (greater than 100% sulfuric acid) were effective for catalyzing isomerization of n-paraffins at much lower temperatures⁽⁴¹⁾, even at or below room temperature. Use of a strong superacid as a catalyst for hydrocracking and hydroisomerization of n-paraffins seems to be a promising way to obtain high quality automotive fuels.

2.3 Superacid Catalysis

2.3.1 Superacids

In 1968, the term superacid was first proposed by Gillespie⁽⁴⁴⁾ as an acid whose acidity is higher than that of 100% sulfuric acid. Since then, superacidic media have been extensively

studied and used as catalysts for hydrocarbon reactions.

Liquid acidic media are widely used for organic reactions. However, they have several disadvantages for industrial applications: need for large amounts of catalysts, corrosion of reactors, pollution by acidic waste water and difficulty of catalyst recovery. Therefore, utilization of heterogeneous processes has become, in principle, an attractive alternative. In recent years, there has been renewed interest in research on the preparation, structure and catalytic properties of solid superacids. Solid superacids can be divided into two groups based on the origin of the acid sites⁽⁴¹⁾, Lewis acids and Brønsted acids. Acidity may be a property of the solid as part of its chemical structure. Solid superacids can be obtained by several approaches:⁽⁴⁵⁾ (a) liquid superacids mounted on a suitable carrier; (b) superacid-intercalated graphites; (c) combination of inorganic salts (e.g. $\text{AlCl}_3\text{-CuCl}_2$, $\text{AlCl}_3\text{-CuSO}_4$); (d) sulfate-promoted metal oxides (e.g. ZrO_2/SO_4); and possibly (f) zeolites (e.g. ZSM-5).

The reported ability of superacids to bring about hydrocarbon transformations, even to activate methane, can open up new fields in chemistry^(43,46). Strong solid acids have been widely used as catalysts for isomerization, cracking, dehydration, alkylation, acylation, conversion of methanol to gasoline, etc. Because of reported advantages of solid catalysts, recent research has focused on the preparation and characterization of strong solid acids.

2.3.2 Characterization of Solid Acids

A complete description of acidic properties on solid surfaces requires the determination of acid strength, and the number and nature of acid sites⁽¹⁰⁾. Based on a method for measuring acid strength proposed by Hammett and Deyrup⁽⁴⁷⁾ in 1932, acid strength can be expressed by the Hammett acidity function H_0 , which is associated with the ability of an acid to protonate a basic indicator. For dilute aqueous solutions, H_0 becomes identical to pH. The number of acid sites on a solid is usually expressed as the number or mmoles of acid sites per unit weight or per unit surface area of the solid, and is obtained by measuring the amount of a base which reacts with the solid acid. The acid sites can be classified as Brønsted and Lewis types in terms of the IR structures.

Several methods are available for characterizing acidic properties on a solid surface: titration, spectroscopic measurement by IR or UV ⁽⁴⁸⁾, test reactions⁽⁴⁹⁾ and adsorption-desorption of bases⁽⁵⁰⁾. The most traditional method is titration of the solid acid with a base, using colored indicators. The color of suitable indicators adsorbed on a surface will give a measure of acid strength; the number of acid sites will be measured by base titration immediately after determination of acid strength. However, the major criticism of the titration method arises from the question of its reproducibility in view of the difficulty in reaching equilibrium⁽⁵⁰⁾. This technique is very difficult to apply to colored catalysts, as well as to catalysts deactivated and darkened by coke. Another technique widely practiced in characterization of acidic properties on a solid surface is gaseous base adsorption-desorption^(50,51). The major advantages of this technique are its simplicity and reproducibility. The acidity can be quantitatively determined by the amount of adsorbed base from desorption measurements, and the desorption temperatures are related to acid strength distribution. A combined technique employing IR spectroscopy and temperature programmed desorption (TPD) has been successfully used to study the acidic properties of solid acid catalysts⁽⁵²⁾. It can give information about acidity, acid strength and nature of acid sites in a single experiment. More recently, several novel techniques such as ESR and NMR have been employed to characterize surface acidity of solid acid catalysts⁽⁵³⁻⁵⁶⁾.

2.3.3 Hydrocarbon Transformation in Superacids

Protonation of exceedingly weak bases can occur with superacids. Not only can almost all π -electron donors such as olefins, acetylenes and aromatics be protonated, but even weak α -electron donors such as saturated hydrocarbons can be protonated⁽⁴²⁾. Existence of the structures of alkylcarbenium ions, arylcarbenium ions, vinylcarbenium ions, acyl cations and so on has been spectrometrically identified by NMR in highly acidic media⁽⁴²⁾. A characteristic of protonation in superacidic media is that it takes place on C-H or C-C bonds to form two-electron-three center carbonium ions⁽⁴¹⁾. Although direct evidence for the presence of carbocations on the surface of a solid catalyst has not been provided, it has been postulated that carbocations can be reaction intermediates in the conversion of hydrocarbons. Arguments in favor of the occurrence of

carbocation intermediates have been that the reaction pathways of hydrocarbons can be predicted by considering the stability of the carbocations that may be formed and the rearrangement pathways these cations might follow⁽⁵⁷⁾.

Before the turn of the 20th century, saturated hydrocarbons (paraffins) played only a minor role in industrial chemistry because of their chemical inertness. After the first World War, the ever increasing demand for gasoline initiated study of isomerization and cracking reactions of petroleum fractions⁽²¹⁾. In the early 1960s, the study of the behavior of saturated hydrocarbons in highly acidic media led to the discovery of hydrocarbon reactions, such as isomerization, Friedel-Crafts alkylation and cracking⁽⁵⁸⁾. The fundamental step in these acid-catalyzed hydrocarbon conversion processes is the formation of intermediate carbocations⁽⁴¹⁾.

Carbenium intermediates may be formed from a feed paraffin in the following ways⁽⁵⁹⁾: (a) by abstraction of a hydride ion at a Lewis acid site, (b) by dehydrogenation of the hydrocarbon and proton addition to the olefinic molecule at a strong Brönsted acid site, and (c) by hydride transfer with a surface carbenium ion formed as in (a) or (b). The carbenium ion may undergo isomerization, cracking or alkylation, and hence strong acids are suitable reagents for chemical transformation, particularly of alkanes.

2.4 Sulfate Promoted Metal Oxides

Among solid superacids, sulfate promoted metal oxides, an interesting class of relatively new solid acids, have gained attention because of their high catalytic activity. The enhancement of acidities and catalytic activities by addition of small amounts of sulfate ions (0.5-3 wt. %) has been reported for certain metal oxides such as ZrO_2 ⁽⁶⁰⁾, TiO_2 ⁽⁶¹⁾, Fe_2O_3 ⁽⁶²⁾, HfO_2 ⁽⁶³⁾ and SnO_2 ⁽⁶⁴⁾, oxides which themselves are neutral or very weakly acidic or basic. The high activities of these

sulfate doped metal oxides for acid-catalyzed reactions are considered to be due to generation of strong acid sites on the metal oxides. These materials are being explored as catalysts for hydrocarbon conversions. Their activities are strongly affected by preparation methods and reaction conditions.

2.4.1 Synthesis of Sulfate Promoted Metal Oxides

Sulfate promoted metal oxides are usually prepared by adding $(\text{NH}_4)_2\text{SO}_4$ or H_2SO_4 to the precipitates of their corresponding hydroxides, followed by calcination at desired temperatures (773 - 923 K)⁽⁶⁵⁾. For example, ZrO_2/SO_4 is often prepared by hydrolyzing commercially available ZrOCl_2 or $\text{ZrO}(\text{NO}_3)_2$ with aqueous ammonia (28%), and the precipitated $\text{Zr}(\text{OH})_4$ is then treated with $(\text{NH}_4)_2\text{SO}_4$ or H_2SO_4 , followed by calcination in air or in vacuum at 773 - 923 K. This preparation method is applicable to other metal oxides. It was found that superacid sites were not created during impregnation of sulfate groups on the crystallized metal oxides, but on the amorphous forms of hydroxides, $\text{M}(\text{OH})_x$ on calcination to convert them to the crystalline form⁽⁶⁶⁾.

2.4.2 Structure and Properties of Sulfate Promoted Metal Oxides

The oxides of metals such as Zr, Ti, Hf, Fe and Sn, whose metal cations have high coordination numbers and high electronegativities, can be effectively promoted by the sulfate group to become superacids⁽⁶⁷⁾. X-ray photoelectron spectroscopy of $\text{Fe}_2\text{O}_3/\text{SO}_4$ and $\text{Fe}_2\text{O}_3/\text{H}_2\text{S}$ treated under oxidizing and reducing conditions, respectively, revealed that the oxidation state of sulfur is S^{6+} and S^{2-} , respectively. No intermediate oxidation states were found during in-situ oxidation and reduction⁽⁶⁸⁾. Since high acidic properties as well as high catalytic activity were observed for $\text{Fe}_2\text{O}_3/\text{SO}_4$ and oxidized $\text{Fe}_2\text{O}_3/\text{H}_2\text{S}$ but not for $\text{Fe}_2\text{O}_3/\text{H}_2\text{S}$ and reduced $\text{Fe}_2\text{O}_3/\text{SO}_4$, it was concluded that generation of strong acidity on metal oxides was independent of the sulfur source provided that the oxidation state of sulfur is $+6$ ⁽⁶⁹⁾. The existence of covalent $\text{S}=\text{O}$ bonds on a metal oxide probably accounts for the enhanced acidic properties⁽⁷⁰⁾. The IR spectra of strong solid acids (ZrO_2/SO_4 ⁽⁷¹⁾, TiO_2/SO_4 ⁽⁷¹⁾, $\text{Fe}_2\text{O}_3/\text{SO}_4$ ⁽⁶⁹⁾ and SnO_2/SO_4 ⁽⁶⁴⁾) show a strong adsorption band at about 1375 cm^{-1} and broad bands located between 1200 and 900 cm^{-1} in the $\text{S}=\text{O}$

stretching frequency region, which were different from the corresponding metal sulfates. The structure of a chelating bidentate sulfate coordinated to metal elements^(70,72), was proposed to be responsible for the generation of strong acidity; the central metal served as a Lewis acid site, and the acid strength was strongly enhanced by the inductive effect of $S=O$ ⁽⁷³⁾. Traces of moisture in such a formulation convert Lewis acid sites to Brønsted acid sites.

The appearance of oxide catalysts treated with the sulfate group differs greatly from that without treatment. It was found⁽⁶⁶⁾ that the former were finely powdered solids which coated the wall of glass ampules obscuring vision, whereas the latter did not. The highest acid strengths of TiO_2/SO_4 and ZrO_2/SO_4 , measured by the Hammett indicator method using sulfuryl chloride as a solvent, were $H_0 \leq -14.5$ ⁽⁷⁴⁾ and $H_0 \leq -16.04$ ⁽⁷⁵⁾, respectively. The acid strength of the ZrO_2/SO_4 was 10,000 times higher than that of 100% H_2SO_4 ($H_0 = -11.9$). The acid strength of Fe_2O_3/SO_4 and HfO_2/SO_4 could not be measured by the Hammett indicator method because of their colors; their relative acid strength could be estimated by model reactions. The surface areas of these sulfate-promoted metal oxides were much larger than their corresponding counterparts without sulfate treatment (the specific surface area of TiO_2 increased from 55 to 100 m^2/g when treated with sulfate group). Analysis by scanning electron microscope showed that, after the sulfate treatment, the ZrO_2 catalyst disintegrated into fine particles⁽⁶⁶⁾. XPS analysis showed that the surface of the ZrO_2/SO_4 was composed of ZrO_2 and SO_4 , not $Zr(SO_4)_2$ ⁽⁶⁷⁾. The same finding was also observed in the XPS spectra of TiO_2/SO_4 ⁽⁶⁷⁾. They showed that crystallization of metal oxides during calcination was retarded upon addition of a sulfate group; the most active TiO_2/SO_4 was in the anatase form⁽⁶⁶⁾, and ZrO_2/SO_4 , whose acidity was higher, was in the tetragonal form⁽⁷⁶⁾.

2.4.3 Hydrocarbon Reactions Catalyzed by Sulfate Promoted Metal Oxides

Sulfate-promoted metal oxides have been used extensively in hydrocarbon reactions. Skeletal isomerization of n-butane, n-pentane and other n-paraffins did not occur at room temperature, even in the presence of H_2SO_4 (100%) as a catalyst. But n-butane was isomerized in the presence of Fe_2O_3/SO_4 , TiO_2/SO_4 or ZrO_2/SO_4 at temperatures between 293 and 323

K^(74,77), the main product being 2-methylpropane. A ZrO₂/SO₄ catalyst exhibited high activity for acylation of chlorobenzene with o-chlorobenzoyl chloride at about 407 K, and the conversion was 100% after ten hours of reaction⁽⁷⁸⁾. Disproportionation of alkylsilanes⁽⁷⁹⁾ and dehydrocyclization of hexane to benzene⁽⁸⁰⁾ could also be effectively catalyzed by ZrO₂/SO₄ under mild reaction conditions. Fe₂O₃/SO₄ containing 2 wt. % of SO₄²⁻ was highly active for dehydration of alcohols (2-propanol, ethanol⁽⁸¹⁾, etc.), double bond isomerization of 1-butene⁽⁷⁰⁾ and isomerization of cyclopropane to propylene⁽⁶²⁾. TiO₂/SO₄ calcined at 773 K was much more active than SiO₂-Al₂O₃ for esterification of terephthalic acid with ethylene glycol at 473 K⁽⁶⁶⁾. The catalytic activity of SnO₂/SO₄ for the isomerization of cyclopropane at 373 K was found to be 100 times greater than SnO₂ alone for the same reaction at 573 K⁽⁸²⁾. The SnO₂/SO₄ was also found to be highly effective for the dehydrogenation of cyclohexanol to cyclohexanone in the presence of water, with a selectivity of as high as 99% for a conversion of 90%⁽⁸³⁾.

2.4.4 Sulfate Promoted Zirconium Oxide

Among the sulfate-promoted metal oxides, ZrO₂/SO₄ is probably the highest in terms of its acid strength and reactivity in isomerization, cracking and alkylation of hydrocarbons. Tanabe and Yamaguchi⁽⁷⁶⁾ found that changing the mode of preparation of zirconium hydroxide and the source of the sulfate gave slightly different ZrO₂/SO₄ products. They also demonstrated that the stability of sulfate-promoted zirconium oxide was strengthened when it existed in the tetragonal phase.

Hino and Arata⁽⁷⁵⁾ found that ZrO₂/SO₄ could isomerize and crack n-butane at room temperature. Addition of the sulfate group to ZrO₂ caused a significant increase in its surface area. More recently, it was claimed that ZrO₂/SO₄ containing Fe and Mn prepared by the heterogeneous co-precipitation method^(94,95) exhibited higher activity for isomerization of n-butane at 301 K than that of ZrO₂/SO₄ alone. It was also claimed that the acid sites generated in the Fe or Mn doped ZrO₂/SO₄ were probably much stronger than those in ZrO₂/SO₄⁽⁹⁶⁾.

Recently, other efforts have been made to disperse ZrO₂/SO₄ on carriers of high surface area, such as SiO₂^(97,98,99), Al₂O₃⁽¹⁰⁰⁾ or active carbon⁽¹⁰¹⁾, with the aim of increasing the number of

acid sites. Such supported catalysts could be important for use in industry from the viewpoint of increased mechanical strength and low cost of solid acid catalysts. Mixed metal oxides treated with the sulfate group, $(\text{ZrO}_2\cdot\text{SnO}_2)/\text{SO}_4$, were reported to exhibit higher activity for isomerization of cyclopropane than that of $\text{ZrO}_2/\text{SnO}_2$ and even higher than that of ZrO_2 or SnO_2 containing a similar amount of sulfate group⁽¹⁰²⁾. Zirconium oxide promoted with other metal oxides (WO_3 ⁽¹⁰³⁾ and MoO_3 ⁽¹⁰⁴⁾) has also been prepared. The ZrO_2/WO_3 catalyst was active for acylation of toluene with benzoic anhydride at 303 K and the skeletal isomerization of n-butane and n-pentane at 373 K. The $\text{ZrO}_2/\text{MoO}_3$ was effective for acylation of toluene with benzoic anhydride at 373 K.

Vedrine et al.⁽¹⁰⁵⁾ employed infrared spectroscopy to study the nature of acid sites of the ZrO_2/SO_4 catalyst that might be responsible for isomerization of n-butane. They claimed that the activity of ZrO_2/SO_4 catalyst correlated with the intrinsic sulfur content despite the finding that part of the sulfur was in the bulk. The maximum activity happened to be the case where the intrinsic sulfur content corresponded roughly to a full coverage of the catalyst surface with a monolayer of sulfur. The maximum catalytic activity for isomerization of n-butane to isobutane was related to the presence of both Brönsted and Lewis acid sites with a ratio of Brönsted to Lewis infrared band intensities close to one. It was concluded that both Brönsted and Lewis acid sites must be present in the catalyst for it to have a high catalytic activity.

Hosoi et al.⁽¹⁰⁶⁾ reported that introduction of a small amount of a transition metal such as Pt or Pd on ZrO_2/SO_4 could effectively avoid catalyst deactivation when the reaction was carried out in the presence of hydrogen. The presence of hydrogen seemingly prevented coke formation during the reaction. Among the eight transition metals (Pt, Pd, Ni, Ru, Rh, Fe, W and Mo), Pt doped ZrO_2/SO_4 exhibited the highest activity and selectivity for the skeletal isomerization of n-pentane in the presence of hydrogen, without catalyst deactivation. Its activity remained unchanged after 1000 hours of use in the isomerization of light straight-run naphtha composed of mainly C5 and C6 hydrocarbons^(106,107). This was considered to be due to reduced coke formation in the presence of Pt^(108,109). Recent studies by Hattori and coworkers^(110,111,112) have provided evidence that Pt added to ZrO_2/SO_4 not only prolongs its lifetime due to reduced coke formation,

but also preserves its acidity. IR studies of pyridine adsorption have showed that, upon heat treatment of Pt/ZrO₂/SO₄ in the presence of hydrogen in the temperature range between 373 and 623 K, protonic acid sites were formed with a concomitant decrease in the number and strength of Lewis acid sites⁽¹¹¹⁾.

The oxidative state of Pt on the ZrO₂/SO₄ surface in the presence of hydrogen remains controversial. Ebitani et al.⁽¹¹³⁾ using in-situ XPS analysis claimed that platinum particles consisted mainly of platinum cations, a mixture of platinum oxide and platinum sulfate, dispersed on the ZrO₂/SO₄ surface in the presence of hydrogen. However, Para et al.^(114,115) suggested that platinum was mostly in the metallic state. More recently, Sayari et al.⁽¹¹⁶⁾ claimed that Pt was reduced to the metallic state upon calcination of the sulfate zirconium oxide at 873 K, whereas Pt in the zirconium oxide without sulfate treatment remained in an oxidized form after calcination at the same temperature.

Pt/ZrO₂/SO₄ showed high activity not only for isomerization of short paraffins at room temperature but also for hydrocracking and hydroisomerization of long chain paraffins such as n-hexadecane under mild reaction conditions⁽⁹⁾ (T < 473 K, P < 400 psig of hydrogen). Typical features of a useful acid catalyst in hydrocracking of long chain alkanes should be that (a) its activity and selectivity for isomerization are high at low reaction temperatures, (b) primary cracking predominates over secondary and further cracking⁽¹⁵⁾, and (c) its environmental effects can be tolerated. Compared with conventional amorphous hydrocracking catalysts or platinum-doped zeolite catalysts, Pt/ZrO₂/SO₄ (Table 1) exhibited high activity in hydrocracking and hydroisomerization of n-hexadecane at mild temperatures; moderate conversion levels of 60%-80% were achieved in the temperature range of 413 - 443 K. Gasoline and kerosene fractions predominated in the hydrocracked products. A small amount of gaseous products (~3%) was also produced, consisting of butanes and propane; no methane and ethane were obtained. With n-hexadecane, this catalyst showed a high selectivity to isoparaffins (> 90%), of which more than 50% of the isohexadecane and C10-C13 isoparaffins were multibranched. In terms of reactivity and product quality for hydrocracking and hydroisomerization of long chain paraffins, the

Pt/ZrO₂/SO₄ catalyst showed some advantages over industrial commercial catalysts.

Table 1. Reactivity Comparison of Various Catalysts for the Hydrocracking and Hydroisomerization of Hydrocarbons

Feed	Catalyst	Temp (K)	H ₂ Press (psig)	Products	Conv.	Ref.
n-C16	Pt/ZrO ₂ /SO ₄	403-443	300	C3-C13 & Iso-C16	56-73	9
n-C16	Pt/SiO ₂ -Al ₂ O ₃	643-667	1000	C1-C15 & Iso-C16	>53	30
n-C20	Pt/Cl-F-Al ₂ O ₃	643	500	12.5% Gas 14.6% Liq. 70.8% Iso-C20	48	25
C11-C15	Pt/F-Al ₂ O ₃	643	50-1000	Fractions	5-70	24
n-C12	Pt/Ca/Y-Zeolite	538-623	600	C3-C9 & Iso-C12	39-100	31
n-C12	Pt/USY-Zeolite	403-523	87-1465	C3-C9 & Iso-C12	0-100	32
n-C15	Pt/Ca/Y-Zeolite	513	540	Cracked Prod. & Iso-C15	95	26
n-C15	Pt/HZSM-5	483-533	300	C3-C12 & Iso-C15	9-99	33
n-C16	Pt/USY-Zeolite	415-436	30-300	C3-C13 & Iso-C16	20-49	34
n-C10	Pt/USY-Zeolite	434	30	C3-C7 & Iso-C10	27	117
n-C7	Pt/HY-Zeolite	523	30	C3-C6 & Iso-C7	0-80	118
n-C7	Pt/H-OFF-Zeolite	523	30	C3-C6 & Iso-C7	0-90	119

2.5 Mechanism of Bifunctional Catalysis in Hydrocracking and Hydroisomerization

The generally accepted mechanism of hydrocracking and hydroisomerization of long chain hydrocarbons catalyzed by a bifunctional catalyst was proposed by Weisz⁽¹²⁰⁾ and by Goonrad⁽³⁰⁾, as shown in Figure 1.

Figure 1. Proposed Mechanism of Bifunctional Catalysis in Hydrocracking and Hydroisomerization of Alkanes

An equilibrium between alkanes and alkenes as a result of dehydrogenation and hydrogenation is established on the metal of the catalyst. Alkylcarbenium ions are formed upon protonation of the alkenes on the Brønsted acid sites. The alkylcarbenium ions can either undergo β -scission to form carbenium ions of lower carbon number and olefins as cracked fragments or isomerized to produce branched hydrocarbons. Carbenium ions play a role as key intermediates in hydrocracking and hydroisomerization, and the overall reaction rate is limited by their rate of formation. There are five modes of β -scission reactions.⁽³³⁾ Starting from a secondary carbenium ion derived from a normal paraffin, primary carbenium ions, which are energetically unfavorable, are formed. The only way to avoid this problem by β -scission is to isomerize the normal paraffins into multibranched ones, which are cracked to form olefins and tertiary or secondary carbenium ions. Unfortunately, many experimental observations cannot be reasonably explained on the basis of this requirement. Sie^(121,122,123) has proposed a somewhat different reaction mechanism to account for acid catalyzed hydrocracking of n-paraffins. The only new feature of this mechanism is a postulation of 1,3-hydrogen shifts, which are known to be unfavorable relative to consecutive 1,2-shifts.

Starting from a straight-chain paraffin, the classic carbenium ion is generated by hydride abstraction or protonation of an olefin derived from dehydrogenation of a paraffin. Through

cyclization of the alkylcarbenium ion, a non-classical carbonium ion is formed. The cracking step is completed by a hydride shift from a carbon atom in the β -position of the cyclopropyl ring to the nearest ring carbon atom, followed by a hydride shift between two carbon atoms of the cyclopropane ring and bond scission, which leads to a tertiary carbenium ion and a linear olefin. The main difference between Sie's mechanism and the classical β -scission one is that in the former mechanism, a non-classical carbonium ion is formed at the cracking step instead of a classical carbenium ion. Sie claimed that this mechanism not only avoided formation of an energetically unfavorable primary carbenium ion but also logically explained the features of acid catalyzed cracking and hydrocracking.

3.0 RESEARCH OBJECTIVES

The main objective of this project was to study the use of anion promoted metal oxides for converting long chain hydrocarbons such as F-T waxes into liquid fuels by hydrocracking and hydroisomerization processes under relatively mild reaction conditions. Specific goals were as follows:

(1) To investigate the effect of the method of synthesis of anion-modified metal oxides (especially zirconium oxide) and mixed metal oxides on the activity of the resulting catalysts for the hydrocracking and hydroisomerization of long chain hydrocarbons. The method of synthesis includes the nature of the starting zirconia precursor, the precipitation route, the concentrations of H_2SO_4 and calcination temperatures.

(2) To establish the relationship between the acidic properties of anion-promoted metal oxides and their activities for hydrocracking and hydroisomerization of Fischer-Tropsch waxes.

(3) To determine the variation in the acidic properties, catalytic activity and product selectivity of sulfate promoted zirconium oxide (ZrO_2/SO_4) with catalyst parameters such as the amount of sulfate group and the nature and amount of dopant metal.

(4) To compare the effect of anions such as SO_4^{2-} , MoO_4^{2-} and WO_4^{2-} on the acidic properties and catalytic activity of platinum doped on ZrO_2 .

(5) To study the effects of hydrogen pressure, reaction time, the presence of a hydride transfer agent or an olefin, on the catalytic activities and product selectivities of $\text{Pt}/\text{ZrO}_2/\text{SO}_4$.

(6) To gain an insight into the reaction mechanism of hydrocracking and hydroisomerization of long chain hydrocarbons and F-T waxes catalyzed by $\text{Pt}/\text{ZrO}_2/\text{SO}_4$.

4.0 SYNTHESIS OF ANION-MODIFIED METAL OXIDES

4.1 Objectives

(1) To synthesize Pt-promoted zirconium oxide products starting from various zirconia precursors, by different precipitation procedures. These products were then modified by SO_4^{2-} , MoO_4^{2-} or WO_4^{2-} .

(2) To prepare Pt/ZrO₂/SO₄ catalysts containing various amounts of sulfate and Pt loadings.

(3) To synthesize Pt doped sulfate promoted mixed metal oxides.

(4) To develop better routes for obtaining sulfate-modified metal oxide catalysts and Pt/ZrO₂/SO₄ in particular.

4.2 Background

Considering the role of superacids in hydrocarbon chemistry and the advantages of solid catalysts in industry, it is not surprising that research activities on catalysis by solid acids have been increasing. It was found that when a few percent of some anions such as a sulfate group was introduced to certain metal oxides and then subjected to heat treatment, their surface acidity and catalytic activity increased greatly^(10,41,45). The most common method for synthesizing sulfate-modified metal oxides is based on aqueous precipitation of the hydroxides of metals followed by drying, treatment with an appropriate sulfate containing material like aqueous sulfuric acid or aqueous ammonium sulfate, and calcination at appropriate temperatures. Calcination allows the products to form stable crystalline phases. A procedure of precipitation-sulfation-calcination has been patented and used by several researchers^(63-65,71). Our catalyst preparation follows this general route with a modification in the synthesis of sulfate-promoted zirconium catalysts: instead of ZrOCl₂ or ZrO(NO₃)₃ which have been used frequently by many researchers, Zr(SO₄)₂·4H₂O is employed as a starting material for catalyst preparation. The main advantage of this modification lies in that, unlike ZrOCl₂ or ZrO(NO₃)₃ which contain unwanted anions requiring thorough water

washing of precipitates, the use of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ as the starting material simplifies water washing greatly. Zirconium oxides modified by other anions such as WO_4^{2-} and MoO_4^{2-} were prepared by heterogeneous coprecipitation of the hydroxide of zirconium with the hydroxide of tungsten or molybdate followed by calcination. Hydrogenation metals were usually introduced into the precipitates by the method of incipient wetness before calcination. Both homogeneous and heterogeneous precipitation methods were used for the synthesis of anion-modified metal oxides. The heterogeneous precipitation method consisted of dropwise addition of aqueous ammonium hydroxide as the precipitating agent to a solution of starting metal salts. In this case, the concentration of ammonium hydroxide was not uniform locally during the formation of precipitates. The homogeneous precipitation method used an excess of urea (NH_2CONH_2) instead of ammonia. The precipitates were formed from the homogeneous solution of hydroxide ion as urea decomposed to ammonium hydroxide at temperatures above 343 K.

4.3 Experimental

4.3.1 Chemicals and Materials Used

The starting materials used for the synthesis of bifunctional anion-modified metal oxides and mixed oxides are shown in Table 2.

4.3.2 Heterogeneous Precipitation Method

4.3.2.1 Synthesis of ZrO_2/SO_4 and $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ Using $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$.

(i) *Dissolution*: 50 g of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, a water-soluble salt, was added to 564 ml of distilled water. The resulting solution was stirred using a magnetic bar for one hour at room temperature.

(ii) *Hydrolysis*: Aqueous ammonia (28%) was added dropwise through a burette (10 -15 drops/min) to the solution with constant stirring while monitoring the pH of the hydrolyzing solution. A white gel was formed immediately after several drops of the aqueous base were added. The addition rate of the base was raised to 20 drops/min after the pH of the solution reached 5.0. This continued to the point where the final pH reached 10.0. Thereafter the solution

was stirred continuously for an additional five minutes before it was allowed to age overnight. About 90 ml of the aqueous ammonia was used in the precipitation process. The final product obtained consisted of fine particles of zirconium hydroxide ($\text{Zr}(\text{OH})_4$).

(iii) *Water washing of precipitates*: The precipitates after hydrolysis were washed twice with 600 ml of distilled water under constant stirring for about 10 minutes at room temperature in order to remove impurities and unreacted aqueous ammonia.

Table 2. Chemicals for the Preparation of Bifunctional Anion-modified Metal Oxides

Description	Chemical	Purity (%)	Supplier
Starting salt	Zirconium sulfate	99.0	Pfaltz & Bauer
	Zirconium dichloride oxide octahydrate	99.998	Strem Chemical
	Zirconium dinitrate oxide hydrate	unavailable	Strem Chemical
	Hafnium dichloride oxide octahydrate	> 98	Stream Chemical
Precipitating agent	Aqueous ammonium hydroxide (28%)	not given	Fisher Scientific
	Urea	99.99	EM industries
Anion	Sulfuric Acid	95.9	Mallinckrodt
	Ammonium metatungstate	> 99.9	Strem Chemical
	Ammonium molybdate tetrahydrate	99.999	Strem Chemical
Hydrogenation Metal	Chloroplatinic acid hexahydrate	99.9	Strem chemical
	Palladium (II) chloride	99.9	Strem Chemical
	Nickel (II) nitrate hexahydrate	99.999	Aldrich Chemical

(iv) *Filtration and collection of precipitates*: The washed precipitates were then filtered under vacuum using a Whatman No.1 filter paper. Some very fine particles of the precipitates were lost during filtration as they passed through the filter. The final precipitates were collected from the filter and placed in a glass beaker.

(v) *Drying*: The precipitates of zirconium hydroxide after filtration were dried in an oven at 383 K for 24 hours in order to remove water and other volatile impurities such as ammonia.

(vi) *Grinding*: The dried precipitates were ground into powder, which could pass through a -100 mesh sieve (149 microns).

(vii) *Sulfation and Drying*: The dried and ground precipitates were weighed to determine the yield of the hydrolysis reaction (18.2 g of $\text{Zr}(\text{OH})_4$ was obtained). The precipitates were slurried and digested for one hour with 180 ml of sulfuric acid (1 N) (10 ml of the sulfuric acid solution per gram of precipitates). The slurry was then filtered to remove excess water, dried in an oven at 383 K for 24 hours in order to remove physically adsorbed water. The product thus dried was then powdered to -100 mesh.

(viii) *Impregnation*: The dried sulfated precipitates ($\text{Zr}(\text{OH})_4/\text{SO}_4$) were impregnated with an aqueous solution containing $\text{H}_2\text{PtCl}_6 \cdot 3\text{H}_2\text{O}$ (0.5 wt. % Pt per gram of ZrO_2) using the method of incipient wetness. The amount of distilled water used in the aqueous solution was 0.9 ml per gram of the sulfated precipitate.

(ix) *Drying and Calcination*: The precipitates after impregnation were dried in an oven at 383 K for 12 hours to remove excess water, and then powdered to -100 mesh. The powdery product was then calcined at 873 K in air for three hours to convert the amorphous zirconium hydroxide to zirconium oxide to a stable crystalline state. The final product (denoted as **SZD1**) was stored in desiccator. The dried precipitates before impregnation with platinum were also calcined following the same procedure. This catalyst will be denoted as **SZD2**.

4.3.2.2 Synthesis of $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ Using Zirconium Oxide Dichloride and Zirconium Oxide Dinitrate.

This was done under the same conditions as those used for the preparation of **SZD1** with

modifications concerning the starting zirconia material and the water washing step. $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ was replaced either by zirconium oxide dichloride (ZrOCl_2) or zirconium oxide dinitrate ($\text{ZrO}(\text{NO}_3)_2$). These two zirconia salts are widely used in the literature. As mentioned in the **Background** section of this chapter, the main disadvantage of using ZrOCl_2 or $\text{ZrO}(\text{NO}_3)_2$ lies in that, unlike $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, ZrOCl_2 and $\text{ZrO}(\text{NO}_3)_2$ contain unwanted ions (Cl^- and NO_3^-), thus requiring a considerable amount of water washing effort in order to remove them. The final catalysts obtained using ZrOCl_2 and $\text{ZrO}(\text{NO}_3)_2$ will be denoted as **SZD3** and **SZD4**, respectively. The catalyst, ZrO_2 denoted as **ZD**, was prepared by calcining the precipitates obtained from ZrOCl_2 without sulfation in air at 773 K for three hours.

The precipitates obtained using $\text{ZrO}(\text{NO}_3)_2$ as the starting material after sulfation and impregnation with $\text{H}_2\text{PtCl}_6 \cdot 3\text{H}_2\text{O}$ solution were also calcined in air at 773, 823, 923 and 973 K, respectively. The resulting catalysts will be denoted as **SZD5**, **SZD6**, **SZD7** and **SZD8**, respectively.

In order to obtain the $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ catalysts containing different amounts of sulfate anion, the precipitates obtained using ZrOCl_2 as the starting material were also impregnated with sulfuric acid solutions of different concentrations (0.2, 0.5, 3.0 and 6.0 N). The catalysts obtained after impregnation with $\text{H}_2\text{PtCl}_6 \cdot 3\text{H}_2\text{O}$ solution and calcination under the same conditions as for **SZD3** will be denoted as **SZD9**, **SZD10**, **SZD11** and **SZD12**, respectively.

4.3.2.3 Synthesis of $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ With Various Pt Loadings, $\text{PtO}_2/\text{ZrO}_2/\text{SO}_4$ and $\text{PtO}_2 + \text{ZrO}_2/\text{SO}_4$.

The $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ catalysts containing various platinum loadings (0.2, 1.0, 2.0 and 5.0 wt. % per gram of ZrO_2) were prepared as follows: the precipitates obtained using $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ as the starting salt after sulfation were impregnated with $\text{H}_2\text{PtCl}_6 \cdot 3\text{H}_2\text{O}$ solutions of desired concentrations in platinum; they were then calcined under the same conditions as **SZD1**. These catalysts will be denoted as **SZD13**, **SZD14**, **SZD15** and **SZD16**, respectively.

The same precipitates after sulfation were also impregnated with platinum oxide (PtO_2) dispersed in distilled water. The catalyst containing 0.5 wt. % Pt per gram of ZrO_2

(PtO₂/ZrO₂/SO₄) obtained after calcination under the same conditions as **SZD1** will be denoted as **SZD17**. A mechanical mixture of **SZD2** with PtO₂ powder (PtO₂ + ZrO₂/SO₄) will be denoted as **SZD18**.

4.3.2.4 Synthesis of Pd/ZrO₂/SO₄ and Ni/ZrO₂/SO₄.

The precipitates obtained using Zr(SO₄)₂·4H₂O as the starting material were impregnated after sulfation with an aqueous solution of palladium (II) chloride or nickel (II) nitrate hexahydrate. Palladium (0.5 wt. % per gram of ZrO₂) or nickel (0.5 and 2.0 wt. % per gram of ZrO₂) was added. The products after impregnation were dried and then calcined in air at 873 K for three hours. These catalysts will be denoted as **SZD19**, **SZD20** and **SZD21**, respectively.

4.3.2.5 Synthesis of Pt/ZrO₂/WO₃ and Pt/ZrO₂/MoO₃.

Zirconium oxide promoted either by WO₃ or MoO₃ was prepared by the heterogeneous coprecipitation method. The hydrolysis step was modified and the sulfation step eliminated. The amount of ammonium metatungstate ((NH₄)₆H₂W₁₂O₄₀) or ammonium molybdate tetrahydrate ((NH₄)₆H₂Mo₇O₂₄·4H₂O) (13 wt. % of either W or Mo per gram of ZrO₂) and the calcination conditions followed the literature^(103,104). An aqueous solution of ZrO(NO₃)₂ mixed with (NH₄)₆H₂W₁₂O₄₀ or (NH₄)₆H₂Mo₇O₂₄·4H₂O was hydrolyzed by aqueous ammonia (28%) to a final pH of 10. After impregnation with H₂PtCl₆·3H₂O solution, the precipitates containing WO₄²⁻ were calcined in air at 973 K for three hours, and those containing MoO₄²⁻ at 1073 K for three hours. These catalysts will be denoted as **TZD** and **MZD**, respectively.

4.3.2.6 Synthesis of Pt/HfO₂/SO₄ and Pt/ZrO₂-HfO₂/SO₄.

The Pt/HfO₂/SO₄ catalyst (denoted as **SHD**) was prepared from hafnium oxide dichloride (HfOCl₂) upon following the same procedure as that for **SZD3**. The Pt/ZrO₂-HfO₂/SO₄ catalysts with three different ZrO₂ to HfO₂ molar ratios (0.2, 0.5 and 0.8) were prepared by the heterogeneous coprecipitation method followed by sulfation, impregnation and calcination under the same conditions as those for **SZD3**. They will be denoted as **SZHD1**, **SZHD2** and **SZHD3**, respectively.

4.3.3 Homogeneous Precipitation Method

In addition to the heterogeneous method, the homogeneous precipitation method was also used for the purpose of the preparation of a Pt/ZrO₂/SO₄ catalyst. The latter differs from the former method only in the following steps:

(i) *Dissolution*: 25 g of Zr(SO₄)₂·4H₂O and 75 g of urea were added to 1000 ml of distilled water with constant stirring at room temperature to a complete dissolution of the whole system. The initial pH of the system was about 2.5.

(ii) *Hydrolysis*: The solution was stirred and heated to 368 K. At that temperature urea decomposed into ammonia and carbon dioxide. Ammonia then reacted with water forming NH₄OH. After reaction with NH₄OH for two and a half hours, Zr(SO₄)₂·4H₂O was converted to Zr(OH)₄ in the form of fine particles. At the end of the reaction, the pH of the solution was about 7.5. The whole system was then cooled to room temperature without stirring.

(iii) *Washing*: The precipitates were washed with 500 ml of hot distilled water (343 K) three times to remove impurity ions and excess ammonium hydroxide.

The catalyst obtained by this method will be denoted as **SZD22**.

The synthesis procedures for all metal oxide catalysts used in this study are summarized in Table 3.

4.4 Final Remarks

The method employing the new starting zirconia salt, Zr(SO₄)₂·4H₂O, is novel and very useful in the synthesis of sulfate-promoted zirconium oxides because it does not contain undesirable ions such as Cl⁻ and NO₃⁻ as in the conventional zirconia salts (ZrOCl₂ and ZrO(NO₃)₂); this reduces significantly the water washing effort. Additionally, the sulfate group already present in the starting material would be beneficial for formation of superacid sites on zirconium oxide. The price of Zr(SO₄)₂·4H₂O is cheaper than that of ZrOCl₂ or ZrO(NO₃)₂, and this may be considered another advantage.

Table 3. Summary of the Catalysts Obtained by the Heterogeneous and Homogeneous Methods

Catalyst No.	Catalyst formula	Preparation			
		starting salt	H ₂ SO ₄ (N)	metal loading (wt. %)	calcination temperature (K)
ZD	ZrO ₂	ZrOCl ₂	0	0	773
SZD2	ZrO ₂ /SO ₄	Zr(SO ₄) ₂ ·4H ₂ O	1	0	873
SZD1	Pt/ZrO ₂ /SO ₄	Zr(SO ₄) ₂ ·4H ₂ O	1	0.5	873
SZD3	Pt/ZrO ₂ /SO ₄	ZrOCl ₂	1	0.5	873
SZD4	Pt/ZrO ₂ /SO ₄	ZrO(NO ₃) ₂	1	0.5	873
SZD5	Pt/ZrO ₂ /SO ₄	ZrO(NO ₃) ₂	1	0.5	773
SZD6	Pt/ZrO ₂ /SO ₄	ZrO(NO ₃) ₂	1	0.5	823
SZD7	Pt/ZrO ₂ /SO ₄	ZrO(NO ₃) ₂	1	0.5	923
SZD8	Pt/ZrO ₂ /SO ₄	ZrO(NO ₃) ₂	1	0.5	973
SZD9	Pt/ZrO ₂ /SO ₄	ZrOCl ₂	0.2	0.5	873
SZD10	Pt/ZrO ₂ /SO ₄	ZrOCl ₂	0.5	0.5	873
SZD11	Pt/ZrO ₂ /SO ₄	ZrOCl ₂	3	0.5	873
SZD12	Pt/ZrO ₂ /SO ₄	ZrOCl ₂	6	0.5	873
SZD13	Pt/ZrO ₂ /SO ₄	Zr(SO ₄) ₂ ·4H ₂ O	1	0.2	873
SZD14	Pt/ZrO ₂ /SO ₄	Zr(SO ₄) ₂ ·4H ₂ O	1	1	873
SZD15	Pt/ZrO ₂ /SO ₄	Zr(SO ₄) ₂ ·4H ₂ O	1	2	873
SZD16	Pt/ZrO ₂ /SO ₄	Zr(SO ₄) ₂ ·4H ₂ O	1	5	873

Table 3 (continued)

Catalyst No.	Catalyst formula	Preparation			
		starting salt	H ₂ SO ₄ (N)	metal loading (wt. %)	calcination temperature (K)
SZD17	PtO ₂ /ZrO ₂ /SO ₄	Zr(SO ₄) ₂ ·4H ₂ O	1	0.5	873
SZD18	PtO ₂ + ZrO ₂ /SO ₄	Zr(SO ₄) ₂ ·4H ₂ O	1	0.5	873
SZD19	Pd/ZrO ₂ /SO ₄	Zr(SO ₄) ₂ ·4H ₂ O	1	0.5	873
SZD20	Ni/ZrO ₂ /SO ₄	Zr(SO ₄) ₂ ·4H ₂ O	1	0.5	873
SZD21	Ni/ZrO ₂ /SO ₄	Zr(SO ₄) ₂ ·4H ₂ O	1	2	873
TZD	Pt/ZrO ₂ /WO ₄	ZrO(NO ₃) ₂	NA	0.5	973
MZD	Pt/ZrO ₂ /MoO ₄	ZrO(NO ₃) ₂	NA	0.5	1073
SHD	Pt/HfO ₂ /SO ₄	HfOCl ₂	1	0.5	873
SZHD1	Pt/ZrO ₂ ·HfO ₂ /SO ₄	ZrOCl ₂ + HfOCl ₂ (4:1 by mole)	1	0.5	873
SZHD2	Pt/ZrO ₂ ·HfO ₂ /SO ₄	ZrOCl ₂ + HfOCl ₂ (1:1 by mole)	1	0.5	873
SZHD3	Pt/ZrO ₂ ·HfO ₂ /SO ₄	ZrOCl ₂ + HfOCl ₂ (1:4 by mole)	1	0.5	873
SZD22 ^a	Pt/ZrO ₂ /SO ₄	Zr(SO ₄) ₂ ·4H ₂ O	1	0.5	873

a: obtained by the homogeneous precipitation method

5.0 CATALYST CHARACTERIZATION

5.1 Objectives

The physical and acidic properties of the catalysts in Table 3 were characterized in order to investigate the effects of the catalyst preparation conditions on their physical and acidic properties. The catalyst conditions refer to the precipitation method, the nature and amount of added anion and/or hydrogenation metal, and calcination temperature. The physical properties included sulfate content, crystallography, specific surface area, pore volume and area distributions, thermal stability the number and nature of acid sites.

Sulfate contents were evaluated in terms of the sulfur content which was measured by a sulfur analyzer. The average particle size and crystallography of catalysts were characterized by X-Ray Diffraction (XRD). Their specific surface areas, and pore volume and area distributions were measured by liquid nitrogen adsorption. The nature of the acid sites of the catalysts was identified upon examining the infrared spectrum of adsorbed pyridine. The number of acid sites and acid strength were measured by the method of temperature-programmed desorption of pyridine (TPD).

5.2 Background

The acidity of zirconium oxide (ZrO_2) is weak. It was reported⁽¹⁰⁾ that the highest acid strength (H_0) of the acid sites of ZrO_2 calcined in air at 773 K for three hours was 1.5 with the number of acid sites of $0.06 \text{ mmole g}^{-1}$ for $H_0 \leq 1.5$ and $0.280 \text{ mmole g}^{-1}$ for $H_0 \leq 4.0$. Its acidic properties can be improved greatly by addition of anions such as SO_4^{2-} , MoO_4^{2-} or WO_4^{2-} ^(41,103,104). The acid strength of a sulfate promoted zirconium oxide can be greater than that of 100% sulfuric acid^(41,76); it is considered a strong solid superacid. Addition of the anion also affects the crystallographic phase transformation of ZrO_2 , leading to formation of high surface area and a thermally stable crystalline phase (tetragonal form)^(66,67). Impregnation of the crystallized form

of ZrO_2 with a sulfate group does not create strong acid sites, calcination leading to the tetragonal form does for strong acid sites.⁽⁶⁶⁾

5.3 Experimental

5.3.1 Characterization of the Physical Properties

5.3.1.1 Crystalline Structures and Average Particle Size.

These were determined using a Philips X'Pert X-ray diffractometer. $\text{Cu-K}\alpha$ radiation at 30 kV and 25 Ma was used. Sample preparation consisted of sprinkling and spreading the catalyst powder on a double sided adhesive tape on a microscopic slide. XRD scans were carried out between 20 and 60 degrees, 2θ at a rate of two degrees per minute.

The crystalline structure was identified by the wavelengths (λ) and the intensities of the XRD peaks. The average crystallite size was determined by line broadening, and calculated using the Scherrer equation⁽¹²⁴⁾:

$$t = 0.9\lambda / [B \cos\theta]$$

where t is the thickness of the crystal, and B is the angular width of the diffraction peak in terms of 2θ , measured at half its maximum intensity.

5.3.1.2 BET Surface Area, Pore Volume and Area Distributions.

The specific surface area of the catalysts was measured using the method of nitrogen physisorption. A small amount of sample (0.5 g) was preheated in a sample holder under vacuum for two hours, and cooled to room temperature. The sample holder was then quenched into liquid nitrogen (-198.5°C). Nitrogen adsorption was carried out by introducing nitrogen gas into the system over a range of pressures at less than one atmosphere to avoid nitrogen adsorption of multimolecular layers on the catalyst surface. The amount of nitrogen physically adsorbed on the catalyst surface was measured after the system reached equilibrium. The surface area was calculated using the BET equation. The measurement of the pore characteristics (distribution of incremental pore volume and incremental pore area) of sulfate promoted oxides was also based on the principle of liquid nitrogen physisorption at higher nitrogen pressures, where capillary

condensation occurs. The pore volume and pore area distributions were evaluated using a Micrometrics 2600 Surface Area Analyzer.

5.3.1.3 Sulfur Analysis.

The amount of sulfur in the sulfate-promoted metal oxides was determined using an SC-132 sulfur analyzer. The dried sample was weighed, placed in a high temperature furnace, and burned completely in a flow of oxygen. The sulfate group in the sample was dissociated into SO_2 during combustion. The SO_2 adsorbed IR energy at a specific wavelength of the IR spectrum, and its concentration was detected by an IR detector. Typically, prior to the beginning of an analysis, samples of known sulfur contents were used for calibrating the sulfur determinator.

5.3.1.4 Thermal Stability.

A Hi-Res 2950 thermogravimetric analyzer (TGA) was used to study the thermal stability of sulfate-promoted zirconium oxide. The temperature and amount of decomposition of the sulfate group during calcination were determined in this way.

In a TGA experiment, a small amount (0.04 g) of zirconium precipitates in the presence of sulfate and platinum ($\text{Pt/Zr(OH)}_4/\text{SO}_4$) was placed in a sample holder. The sample holder was then placed in a closed chamber over which nitrogen was continuously passed. The chamber was then heated from room temperature to 973 K at a rate of five degrees per minute. Results were presented in terms of the weight percentage of the remaining sample or the rate of the sample loss versus temperature, as shown later.

5.3.2 Characterization of Acidic Properties

5.3.2.1 Nature of Acid Sites by FTIR.

FTIR was employed to study the binding structure between the sulfate group and zirconium oxide. The nature of the acid sites of this catalyst was identified and its surface acidity and acid strength qualitatively evaluated by a Mattson Polaris FTIR spectrometer coupled with in-situ pyridine adsorption.

A self-supported thin wafer of the catalyst pressed from catalyst powder was placed into an in-situ IR cell with CaF_2 windows. The cell was then heated to a desired temperature (~433K)

in a continuous helium flow for two hours to remove moisture adsorbed on the catalyst surface. Pyridine adsorption was carried out at 433 K using helium as a carrier gas which was first passed through a saturator containing pyridine and then through the IR cell. All IR spectra were recorded at 433 K with a resolution of 4 cm^{-1} and 100 scans from 4000 to 400 cm^{-1} . They were represented either in absorbance or transmittance bands between 2400 and 1200 cm^{-1} . The nature of the acid sites (Lewis and Brönsted acid sites) was determined by wavelengths of the pyridine chemisorbed on the catalyst surface; the shift of the S=O band after pyridine adsorption was used to characterize the acid strength⁽⁶⁹⁾. The effect of hydrogen on the Lewis acid sites, possibly converting them to protonic acid sites, was studied by introducing hydrogen into the IR cell after pyridine adsorption and then recording the IR spectra.

5.3.2.2 Temperature-Programmed Desorption.

The method of temperature programmed desorption (TPD) of basic molecules was used to quantitatively characterize the number of acid sites and acid strength of catalysts.

Pyridine was chosen as the base in the TPD experiments. In a typical run, a small amount of sample (~50 mg) was weighed and preheated in air in a furnace at 723 K for one hour and a half to remove the moisture. The sample was then transferred into a quartz tube, with a quartz wool inside to support the sample. A thermometer was inserted into the quartz tube to monitor the temperature in-situ of the sample. The latter was then preheated in a continuous helium flow at 623 K for twenty minutes to remove adsorbed moisture. Pyridine adsorption was carried out at 433 K using helium as a carrier gas which passed through a saturator containing pyridine and carried pyridine vapor to pass through the catalyst sample. After the catalyst surface was saturated with pyridine (determined by GC when the concentration of pyridine in the carrier gas was constant), the sample was purged with a helium flow for about 40 minutes to remove pyridine physically adsorbed on the catalyst surface. The temperature-programmed desorption of pyridine was carried out by increasing the temperature from 433 to 733 K within 20 minutes under flow rate of helium of 30 ml per minute. The desorbed pyridine was detected by an on-line Varian 3300 gas chromatograph (GC) with a thermal conductivity detector. The desorption peak area was

related to the number of acid sites, and the desorption temperature corresponding to the peak maximum (T_p) was used to characterize acid strength.

5.4 Results and Discussion

5.4.1 Effect of Addition of Sulfate Group on Properties of Zirconium Oxide

The effect of incorporation of a small amount of a sulfate group on the physical and structural properties of zirconium oxide (ZrO_2) was studied by the several techniques described earlier. Some properties of ZrO_2 with and without an added sulfate group are shown in Table 4.

Table 4. Effect of Addition of Sulfate Group on Some Properties of ZrO_2

Cat. No.	Catalyst	Sulfur content (wt. %)	Crystalline form	Specific surface area (m^2/g)	Average particle size (nm)
ZD	ZrO_2	0.0	Tetragonal (773 K) ^a	47.0	13.2
SZD2	ZrO_2/SO_4	2.71	Tetragonal (873 K) ^a	83.4	8.4

a: the temperatures given in the brackets are the calcination temperatures

Note that these two catalysts were calcined at different temperatures. These temperatures were so chosen that **ZD** and **SZD2** had the same crystalline structure, the tetragonal form, making comparison between them more meaningful. A large increase in surface area with a decrease in particle size was observed when a small amount of the sulfate group was added to ZrO_2 ; this agrees qualitatively with experimental findings in the literature^(1,7). The XRD patterns of **ZD** and **SZD2** after calcination at 773 and 873 K, respectively showed that they were in the tetragonal form. The monoclinic form was not found in the case of **ZD**. Results reported in the literature⁽⁶⁶⁾ claimed that ZrO_2 calcined at 773 K consisted of a mixture of tetragonal and monoclinic forms; a higher calcination temperature (973 K) was required to convert the tetragonal form into the

monoclinic one. Also noteworthy is that the calcination temperature necessary for a complete transformation of the amorphous form to the tetragonal crystalline one was at about 100 K higher for the sulfate-treated ZrO_2 than for the sulfate-free ZrO_2 . This indicates that the phase transformation of the sulfated zirconium oxide from the amorphous form to the tetragonal one requires a higher thermal activation, as observed also by other researchers⁽⁶⁴⁾. The distribution of the pore volume is very broad, as indicated by the diameter of the pores which range from 21 to 1083 Å, and a large portion of the pore volume is in the mesopore region (20 - 500 Å). In terms of the pore area distribution, most of the BET surface area of this catalyst is located in a narrow range of the mesopore region, 21 - 60 Å, with a very small portion being located in the larger pore area region.

Formation of acid sites of **SZD2** upon addition of a sulfate group was investigated using FTIR. Before calcination, the absorption bands of the sulfate group could not be identified. The peak at 1610 cm^{-1} was attributed to adsorbed molecular water. After calcination, besides a bending vibration of adsorbed molecular water at 1610 cm^{-1} , four additional strong vibration peaks were observed at 1240, 1140, 1020 and 924 cm^{-1} . These four peaks are assigned to the asymmetric and symmetric stretching frequencies of the S=O and S-O groups of the chelating bidentate sulfate ions coordinated to zirconium cations (Zr^{4+}) in zirconium oxide⁽⁶⁷⁾. The sulfate groups bound to the zirconium cations were formed during calcination which converted the amorphous zirconia to the crystalline one, ZrO_2 .

The nature of acid sites was examined using platinum doped and sulfate-promoted zirconium oxide (**SZD1**). The catalyst was heated in-situ under a helium flow at 423 K while IR spectra were recorded after various heating times. These IR spectra showed that the intensity of the band corresponding to molecular water decreased substantially and a new band at 1378 cm^{-1} appeared, which was characteristic of the asymmetric stretching frequency of the S=O covalent bond⁽⁶⁷⁾. This change of the IR spectrum is due to the removal of molecular water absorbed on the catalyst surface during heating, which transformed the catalyst from one with a chelating inorganic complex to one with an organic sulfate.

After **SZD1** was heated in-situ under a helium flow at 423 K for 60 minutes, pyridine was introduced using helium as a carrier. The presence of pyridine in this catalyst resulted in a shift in the asymmetric stretching frequency of the S=O bond from 1378 cm^{-1} to 1338 cm^{-1} , with three new adsorption bands appearing at 1537, 1491 and 1444 cm^{-1} . This shift is believed to be due to the fact that when pyridine was adsorbed on the central zirconium cation, it changed the nature of the S=O bond from a highly covalent double bond to one with less double bond character. In fact, the magnitude of this shift was used by other researchers for evaluating the acid strength of sulfate-promoted metal oxides⁽⁶⁹⁾.

The nature of the acid sites on **SZD1** can be identified from the three pyridine adsorption bands appearing at 1444, 1491 and 1537 cm^{-1} , respectively. They are assigned to the pyridine chemisorbed on the Lewis acid sites (L-Py), both the Lewis and Brönsted acid sites (L+B-Py), and the Brönsted acid sites (B-Py)^(111,112), respectively.

5.4.2 Effect of the Preparation Procedures on Properties of Pt/ZrO₂/SO₄

5.4.2.1 Precipitation Methods.

Two Pt/ZrO₂/SO₄ catalyst samples, **SZD1** and **SZD22**, were prepared from Zr(SO₄)₂·H₂O using heterogeneous and homogeneous methods, respectively. Some selected physical and acidic properties of these catalysts are shown in Table 5.

Table 5. Comparison of Selected Physical and Acidic Properties Between **SZD1** and **SZD22** Prepared by the Heterogeneous and Homogeneous Precipitation Methods

Cat. No.	Physical Properties				Acidic Properties	
	sulfur (wt. %)	surface area (m ² .g ⁻¹)	crystalline form	average particle size (nm)	T _p (K)	acidity (mmole/g)
SZD1	2.71	83.4	tetragonal	8.4	563	0.358
SZD22	1.34	90.0	tetragonal	8.2	530	0.150

The nature of crystalline phases, specific surface area and average particle size of these two

catalysts were close with a notable difference in sulfur content. On the other hand, their acidic properties were strongly affected by the precipitation method, as revealed by TPD measurements. The peak desorption temperature (T_p) of **SZD1**, which is related to acid strength, was about 30 K higher than that of **SZD22**. This indicates that the acid strength of $\text{Pt/ZrO}_2/\text{SO}_4$ synthesized by the heterogeneous precipitation method (**SZD1**) was higher than the one obtained by the homogeneous method (**SZD22**). The number of acid sites of **SZD1** was also larger than that of **SZD22**, which was probably attributed to the fact that the sulfur content of **SZD22** was lower than that of **SZD1**. The experimental results indicate that the heterogeneous precipitation method is better than the homogeneous one to synthesize the $\text{Pt/ZrO}_2/\text{SO}_4$ catalyst with higher acid strength and acidity.

Additional TPD runs for **SZD1** and **SZD22** were carried out under similar conditions to check the reproducibility of measurements for the acidity and acid strength of these two catalysts.

5.4.2.2 Effect of Calcination Temperature.

Calcination temperature is important as it dictates the degree to which the amorphous phase of such catalysts is converted to crystalline forms. It also affects the sulfur content. The effect of calcination temperature was examined by calcining platinum doped and sulfate-promoted zirconium hydroxide at various temperatures. The results are shown in Table 6.

Table 6. Effect of Calcination Temperature on the Physical Properties of $\text{Pt/ZrO}_2/\text{SO}_4$

Catalyst No.	Calcination Temperature (K)	Sulfur content (wt. %)	Crystalline form	Average particle size (nm)
SZD5	773	4.32	A	not applicable
SZD6	823	4.07	A + T	8.4
SZD4	873	1.58	T	7.0
SZD7	923	1.51	T	7.6
SZD8	973	1.16	T	8.4

A: the amorphous form; T: the tetragonal form

Sulfur is evidently lost upon calcination. The loss was negligibly small when the calcination temperature was below 823 K but it became severe when the calcination temperature was above 873 K. In this later case, more than 70% of the sulfur contained in the catalyst was lost. On the other hand, the TGA profile of the amorphous $\text{Pt/Zr(OH)}_4/\text{SO}_4$ recorded from room temperature to 973 K indicated that the weight loss of the catalyst started in the temperature range between 373 and 473 K, which is related to the amount of the physically adsorbed water and that of the water generated by the decomposition of Zr(OH)_4 into ZrO_2 and H_2O . The weight loss from 573 to 823 K was insignificant; it became important (6.85% of the weight of the initial sample was lost) when temperature was between 873 and 973 K. This later was revealed by a peak which appeared in that temperature range in the TGA profile. This observation indicated that when the calcination temperature exceeded 873K, a significant amount of sulfur was lost due to thermal decomposition of the sulfate group.

The XRD profiles of platinum doped and sulfate-promoted zirconium hydroxide before and after calcination at different temperatures were obtained. Before calcination, the precipitates were amorphous. When they were calcined at 773 K (SZD5), XRD pattern did not eventually change, indicating that they did not crystallize at that temperature. On the other hand, ZrO_2 without a sulfate treatment was found to be only in tetragonal crystalline form when calcined at the 773K for the same period of time. The presence of the sulfate group in the zirconia precipitates evidently retards crystallization of ZrO_2/SO_4 . The XRD spectra also show that the phase transformation of the $\text{Pt/ZrO}_2/\text{SO}_4$ from the amorphous form to the tetragonal one occurred when the calcination temperature reached 823 K. The tetragonal crystalline structure developed further with increasing calcination temperature. When temperature was above 873 K, it was completely converted into the tetragonal form. It was also in the tetragonal form after calcination at 973 K. By contrast, ZrO_2 without sulfate treatment was converted from the tetragonal into the monoclinic form at 973 K⁽⁶⁶⁾.

The average particle size of the $\text{Pt/ZrO}_2/\text{SO}_4$ catalysts increased visibly with increasing calcination temperature when the latter was above 873 K. This finding agrees reasonably well

with the experimental fact that the surface area of such a catalyst decreased when it was calcined at a temperature above 873 K^(116,126).

5.4.2.3 Effect of the Nature of the Anion.

It is known that when an anion (e.g. SO_4^{2-} , WO_3 or MoO_3) is introduced to certain metal oxides, their surface acidities are strongly enhanced^(103,104). Their effect on the acidic properties of Pt/ZrO₂ was determined by TPD. The experimental results are shown in Table 7.

Among the various anions, the sulfate group gave the best performance in terms of the increase in acidic properties of the Pt/ZrO₂. This may be due to a stronger inductive effect of SO_4^{2-} in the formation of the sulfur surface complex compared to WO_3 and MoO_3 . The XRD profiles of the Pt/ZrO₂ promoted by SO_4^{2-} , WO_3 and MoO_3 were obtained. The Pt/ZrO₂ promoted with WO_3 was in the tetragonal form, and so was the Pt/ZrO₂ promoted with MoO_3 . The Pt/ZrO₂ without anion treatment was in the monoclinic form when it was calcined at 973 K⁽⁶⁶⁾. This leads to the conclusion that during calcination at high temperatures, the presence of WO_3 or MoO_3 stabilizes the tetragonal phase of the Pt/ZrO₂, as does SO_4^{2-} . A similar conclusion has been drawn by other researchers^(103,104).

Table 7. Effect of Addition of Anions on the Acidic Properties of the Pt/ZrO₂ Catalysts

Catalyst No.	Catalyst formula	Anion	Acidic properties	
			Acidity (mmole/g)	T _p (K)
SZD4	Pt/ZrO ₂ /SO ₄	SO ₄ ²⁻	0.358	563
TZD	Pt/ZrO ₂ /WO ₄	WO ₃	0.144	556
MZD	Pt/ZrO ₂ /MoO ₄	MoO ₃	0.085	520

5.4.2.4 Effect of the Concentration of Sulfuric Acid.

The effect of the concentration of sulfuric acid used for sulfation on the physical and acidic properties of sulfate-promoted and Pt doped zirconium oxide metal oxides was investigated. To that end, zirconium hydroxide precipitates were impregnated with sulfuric acid of various

concentrations. The sulfur content and acidity of these catalysts are shown in Table 8. Interestingly, the weight percentage of the sulfate adsorbed on the Pt/ZrO₂ after calcination at 873 K differed only slightly for a relatively wide range of the sulfuric acid concentration (0.2 - 6.0N). Although this finding was unexpected, it should be pointed out that in addition to the concentration of sulfuric acid used for sulfation, the sulfur content also depends, possibly to a great extent, on the calcination temperature. This latter statement is supported by the results in Table 6. It was also reported^(105,126) that, at calcination temperatures below 873 K, the sulfur contents increased with increasing concentration of sulfuric acid; at a calcination temperature above 873 K, the sulfur contents became relatively insensitive to the concentration of sulfuric acid. The surface area of the Pt/ZrO₂/SO₄ impregnated with 1 N H₂SO₄ (SZD3) was 107 m²/g, close to the result reported in the literature^(105,112); the calculated surface sulfur is 14.5·10⁻⁵ g/m². This calculation was done by dividing the amount of sulfur in the catalyst by its surface area. If it is assumed that each sulfur species occupies 25 Å² (corresponding to 21·10⁻⁵ g/m²)⁽¹⁰⁵⁾, the sulfur adsorbed on the surface of the Pt/ZrO₂/SO₄ catalyst would be close to a monolayer.

Table 8. Effect of the Concentration of Sulfuric Acid on the Properties of the Pt/ZrO₂/SO₄ Catalysts (calcined at 873 K in air for three hours)

Catalyst No.	H ₂ SO ₄ (N)	Sulfur (wt. %)	Acidity (mmole/g)	
			Calculated ^a	Experimental
SZD9	0.2	1.48	0.463	0.249
SZD10	0.5	1.51	0.472	0.271
SZD3	1.0	1.56	0.488	0.358
SZD11	3.0	1.58	0.494	0.263
SZD12	6.0	1.56	0.488	0.323

a: the calculation was based on the assumption that each sulfate group incorporated in the catalyst forms an acid site.

The number of acid sites of the Pt/ZrO₂/SO₄ catalyst increased with increasing H₂SO₄

concentration in the range of 0.2 - 1 N. With further increase in the H_2SO_4 concentration, the number of acid sites decreased first and then increased. The $\text{Pt/ZrO}_2/\text{SO}_4$ catalyst prepared by impregnation of zirconium precipitates with 1 N H_2SO_4 concentration gave the highest number of acid sites. The calculated number of acid sites of the $\text{Pt/ZrO}_2/\text{SO}_4$ catalysts were higher than the experimental ones determined by TPD. This may be understood by stating that the acid sites distributed on the catalyst surface may possess different acid strengths with some weak acid sites being unable to adsorb pyridine. On the other hand, not all of the adsorbed sulfate species would form a bidentate complex with the zirconium cations responsible for generation of highly acidic sites.

5.4.3 Properties of Pt and Sulfate-Promoted Mixed Zirconium and Hafnium Oxides

Platinum and sulfate-promoted mixtures of zirconium and hafnium oxides, $\text{Pt/ZrO}_2\cdot\text{HfO}_2/\text{SO}_4$, were prepared by the heterogeneous coprecipitation method. Their acidic properties were compared with platinum and sulfate promoted zirconium oxide and hafnium oxide, respectively (Table 9).

Table 9. Acidic Properties of Pt and Sulfate-Promoted ZrO_2 , HfO_2 and Their Mixtures (calcined at 873 K for three hours)

Catalyst No.	Catalyst formula	Zr/(Hf+Zr) molar fraction	Acidic properties	
			Acidity (mmole/g)	T_p (K)
SZD3	$\text{Pt/ZrO}_2/\text{SO}_4$	1	0.358	553
SZHD1	$\text{Pt/ZrO}_2\cdot\text{HfO}_2/\text{SO}_4$	0.8	0.228	543
SZHD2	$\text{Pt/ZrO}_2\cdot\text{HfO}_2/\text{SO}_4$	0.5	0.215	533
SZHD3	$\text{Pt/ZrO}_2\cdot\text{HfO}_2/\text{SO}_4$	0.2	0.198	533
SHD	$\text{Pt/HfO}_2/\text{SO}_4$	0	0.186	533

The number of acid sites of the $\text{Pt/ZrO}_2/\text{SO}_4$ catalyst (SZD3) was much higher than that of the $\text{Pt/HfO}_2/\text{SO}_4$ catalyst (SHD). Its number of acid sites was reduced when HfO_2 was present.

The acid strength, characterized by the peak desorption temperature (T_p) of the $\text{Pt/ZrO}_2/\text{SO}_4$ was also higher than that of the $\text{Pt/HfO}_2/\text{SO}_4$ and the mixtures, $\text{Pt/ZrO}_2\cdot\text{HfO}_2/\text{SO}_4$.

The metal oxide that can be effectively promoted by a sulfate group to form strong acid sites should have a metal atom with high electronegativity and high coordination number⁽⁶⁷⁾. Zirconium and hafnium cations of the same group in the periodic table have the same charge, same size and same electronegativity⁽¹²⁷⁾. The difference in acidic properties between sulfate-promoted and platinum-doped zirconium oxide and hafnium oxide may be related to the different structures of these two catalysts. The XRD pattern of the $\text{Pt/ZrO}_2/\text{SO}_4$ calcined at 873 K showed a completely tetragonal form. The XRD pattern of $\text{Pt/ZrO}_2\cdot\text{HfO}_2/\text{SO}_4$ consisted of a mixture of the tetragonal and monoclinic forms. However, the XRD pattern of the $\text{Pt/HfO}_2/\text{SO}_4$ catalyst calcined at the 873 K was in the mixture of monoclinic form and amorphous. It has been reported⁽⁶⁶⁾ that the ZrO_2/SO_4 catalyst in the tetragonal form was more active than that in the monoclinic form or amorphous. This suggests that the $\text{Pt/HfO}_2/\text{SO}_4$ catalyst in the mixture of monoclinic form and amorphous might account for its low number of acid sites and weak acid strength compared to those of the $\text{Pt/ZrO}_2/\text{SO}_4$ catalyst in the tetragonal form.

5.4.4 Effect of Addition of Hydrogenation Metals on the Acidic Properties of ZrO_2/SO_4

Addition of a hydrogenation metal to the ZrO_2/SO_4 catalyst not only prolongs its catalytic life but also affects its acidic properties. FTIR technique was mainly employed for this study.

The IR spectra of pyridine adsorbed on the ZrO_2/SO_4 doped with 1.0 wt. % of Pt (SZD14) and 2.0 wt. % of Ni (SZD21) and the IR spectrum of the ZrO_2/SO_4 catalyst (SZD2) were obtained.

After 60 minutes of in-situ preheating of these samples in the presence of helium, the band at 1616 cm^{-1} , corresponding to physically adsorbed molecular water, decreased substantially, and a new band at 1398 cm^{-1} in the case of SZD2, and 1385 cm^{-1} in the case of SZD21, due to S=O appeared. Upon introducing pyridine carried by helium, three new bands appeared in the wavelength region between 1440 and 1550 cm^{-1} ; the ones at 1444 , 1491 and 1537 cm^{-1} were attributed to pyridine chemisorbed on Lewis acid sites (L-Py), on both the Lewis and Brönsted acid sites (L+B-Py) and the Brönsted acid sites (B-Py), respectively. The band at 1398 cm^{-1}

corresponded to the S=O in the ZrO_2/SO_4 ; it shifted to 1378 cm^{-1} when 0.5 wt. % of Pt was added to the ZrO_2/SO_4 . After adsorption with pyridine, this band shifted to 1330 cm^{-1} in the case of ZrO_2/SO_4 , and to 1338 cm^{-1} in the case of Pt doped ZrO_2/SO_4 . The amount of the shift in the wavelength of the S=O was lower in the case of the Pt doped ZrO_2/SO_4 , indicating that the acid strength of the ZrO_2/SO_4 catalyst decreased upon addition of Pt. The amount of shift of the S=O was used to quantify the acid strength of sulfated metal oxides⁽⁶⁹⁾.

The effect of the presence of hydrogen on the acidic properties of the ZrO_2/SO_4 with or without an added hydrogenation metal was also studied by FTIR. The IR spectrum showed that when hydrogen was introduced to the Pt/ ZrO_2/SO_4 (SZD14), the band at 1491 cm^{-1} due to the L+B-Py increased significantly with a concomitant decrease in that at 1444 cm^{-1} due to the L-Py. This experimental finding agrees with published work^(111,112). The conversion between the Lewis and Brönsted acid sites in the Pt/ ZrO_2/SO_4 in the presence of hydrogen was explained by the dissociation of the hydrogen molecules adsorbed on Pt into hydrogen atoms, their spillover onto the ZrO_2/SO_4 surface and electron transfer from hydrogen atoms to the Lewis acid sites producing protonic acid sites⁽¹¹²⁾. Interestingly, the presence of hydrogen with ZrO_2/SO_4 in the absence of a hydrogenation metal did not have any effect on the bands of the L-Py and L+B-Py mentioned above (Figure 20a). This was also observed with Ni/ ZrO_2/SO_4 . The fact that platinum and nickel did not play the same role with ZrO_2/SO_4 may be understood as follows: nickel is not as good a hydrogenation metal as is platinum, so that there is little hydrogen spillover from nickel.

5.5 Summary

We have demonstrated that addition of SO_4^{2-} , WO_3 and MoO_3 , to platinum promoted zirconium oxide is instrumental in changing both physical and acidic properties. Small amounts of these materials (~2%) on the zirconium oxide significantly increased its surface area and improved the thermal stability of its tetragonal phase. As a result, its surface acidic properties increased greatly. Among these anions, the sulfate gave the best promotional effect on acidic properties of zirconium oxide. It was found that the method of preparation of catalyst, the nature

of the anion and that of hydrogenation metal were also important for modifying the physical and acidic properties of the catalyst. A Pt/ZrO₂/SO₄ sample prepared by heterogeneous precipitation with 1 N sulfuric acid for sulfation and calcination for three hours at 873 K gave better acidic properties. We have found that, in the presence of hydrogen, protonic acid sites could be formed on platinum doped ZrO₂/SO₄ but not on nickel doped ZrO₂/SO₄.

6.0 ACTIVITY OF ANION-MODIFIED METAL OXIDES FOR HYDROCRACKING AND HYDROISOMERIZATION OF ALKANES

6.1 Objectives

The activity of anion-modified metal oxides for hydrocracking and hydroisomerization of long chain hydrocarbons was measured experimentally. Normal hexadecane was chosen as a model compound to represent the behavior of F-T waxes. A batch reactor was used to carry out the reactions. The main objectives of this study were:

(1) to investigate the effect of catalyst preparation conditions on the catalytic activity for the hydrocracking and hydroisomerization of n-hexadecane. These catalyst preparation conditions included the nature of the starting zirconia precursor, the precipitation method, the nature and amount of anion, and the calcination temperature. It was also hoped to gain an insight into the relationship between catalytic activity and acidic properties of $\text{Pt/ZrO}_2/\text{SO}_4$.

(2) to study the effect of addition of various hydrogenation metals on the catalytic activity and product selectivity of ZrO_2/SO_4 toward hydrocracking and hydroisomerization of n-hexadecane.

(3) to determine the activity of sulfate promoted bimetallic oxides ($\text{Pt/ZrO}_2\text{-HfO}_2/\text{SO}_4$) for hydrocracking and hydroisomerization of n-hexadecane.

6.2 Background

Addition of a sulfate group to certain metal oxides such as ZrO_2 , HfO_2 and TiO_2 enhances their surface acidity significantly^(63,74,75). Consequently, their catalytic activity for acid-catalyzed reactions increases to a great extent. Hino and Arata⁽⁷⁵⁾ found that sulfated zirconium oxide catalyst could be used to isomerize light alkanes at low temperatures (~423 K). Formation of multibranched isomers was favored at these low temperatures. Hosoi et al.^(106,107,110) reported that incorporation of certain transition metals such as Pt, Pd and Ni on ZrO_2/SO_4 enhanced catalytic performance for isomerization of n-pentane in the presence of hydrogen; a major purpose of the

metal was to prevent deactivation of the catalyst due to coke formation. Wen et al.^(9,128) found that Pt/ZrO₂/SO₄ was highly active in hydrocracking and hydroisomerization of n-heptane and n-hexadecane under relatively mild reaction conditions (383 - 443 K; 200 - 300 psig of hydrogen pressure) obtaining a high selectivity (> 90%) to hydrocracked isoparaffins. In terms of catalytic activity and product selectivity, the Pt/ZrO₂/SO₄ catalyst seemed to be promising for upgrading F-T waxes to obtain liquid fuels.

It is believed that the catalytic activity of Pt/ZrO₂/SO₄ for acid catalyzed hydrocracking and hydroisomerization of hydrocarbons is related to its acidic properties. The latter can be affected by several parameters, such as the preparation procedure, the amount and nature of the anion and the hydrogenation metal. A main objective of our work was to explore the effects of these parameters on the catalytic activity and product selectivity of the Pt/ZrO₂/SO₄ catalyst for hydrocracking and hydroisomerization, and to gain insights into the relationship between the catalyst activity and acidic properties of this metal oxide.

6.3 Experimental

n-Hexadecane (99%) was purchased from Aldrich Chemical Company, and used as received.

6.3.1 Experimental Setup

A horizontal shaking microreactor system (Figure 2), providing good catalyst-reactant mixing and gas-liquid mass transfer, was used to carry out hydrocracking and hydroisomerization experiments with n-hexadecane. The microreactor consisted of three portions: a horizontal reactor tube (1 in.o.d. x 4.625 in.), a vertical reactor stem (1/2 in.o.d. x 10 in.), and a multiport valve connected on top of the reactor stem. The horizontal tube was sealed at one end, and the other end was fitted with a cap to allow charging of the catalyst and discharging of the products. The reactor stem isolated the multiport valve from the heating source (a fluidized sandbath), and accommodated a pressure transducer, a thermocouple and a quick connector to allow for monitoring of the reaction variables and charging and discharging of gases.

6.3.2 Reaction Procedure

In a typical experiment, one gram of catalyst was activated in a furnace at 723K for one hour and a half, then quickly transferred to a predried hot tubing bomb microreactor. After the catalyst was placed in the horizontal reactor, the open end was immediately closed and the top of the reactor stem plugged. The horizontal portion of the reactor was cooled to room temperature with water. Upon removal of the plug, six grams of n-hexadecane was charged into the reactor through the reactor stem. After connecting the multiport valve to the reactor stem, the reactor was

Figure 2. Schematic Drawing of Microautoclave Reactor.

mounted on the stand, purged with hydrogen (99.99%) three times, and then pressurized to a desired pressure (360 psig). The reactor was shaken for about three minutes at room temperature at 160 cycles per minute to allow for pre-reaction feed mixing and hydrogen dissolution in the slurry. At time zero, the reactor was immersed in the sandbath which was preheated to the reaction temperature (433 K). Typically, the reactor reached the reaction temperature in three minutes while being shaken at 160 cycles per minute during which the initial pressure increased to about 440 psig at the reaction temperature of 433 K. After reaction, the reactor was removed from the sandbath and quenched to a cooling water bath for about ten minutes. Because the yield of gas products obtained in our reactions was less than 3 wt. %, they were considered negligible and were vented after cooling. The liquid products were filtered to remove suspended catalyst powder and analyzed using an HP-5890 gas chromatograph through a 30 m x 0.25 mm i.d. DB-1 capillary column with an injection split ratio of 50 to 1. A flame ionization detector was used for product analysis. The hydrocarbon components were identified upon comparing their retention times with those known standards calibrated in the same GC. The conversion was defined as the disappearance of n-C16 in the liquid phase, isomerization as the mass of isohexadecanes (i-C16) and cracking as the mass of compounds with carbon numbers less than 16. The selectivity of cracking was the mass of cracked products (C5-C13) divided by the mass of n-C16 converted, and correspondingly the selectivity of isomerization was the mass of i-C16 divided by the mass of n-C16 converted.

6.4 Results and Discussion

6.4.1 Effect of Preparation Procedure on Catalytic Activity

6.4.1.1 Effect of the Precipitation Method and Nature of Zirconia Precursor.

Four Pt-doped sulfated zirconium oxide samples were prepared from different precursors and under different precipitation conditions, as described in Table 3 of Section 4.3.3. Their activity was tested using the hydrocracking and hydroisomerization of n-hexadecane as the reaction model. The experimental results are given in Table 10.

Under the same reaction conditions, the Pt/ZrO₂/SO₄ catalysts (**SZD1**, **SZD2** and **SZD4**) prepared by the heterogeneous method using Zr(SO₄)₂·4H₂O, ZrOCl₂ and ZrO(NO₃)₂ as zirconia precursors showed similar activities and product selectivities towards hydrocracking and hydroisomerization of n-hexadecane. This indicates that the activity and product selectivity of the Pt/ZrO₂/SO₄ catalyst evidently does not depend on the particular starting zirconia precursor. As mentioned earlier, the use of Zr(SO₄)₂·4H₂O as a zirconia precursor greatly reduced the washing effort involved in the synthesis procedure. Thus, Zr(SO₄)₂·4H₂O was a good replacement for the conventional zirconia precursors: ZrOCl₂ and ZrO(NO₃)₂. Duplicate runs for hydrocracking and hydroisomerization of n-hexadecane were carried out under similar reaction conditions in the presence of the Pt/ZrO₂/SO₄ catalysts; these catalysts were prepared from the same or different batch reactions, using Zr(SO₄)₂·4H₂O as the zirconia precursor. The experimental data obtained were reproducible, within 4% of experimental error.

The catalyst **SZD22** prepared by the homogeneous precipitation method showed a lower activity than that of the catalyst **SZD1** obtained by the heterogeneous precipitation method; both **SZD22** and **SZD1** used Zr(SO₄)₂·4H₂O as the zirconia precursor. The lower activity of **SZD22** agrees with the finding that the number of acid sites and acid strength of **SZD22** were much lower than those of **SZD1** (see Table 5 of Section 5.4.2.1).

Table 10. Comparison of Activity Among the Various Pt/ZrO₂/SO₄ Catalysts Prepared from Different Precursors or under Different Precipitation Conditions

Run No.	Catalyst No.	Conversion (wt. %)	Selectivity (wt. %)		
			C5-C9	C10-C13	i-C16
R001	SZD1	68.0	58.8	17.6	23.6
R002	SZD3	66.0	56.1	21.2	22.7
R003	SZD4	67.9	57.2	18.6	24.2
R004	SZD22	30.0	57.1	23.3	19.6

(Reaction conditions: cat./feed: 1/6, 433 K, 300 psig H₂ (cold) and 50 min)

In sum, a highly active Pt/ZrO₂/SO₄ catalyst was successfully prepared by the heterogeneous precipitation method using Zr(SO₄)₂·4H₂O as a zirconia precursor to obtain zirconium hydroxide precipitates. This zirconia precursor reduces a considerable amount of water washing effort in the synthesis compared to the use of the conventional precursors (ZrOCl₂ and ZrO(NO₃)₂).

6.4.1.2 Effect of Calcination Temperature.

Five Pt/ZrO₂/SO₄ catalysts (SZD4-SZD8) obtained after calcination at different temperatures (773 - 973 K) were used for hydrocracking and hydroisomerization of n-hexadecane.

The conversion of n-hexadecane with respect to the calcination temperature is shown in **Figure 3**. Clearly, the catalyst activity depends strongly on the calcination temperature. The conversion of n-hexadecane increased with the increase in calcination temperature when the latter was between 773 and 873 K. It reached its highest value when the catalyst was calcined at 873 K (SZD4). With a further increase in calcination temperature, however, the conversion decreased.

The catalyst calcined at 973 K (SZD8) was almost inactive for the hydrocracking and hydroisomerization of n-hexadecane.

Figure 3. Effect of Calcination Temperature on the Conversion of n-C16 Using a $\text{Pt/ZrO}_2/\text{SO}_4$ Catalyst (433 K, 360 psig H_2 cold, 60 min).

The effect of calcination temperature on the catalytic activity of $\text{Pt/ZrO}_2/\text{SO}_4$ is connected to the phase transformation. The amorphous zirconium hydroxide crystallized above 823 K. At low calcination temperatures (< 823 K), the degree of crystallization of $\text{Pt/ZrO}_2/\text{SO}_4$ (SZD5) was low, consisting mainly of the amorphous form. It has been reported that highly acidic and catalytically active $\text{Pt/ZrO}_2/\text{SO}_4$ was completely in the tetragonal form⁽⁶⁶⁾. The low activity of the $\text{Pt/ZrO}_2/\text{SO}_4$ catalyst calcined at low temperatures was mainly attributed to the fact that the amount

of tetragonal phase responsible for the formation of highly acidic sites was low. When Pt/ZrO₂/SO₄ was calcined at 873 K (SZD4), it consisted only of the tetragonal form, exhibiting the highest activity towards hydrocracking and hydroisomerization of n-hexadecane, although its sulfate content was much lower than that of the catalysts calcined at lower temperatures (see Table 6 of Section 5.4.2.2).

Similar findings have been reported by other researchers^(105,126). This indicates that the total sulfur content does not necessarily reflect the amount of the surface sulfur complex responsible for formation of highly acidic sites. Although the Pt/ZrO₂/SO₄ catalyst calcined at a temperature above 873 K (SZD7-8) remained in the tetragonal form, its catalytic activity for conversion of n-hexadecane decreased. Calcination at high temperatures not only reduced the content of the surface sulfur species but the catalyst surface area as well^(105,126). As the total number of the active sites is proportional to each of these two parameters, the calcination temperature is critical for obtaining Pt/ZrO₂/SO₄ catalyst with high activity. The catalyst (SZD8) calcined at 973 K lost about 28 wt. % of sulfur compared to that of SZD4,; however it gave a low conversion of n-C16.

6.4.1.3 Effect of the Nature of the Anion.

The catalytic properties of anion modified metal oxides are strongly related to the nature of anion. In this study, Pt/ZrO₂ was promoted with SO₄²⁻, WO₄²⁻ and MoO₄²⁻, respectively. The use of WO₄²⁻ and MoO₄²⁻ was motivated by the results reported in the literature that Pt/ZrO₂ promoted with WO₄²⁻ or MoO₄²⁻ was active for the isomerization of n-butane^(114,115). The preparation conditions for these catalysts are specified in Table 3 of Section 4.3.3 and their activity for the hydrocracking and hydroisomerization of n-hexadecane are shown in Table 11. Addition of a sulfate group to the Pt/ZrO₂ (SZD4) greatly enhanced its catalytic activity while the activities of Pt/ZrO₂ promoted by WO₃ (TZD) and MoO₃ (MZD) were much lower. This agrees with the fact that the number of the acid sites and acid strength of the SO₄²⁻ promoted Pt/ZrO₂ were much higher than those of WO₃ or MoO₃ promoted Pt/ZrO₂ (see Table 9 of Section 5.4.3). The weak capability for WO₃ and MoO₃ to improve the surface acidic properties of ZrO₂ compared to that of SO₄²⁻ may be related to their weak inductive effects. On the other hand, most

of the WO_3 or MoO_3 , which could be responsible for the formation of strong acid sites for the reaction of n-C16, may be in the bulk rather than on the ZrO_2 surface.

Table 11. Comparison of the Catalytic Activity of Pt/ZrO_2 Promoted by Various Anions
(Reaction conditions: feed/cat.: 6/1, 433 K, 360 psig H_2 (cold) and 60 min)

Run No.	Catalyst No.	Catalyst formula	Anion	Conversion (wt. %)
R005	SZD4	$\text{Pt/ZrO}_2/\text{SO}_4$	SO_4^{2-}	83.9
R006	TZD	$\text{Pt/ZrO}_2/\text{WO}_3$	WO_4^{2-}	1
R007	MZD	$\text{Pt/ZrO}_2/\text{MoO}_3$	MoO_4^{2-}	0

6.4.1.4 Effect of H_2SO_4 Concentration.

Addition of a sulfate group to ZrO_2 greatly enhances its surface acidity. The most common way to introduce a sulfate group is to impregnate zirconium hydroxide precipitates (Zr(OH)_4) with an H_2SO_4 solution. While the effect of the concentration of H_2SO_4 solution on sulfate adsorption and surface area of catalysts has been reported in the literature,⁽¹²⁹⁾ its effect on the activity of the resulting catalysts has received little attention. The effect of the concentration of H_2SO_4 solution on the physical and acidic properties of the $\text{Pt/ZrO}_2/\text{SO}_4$ catalyst was discussed earlier. To that end, zirconium hydroxide precipitates were impregnated with H_2SO_4 solutions of various concentrations ranging from 0.2 to 6.0 N. They were then calcined at 873 K for three hours.

The activity and product selectivity of these catalysts were compared using the hydrocracking and hydroisomerization of n-hexadecane as the reacting system. The conversion of n-hexadecane obtained with a particular $\text{Pt/ZrO}_2/\text{SO}_4$ catalyst and the number of acid sites for this catalyst as a function of H_2SO_4 concentration are shown in Figure 4.

Conversion first increased with increasing H_2SO_4 concentration, reaching the highest conversion at a concentration of H_2SO_4 of about 1N. It then decreased slightly with a further

Figure 4. Effect of the Concentration of H₂SO₄ on the Number of Acid Sites of Pt/ZrO₂ and the Conversion of n-16, 433K, 360 psig H₂ cold, 40 min.

increase in the concentration of H₂SO₄. An important finding was that there was a similarity between the dependency of the conversion of n-hexadecane and that of the number of acid sites of the Pt/ZrO₂/SO₄ catalyst on the H₂SO₄ concentration used for sulfation of these catalysts (Figure 4) when the H₂SO₄ concentration is less than 1N. However, when the H₂SO₄ concentration was higher than 1N, the dependency of the conversion of n-hexadecane and that of the number of the acid sites of the Pt/ZrO₂/SO₄ catalyst on the H₂SO₄ concentration was different. The number of acid sites of Pt/ZrO₂/SO₄ at 3N was lower than that of Pt/ZrO₂/SO₄ at 1N or 6N,

which was unexpected, because the sulfur content of the former one was similar to that of the latter one. This might be due to the error of TPD measurements. The use of these catalysts led to a similar product selectivity (Figure 5).

In sum, the activity of $\text{Pt/ZrO}_2/\text{SO}_4$, which depended on its surface acidity, was affected by the concentration of the H_2SO_4 solution used in the preparation of the catalysts. A $\text{Pt/ZrO}_2/\text{SO}_4$ sample prepared from 1 N sulfation gave the highest activity for conversion of n-C16.

Figure 5. Effect of the Concentration of H_2SO_4 on the Product Selectivity from the Reaction of n-C16 and H_2 .

6.4.2 Effect of Addition of Hydrogenation Metals on the Catalytic Activity of ZrO_2/SO_4

6.4.2.1 Hydrogenation Metal.

Bifunctional catalysts, consisting of both a hydrogenation metal and an acidic support, are widely used in the hydrocracking and hydroisomerization of hydrocarbons; the balance between the hydrogenation capacity and the acidic function strongly affects catalytic activity and product selectivity. In order to investigate the role of addition of a hydrogenation metal during the reaction, and its effect on catalytic activity, ZrO_2/SO_4 doped with various hydrogenation metals was used in experiments on hydrocracking and hydroisomerization of n-hexadecane. The preparation conditions of these catalysts have been specified in Table 6 of Section 4.3.3. The catalytic activities of these catalysts are shown in Table 12.

The conversion of n-C16 using the ZrO_2/SO_4 catalyst (SZD2) was low, likely due to rapid formation of coke. Addition of a hydrogenation metal such as Pt is known to be effective in reducing coke formation^(106,107). In this study, platinum was introduced to the ZrO_2/SO_4 catalyst in three different ways: (a) the classic way: impregnation of $\text{Zr}(\text{OH})_4/\text{SO}_4$ precipitates with H_2PtCl_6 using the method of incipient wetness followed by calcination at 873 K (SZD1), (b) PtO_2 powder suspended in distilled water was impregnated with $\text{Zr}(\text{OH})_4/\text{SO}_4$ precipitates and then calcined together at 873 K (SZD17), and (c) PtO_2 powder was mechanically mixed with the ZrO_2/SO_4 catalyst (SZD2) which was already calcined at 873 K (SZD18).

There was an increase in the conversion of n-hexadecane with all three Pt doped ZrO_2/SO_4 catalysts (SZD1, SZD17 and SZD18) compared to that of the untreated ZrO_2/SO_4 catalyst (SZD2). Specifically, the use of the $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ or $\text{PtO}_2/\text{ZrO}_2/\text{SO}_4$ as the catalyst gave high conversions (about 72 wt. %). A conversion of only 11.0 wt. % was obtained upon using the mechanically mixed $\text{PtO}_2 + \text{ZrO}_2/\text{SO}_4$ as the catalyst. Deactivation was not found in the case of $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ and $\text{PtO}_2/\text{ZrO}_2/\text{SO}_4$ during reaction, as suggested by the fact that their colors did not change after reaction. For the $\text{PtO}_2 + \text{ZrO}_2/\text{SO}_4$ catalyst, deactivation seemed to occur during reaction.

The presence of platinum as a hydrogenation metal component was indeed effective in

reducing coke formation of the ZrO_2/SO_4 . Perhaps more important, the activity of the platinum doped ZrO_2/SO_4 catalyst after calcination apparently did not depend on the nature of starting platinum material used for impregnation. The difference in activity between the calcined $\text{PtO}_2/\text{ZrO}_2/\text{SO}_4$ (SZD17) and mechanically mixed $\text{PtO}_2 + \text{ZrO}_2/\text{SO}_4$ (SZD18) catalysts suggests that there was modification of the PtO_2 after calcination which favored the catalytic activity.

Table 12. Conversion of n-C16 Using ZrO_2/SO_4 Doped with Various Hydrogenation Metals with 0.5 wt. % of Metal

(Reaction conditions: feed/cat.: 1/6, 433 K, 360 psig H_2 (cold) and 60 min)

Run No.	Catalyst No.	Catalyst formula	Conversion (wt. %)	Selectivity (wt. %)	
				C5 - C13	i-C16
R008	SZD2	ZrO_2/SO_4	0	0	0
R009	SZD1	$\text{Pt}/\text{ZrO}_2/\text{SO}_4$	71.7	82.5	17.5
R010	SZD17	$\text{PtO}_2/\text{ZrO}_2/\text{SO}_4$	72.5	88.4	11.6
R011	SZD18	$\text{PtO}_2 + \text{ZrO}_2/\text{SO}_4$	11	10	90
R012	SZD19	$\text{Pd}/\text{ZrO}_2/\text{SO}_4$	50	76.4	23.6
R013	SZD20	$\text{Ni}/\text{ZrO}_2/\text{SO}_4$	0	0	0

Recently, Ebitani et al.⁽¹¹³⁾ investigated the state of platinum in the $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ catalyst by means of XPS technique. They found that platinum was essentially in an oxidized state, even after hydrogen reduction at 673 K for one hour. On the contrary, Sayari et al.⁽¹¹⁶⁾ found that it was in the metallic state (Pt^0) in $\text{Pt}/\text{ZrO}_2/\text{SO}_4$, as also revealed by XPS; however, it was in an oxidized form in a non-sulfated Pt/ZrO_2 catalyst. They further suggested that platinum in $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ was reduced to the metallic state by SO_2 generated from the decomposition of the sulfate group during calcination at high temperatures (873 K). In our opinion, the evidence provided by Sayari et al. appears to be more convincing. The effect of calcination observed in this study on the activity of the Pt doped ZrO_2/SO_4 catalysts can thus be explained: platinum was

reduced to its metallic state after calcination regardless of the nature of starting platinum material used for impregnation. The low conversion of n-C16 using the mechanically mixed $\text{PtO}_2 + \text{ZrO}_2/\text{SO}_4$ catalyst without calcination may be due to the fact that the hydrogenation ability of PtO_2 is poorer than that of platinum in the metallic state.

The activities of the ZrO_2/SO_4 doped, respectively, with Pt, Pd and Ni which are in the same group in the periodic table, were investigated for the hydrocracking and hydroisomerization of n-hexadecane (see Table 12). The conversion of n-hexadecane using the ZrO_2/SO_4 catalyst doped with Pt (SZD1) was higher than that doped with Pd (SZD19); the ZrO_2/SO_4 catalyst doped with Ni (SZD20) had virtually no activity. The striking difference in activity between the Pt and Ni doped ZrO_2/SO_4 catalysts can be explained by the fact that protonic acid sites were generated on the former catalyst, but not on the latter one, as supported by the IR spectra of the pyridine adsorbed on these two catalysts in the presence of hydrogen. The generation of the active protonic acid sites was thought to be via dissociative adsorption of hydrogen molecules on Pt, followed by spillover of hydrogen atoms onto the ZrO_2/SO_4 and electron transfer from hydrogen atoms to give protonic acid sites.^(111,112) Electrons released from the hydrogen atoms to Lewis acid sites reduced their acid strength. As a result, such weakened Lewis acid sites generated less coke, increasing the lifetime of the catalyst. We may conclude that the high catalytic activity of the ZrO_2/SO_4 catalyst doped with Pt or Pd compared to that doped with Ni was due to generation of highly active protonic acid sites and reduced coke formation. Nickel may not be reduced to its metallic state after calcination, and it could not play the same role as Pt in generation of highly protonic acid sites on Ni/ ZrO_2/SO_4 under given reaction conditions.

The Pt and Pd doped ZrO_2/SO_4 catalysts gave similar selectivities to cracked products (C5-C13) and isomerized hexadecanes (i-C16). The carbon number distributions of the products with these two catalysts are shown in Figure 6. Methane (C1), ethane (C2), tetradecane (C14), pentadecane (C15) or compounds greater than C16 were not detected in the cracked products using either of these two catalysts. The carbon number distributions obtained were asymmetrical. Similar experimental findings have been reported by others.^(9,128) The conversion of n-C16 as a

function of reaction time using the Pt and Pd doped ZrO_2/SO_4 catalysts is shown in Figure 7. The conversion of n-C16 by Pt/ ZrO_2/SO_4 (SZD1) was higher than that by Pd/ ZrO_2/SO_4 (SZD19), probably due to the higher hydrogenation capability of Pt.

Figure 6. Comparison of Product Distributions Obtained Using Pd and Pt Dopants on the Reaction of n-C16 and H_2 .

6.4.2.2 Platinum Loading.

The effect of Pt loading on catalytic activity was studied by varying the weight percent of Pt (0.2 - 5.0 wt. %) on the catalyst. The conversion of n-hexadecane as a function of reaction time using different amounts of Pt loaded on the ZrO_2/SO_4 catalyst is shown in Figure 8. The conversion was 74.4 wt. % in the case of the 5.0 wt. % Pt doped catalyst (SZD16) after 10 minutes of reaction, much higher than that for the 0.5 wt. % Pt doped catalyst (SZD1) with a conversion

Figure 7. Comparison of Conversion of n-C16 Using Pd and Pt Dopants on ZrO_2/SO_4 Catalyst at 433K and 360 psig H_2 cold.

of 36.5 wt.% after 20 minutes of reaction. It can be concluded that the catalytic activity of Pt/ZrO₂/SO₄ increases with increasing Pt loading.

Our results have shown that addition of platinum to the ZrO₂/SO₄ not only prolongs catalyst life by preventing coke formation, but also modifies its acidic properties. The role of Pt in an acid catalyzed reaction was investigated by examining the IR spectrum of pyridine adsorbed on the Pt/ZrO₂/SO₄ catalyst in the presence of hydrogen. The amount of the pyridine adsorbed on the Lewis acid sites (L-Py) decreased upon introduction of hydrogen with a concomitant

Figure 8. Effect of Pt loading on the Conversion of n-C16 Using a Pt/ZrO₂/SO₄ Catalyst at 433K and 360 psig cold.

increase in that of the pyridine adsorbed on the Brønsted acid sites (B-Py). Similar findings have been reported by others^(111,112). Ebitani et al.⁽¹¹²⁾ proposed a mechanism for the generation of the protonic acid sites which involved: (a) dissociation of hydrogen molecules on Pt into hydrogen atoms; (b) spillover of hydrogen atoms onto the ZrO_2/SO_4 surface; and (c) electron transfer from hydrogen atoms to the Lewis acid sites forming protonic acid sites. According to this mechanism, the role played by a Pt doped ZrO_2/SO_4 catalyst in a hydrocracking and hydroisomerization reaction differs from that of a hydrogenation metal in the conventional bifunctional mechanism. In the latter, the proposed role of the metal in a bifunctional catalyst system was to dehydrogenate

Figure 9. Conversion of n-C16 as a Function of Platinum Loading over a $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ Catalyst at 433K, 360 psig H_2 cold and 60 min.

hydrocarbons to the corresponding olefins and to hydrogenate cracked olefins.^(30,120) It was reported⁽¹¹²⁾ that a Pt/ZrO₂/SO₄ catalyst with a higher platinum loading accelerated hydrogen spillover, which favored generation of more active protonic acid sites. This agrees with our experimental finding that an increase in Pt loading on the Pt/ZrO₂/SO₄ catalyst enhanced its catalytic activity for conversion of n-C16 significantly. The conversion of n-hexadecane (after 60 minutes of reaction) as a function of Pt loading is shown in Figure 9. The conversion increased significantly with increasing amount of Pt in the Pt/ZrO₂/SO₄ catalyst when Pt loading

Figure 10. Effect of Pt Loading on the Product Distribution from Hydrocracking of nC-16 over a Pt/ZrO₂/SO₄ catalyst at 433K and 360 psig H₂ cold.

was between 0 and 0.5 wt.%. It then leveled off when Pt loading exceeded 0.5 wt.%. The product distributions at similar conversion levels of n-hexadecane, obtained from three different Pt loadings, 0.5 wt.%, 1.0 wt.%, and 5.0 wt.%, on ZrO_2/SO_4 catalysts (SZD1, SZD14 and SZD16), are shown in Figure 10. All of the carbon number distributions appeared to be asymmetric. No C1, C2, C14, C15 and products higher than C16 were detected. A high Pt loading favored cracking activity, shifting products to shorter chain compounds.

6.4.3 Catalytic Activity of Sulfate-Promoted Bimetallic Oxides ($\text{Pt}/\text{ZrO}_2\text{-HfO}_2/\text{SO}_4$)

Sulfate promoted-bimetallic oxides, $\text{Pt}/\text{ZrO}_2\text{-HfO}_2/\text{SO}_4$, with various molar ratios of Zr to Hf were prepared and their activities tested for hydrocracking and hydroisomerization of n-hexadecane. The amount of reacted n-hexadecane per millimole of acid sites of the catalyst versus molar fraction of ZrO_2 in the bimetallic oxides is shown in Figure 11, and it increased significantly with an increase in molar fraction of ZrO_2 , reaching a maximum when the mole fraction of ZrO_2 equaled 0.5 and then decreased slightly when the molar fraction of ZrO_2 exceeded 0.5.

The results can be explained as follows: catalyst activity is dictated by acidic properties, i.e., acidity and acid strength. A decrease in the number of acid sites results in a decrease in catalytic activity. On the other hand, a decrease in the acid strength reduces coke formation and favors product desorption. As both the total number of acid sites and the acid strength of these bimetallic oxides decreased with a decrease in the mole fraction of ZrO_2 (see Table 9 of Section 5.4.3), it is thought that the high activity of $\text{Pt}/\text{ZrO}_2\text{-HfO}_2/\text{SO}_4$ with a molar ratio of $\text{ZrO}_2/\text{HfO}_2$

Figure 11. Effect of Molar Fraction of ZrO_2 in a Mixture of ZrO_2 and HfO_2 on the Conversion of n-C16 Using a $\text{Pt}/\text{ZrO}_2\text{-HfO}_2/\text{SO}_4$ at 433K and 360 psig H_2 cold.

being 1:1 (SZHD2), was due to a good balance between the number of acid sites and acid strength. The XRD profiles of these bimetallic oxides showed that the crystalline phase of the sulfate promoted mixtures of zirconium and hafnium oxides consisted of a mixture of tetragonal and monoclinic forms, while the $\text{Pt}/\text{HfO}_2/\text{SO}_4$ alone (SHD) had a mixture of monoclinic form and amorphous, which was reported to be less superacidic.⁽⁶⁶⁾ This may explain the low catalytic activity and poor acidic properties of the $\text{Pt}/\text{HfO}_2/\text{SO}_4$ compared with those of the $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ (SZD3).

Figure 12. Effect of the Molar Fraction of ZrO_2 on the Product Selectivity on Hydrocracking of n-C16 Using $\text{Pt}/\text{ZrO}_2\cdot\text{HfO}_2/\text{SO}_4$.

In terms of product selectivity as a function of the molar fraction of ZrO_2 in these bimetallic oxides, (Figure 12), selectivity to cracked products increased while that to isomerized hexadecanes decreased when the molar fraction of ZrO_2 increased. An increase in the acid strength with increasing molar fraction of ZrO_2 was responsible for the increased cracking activity. The product distributions obtained using the $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ (SZD3) and the $\text{Pt}/\text{ZrO}_2\cdot\text{HfO}_2/\text{SO}_4$ ($\text{ZrO}_2/\text{HfO}_2 = 1/1$) catalysts are shown in Figure 13. No methane or ethane was found in the cracked products using either of these two catalysts. The $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ catalyst had a higher selectivity to shorter chain products (C5-C9), but a lower selectivity to isohexadecanes.

Incorporation of HfO_2 resulted in a wider product distribution spectrum and a higher selectivity to isohexadecanes.

6.5 Summary

We have found that the catalytic activity of an anion-modified metal oxide was determined by its number of acid sites as well as its acid strength, both of which depended on catalyst preparation conditions, the nature of the anion and sulfuric acid concentrations, and calcination temperatures. A $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ sample prepared by heterogeneous precipitation with addition of 1N of sulfuric acid for sulfation and calcination of three hours at 873 K gave the highest number of acid sites and conversion of n-hexadecane. Incorporation of hydrogenation metals such as Pt and Pd on ZrO_2/SO_4 greatly improved its catalytic activity in the presence of hydrogen due

Figure 13. A Comparison of the Product Distribution from the Reaction of n-C16 and H_2 Using the $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ and $\text{Pt}/\text{ZrO}_2\cdot\text{HfO}_2/\text{SO}_4$ ($\text{Zr}/\text{Hf} = 1$) Catalysts

to prevention of coke formation as well as modification of its surface acidic properties. We have found that the nature and amount of a particular hydrogenation metal doped on ZrO_2/SO_4 also strongly affected its catalytic activity and product selectivity. Among Pt, Pd and Ni, Pt doped ZrO_2/SO_4 gave the highest conversion of n-hexadecane. The activity of $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ for conversion of n-hexadecane increased greatly with increase in Pt loading. The sulfated promoted bimetallic oxides ($\text{Pt}/\text{ZrO}_2\cdot\text{HfO}_2/\text{SO}_4$) with a molar ratio of $\text{ZrO}_2/\text{HfO}_2$ of one exhibited higher catalytic activity and selectivity to isohexadecanes than those of the platinum doped and sulfate-promoted zirconium oxide.

7.0 EFFECT OF REACTION CONDITIONS ON CATALYTIC ACTIVITY IN HYDROCRACKING AND HYDROISOMERIZATION OF ALKANES

7.1 Objectives

The main objective of this study was to evaluate the catalytic activity of a particular Pt/ZrO₂/SO₄ catalyst (SZD1) for isomerization and hydrocracking of n-hexadecane and FT waxes under various reactions conditions. Emphasis was placed on the effects of operating parameters such as reaction temperature, time, operating hydrogen pressure, and the effect of addition of a hydride transfer agent or olefins on the catalytic activity and product selectivity of SZD1.

7.2 Background

Pt/ZrO₂/SO₄ is an active catalyst for the isomerization of n-butane and n-pentane^(75,106,107) and for the hydrocracking and hydroisomerization of long chain hydrocarbons.^(9,128) We have seen earlier that the catalytic activity and product selectivity of this catalyst were strongly affected by the preparation conditions as well as by its composition. In order to better understand the mechanism of the hydrocracking and hydroisomerization of long chain hydrocarbons, the effects of operating parameters, such as reaction temperature, time, operating hydrogen pressure as well as addition of a hydride transfer agents or olefins, on the catalytic activity and product distribution were investigated. The long-term performance of the Pt/ZrO₂/SO₄ catalyst towards the hydrocracking and hydroisomerization of n-hexadecane was carried out in a continuous fixed-bed reactor constructed by Dr. Jianli Hu in our laboratory.

7.3 Experimental

The chemicals used in this study were purchased from the Aldrich Chemical company except for the FT waxes which were provided by Sasol (Table 13). They were used as received.

All hydrocracking and hydroisomerization reactions of long chain hydrocarbons were performed in a horizontal shaken tube-microreactor (45cm³) described earlier. Hydrogen pressure

in the reactor was varied between 300 and 1600 psig (cold) and reaction temperature between 433 and 453 K. Reactions were carried out at lengths from 10 to 60 minutes.

Table 13 Chemicals Used in This Study

	Chemical	Formula	Purity (%)
Hydrocarbons	n-heptane, n-C7	$\text{CH}_3(\text{CH}_2)_5\text{CH}_3$	99
	n-hexadecane (n-C16)	$\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$	99
	n-dotriacontane (n-C32)	$\text{CH}_3(\text{CH}_2)_{30}\text{CH}_3$	97
	FT waxes	C58 - C64	unknown
Hydride transfer agents	methylcyclopentane (MCP)	$\text{CH}_3(\text{C}_5\text{H}_9)$	98
	adamantane	$\text{C}_{10}\text{H}_{16}$	99+
Olefins	1-heptene	$\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{CH}_3$	97
	5-decene	$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_3\text{CH}_3$	99+
	1-hexadecene	$\text{CH}_2=\text{CH}(\text{CH}_2)_{13}\text{CH}_3$	92

The hydrocracking and hydroisomerization of n-hexadecane was also carried out in a fixed-bed continuous reactor for 96 hours. The reaction temperature was measured with a thermocouple which was placed in the catalyst bed. Before reaction, the Pt/ZrO₂/SO₄ catalyst was pressed into pellets in a hydraulic press at about 20,000 psig. The pellets were crushed and then screened to obtain catalyst beads of 20-30 mesh. They were then loaded to the reactor preheated at 383 K. The catalyst was preheated in a 723 K furnace under a continuous air flow for one hour and a half, and then cooled down to room temperature. The reactor was purged with hydrogen (99.99%) for five minutes, then pressurized to 360 psig. The hydrogen flow rate was controlled by a mass flow controller to obtain a suitable molar ratio of reactant feed to hydrogen. The flow rate of n-hexadecane was controlled by an instrument mini pump (flow rate range: 39 - 390 cm³

per hour; maximum pressure: 5000 psig). After desired flow rates of hydrogen and n-hexadecane were reached, the reactor was heated by the furnace up to the reaction temperature. The system reached a steady state in about 40 minutes with 60 ml per minute of hydrogen and 100 cm³ per hour of n-hexadecane. The liquid products were taken from the product receiver and then analyzed using an HP-5890 II GC.

7.4 Results and Discussion

7.4.1 Catalytic Activity of Pt/ZrO₂/SO₄ Toward Different Long Chain Hydrocarbons

Three long chain hydrocarbons, n-hexadecane, n-dotriacontane and Sasol wax (C58-C64) were chosen for testing the catalytic activity of the Pt/ZrO₂/SO₄ catalyst (SZD1). Under relatively mild reaction conditions (433 - 443 K and 360 psig), this catalyst exhibited a high catalytic activity for long chain hydrocarbons such as n-C16 and n-C32) Sasol wax (Figure 13). After 60 minutes, about 90 wt.% of these paraffins had reacted. Selectivities to cracked products were high, but those to isomerized products (i-C16, i-C32 and isomerized C58-C64) were low (about 10 wt.%). The cracked product distributions of these three feeds are shown in Figure 14. Methane and ethane were not found in the cracked products from these three feeds. In the case of the Sasol wax, the cracked products consisted mainly of C5-C22, encompassing the range of gasoline, diesel and jet fuel; cracked products higher than C22 were not found. It appears that the Pt/ZrO₂/SO₄ catalyst is promising for upgrading FT waxes into valuable liquid fuels.

7.4.2 Effect of Reaction Conditions

The effects of temperature, time and reactant loading on the hydrocracking and hydroisomerization of waxes were investigated. n-Dotriacontane (n-C32) was chosen as a model compound of waxes. Methylcyclopentane (MCP) was chosen as a solvent. In the presence of MCP, the conversion as well as cracked products (C5-C9 and C10-C13), increased with increasing temperature or reaction time. For n-C32, a higher temperature or a longer reaction time favored the production of cracked products rather than i-C32.

Figure 14. Conversion and Product Selectivity from the Hydrocracking and Hydroisomerization of n-C16, n-C32 and Sasol Wax over the Pt/ZrO₂/SO₄ Catalyst (cat./n-C16 = 1/6, cat./n-C32 = 1/3, cat./Sasol wax = 1/3, 433K for n-C16, 443 K for n-C32, 360 psig H₂ (cold) and 60 min)(m: the highest carbon number of cracked products from the reaction of alkanes).

7.4.2.1 Reaction of n-Dotriacontane.

The effect of reactant loading on catalytic activity of Pt/ZrO₂/SO₄ for the hydrocracking and hydroisomerization of n-C32 was studied in the absence of MCP. The conversion of n-C32 decreased dramatically with an increase in the n-C32 to catalyst ratio. It appears that, at high n-C32 loadings (n-C32/cat. ratios greater than 4), the Pt/ZrO₂/SO₄ catalyst was essentially

deactivated during reaction as observed by its color change from grey before reaction to yellow after reaction. The color of this catalyst did not change after the reaction of n-C16 when the ratio of n-C16 / catalyst was 6/1, suggesting that it was not deactivated. It appears that the higher viscosity of n-C32 compared to that of n-C16 was responsible for the catalyst deactivation; a high viscosity reacting medium likely hinders hydrogen transfer from the reactant bulk to the catalyst surface and subsequent hydrogenation of carbocation and possibly olefinic intermediates. These intermediates cannot desorb quickly and so block the active catalytic sites.

Figure 15. Cracked Product Distribution from the Reaction of n-C16, n-C32 and Sasol Wax in the Presence of H_2 Using a $Pt/ZrO_2/SO_4$ Catalyst (same reaction conditions as in Figure 13)

7.4.2.2 Effect of Initial Hydrogen Pressure.

Hydrogen pressure is an important operating parameter, which strongly affects catalytic activity and product selectivity in hydrocracking and hydroisomerization of n-hexadecane catalyzed by Pt/ZrO₂/SO₄. The conversion of n-hexadecane as a function of reaction time at various initial H₂ pressures (cold) at 433 K is shown in Figure 16. The initial reaction rate increased with an increase in the initial hydrogen pressure. For example, the conversions obtained at 460 psig and 700 psig H₂ were 78.0% and 94.3%, respectively, after 40 minutes of reaction; it was reduced to 62% under 360 psig H₂ for the same

Figure 16. Effect of the Initial Hydrogen Pressure (cold) on the Conversion of n-C16 Using the Pt/ZrO₂/SO₄ (0.5 wt. % of Pt) Catalyst at 433 K.

reaction time. A similar experimental finding was also reported when the reactions of n-C16 were carried out in a continuous trickle bed reactor⁽¹²⁸⁾. The significant increase in the catalytic activity of the Pt/ZrO₂/SO₄ catalyst with increasing hydrogen pressure was due to the fact that a high hydrogen pressure favored formation of highly active protonic acid sites^(111,113). The product distributions at similar conversion levels obtained at different initial hydrogen pressures (cold) are depicted in Figure 17. Unlike the effect of the initial hydrogen pressure on the reaction rate, the initial hydrogen pressure did not greatly affected the product distribution.

7.4.2.3 Long-Term Performance of Pt/ZrO₂/SO₄. The long-term performance of the Pt/ZrO₂/SO₄ catalyst was evaluated using the hydrocracking and hydroisomerization of n-hexadecane in a continuous fixed-bed reactor. Hosoi et al.⁽¹⁰⁶⁾ reported that the Pt/ZrO₂/SO₄ catalyst was not deactivated in hydroisomerization of n-butane for as long as 1000 hours at 473 K and 150 psig. However, its catalytic behavior with long chain hydrocarbon reactions has not been studied in a similar manner.

The long-term catalytic performance of Pt/ZrO₂/SO₄ (0.5 wt% of Pt) for the reaction using n-hexadecane as a feedstock was evaluated. After 96 hours on-stream, the activity of the Pt/ZrO₂/SO₄ catalyst remained as high as its initial activity without deactivation. The product distribution obtained from the continuous fixed-bed reactor was similar to that obtained with the batch reactor. A similar finding was also reported in the literature⁽¹²⁸⁾.

It was reported that the catalytic performance of ZrO₂/SO₄ without hydrogenation metal deteriorated as a result of reduction of the sulfate group in a hydrogen environment⁽¹⁰⁸⁾. A hydrocracking and hydroisomerization reaction of n-hexadecane in the presence of SZD1 was carried out in the tubing bomb microreactor at 1600 psig to determine the effect of high hydrogen pressure on its catalytic activity and product selectivity. At 433 K, the overall conversion reached 99.6 wt.% in 30 minutes; the selectivity to cracked products reached 99.9 % with 99.0 % of the cracked products being in the gasoline range (C5-C9). This confirms our earlier experimental finding that cracking activity increased significantly by increasing hydrogen pressure. The sulfur contents of the Pt/ZrO₂/SO₂ catalyst before and after reaction were 1.58 and 1.55 wt.%,

Figure 17. Effect of the Initial Hydrogen Pressure (cold) on the Product Distribution from the Reaction of n-C16 and H₂ Using the Pt/ZrO₂/SO₄ (0.5 wt. % of Pt) Catalyst at 433 K.

respectively, showing that the surface sulfur complex responsible for the generation of highly acidic sites was not reduced under high hydrogen pressures.

7.4.2.4 Effect of Reaction Temperature.

This was examined by carrying out the hydrocracking and hydroisomerization of n-hexadecane in the tubing bomb microreactor at two different temperatures (393 and 433 K) under 1600 psig hydrogen pressure. After 30 minutes of reaction, the conversion of n-hexadecane reached 99.6 wt. % at 433 K, but only 33.4 wt. % at 393 K.

7.4.2.5 Effect of Addition of Hydride Transfer Agents (Methylcyclopentane and Adamantane).

A hydride transfer agent, adamantane or methylcyclopentane (MCP), was added to the hydrocracking and hydroisomerization of n-C16 and n-C32 systems in order to study their influence on the catalytic activity and product selectivity of the Pt/ZrO₂/SO₄. The experimental results are summarized in Table 14.

The conversion and selectivity to i-C16 or i-C32 was increased upon addition of a hydride transfer agent (adamantane or MCP), and the selectivity to cracked products was decreased. Similar experimental findings were also reported when adamantane was added to n-heptane and n-octane feeds^(130,131). The added adamantane was recovered quantitatively, but about 5% of the MCP was lost under the above reaction conditions. The results show that adamantane or MCP is a good hydride transfer agent.

MCP not only played the role of a hydride transfer agent, as did adamantane, but it also served as a solvent to decrease the viscosity of the n-C32 reacting system. The beneficial effect of adding a hydride transfer agent lies in that it acts as a co-catalyst, enhancing the catalytic activity and modifying product selectivities.

A mechanism of hydride transfer of adamantane in the hydrocracking and hydroisomerization of n-hexadecane is proposed and shown in Figure 18.

Adamantane (structure I) possesses a very reactive tertiary hydrogen atom with a low binding energy attached to a tertiary carbon. In the presence of a strong acid catalyst, the more stable bridgehead 1-adamantyl cation (structure II) is readily formed by release of a hydride⁽¹³²⁾.

This hydride transfer leads to rapid termination of the surface carbocation intermediates of isomerized products from hexadecane, decreasing therefore their average surface lifetime. As a result, it suppresses cracking reaction and favors formation of isomerized hexadecanes.

7.4.2.6 Effect of Addition of Olefins.

Commercial raw waxes without being hydrogenated may contain small amounts of olefins⁽¹³³⁾. In this work, the effect of the presence of olefins on the catalytic activity of the

Pt/ZrO₂/SO₄ catalyst for hydrocracking and hydroisomerization of n-heptane and n-hexadecane was studied using three different olefins (1-heptene, 1-hexadecene and 5-decene). The experimental results are given in Table 15.

Table 14. Effect of Addition of a Hydride Transfer Agent on the Catalytic Activity and Product Selectivity of the Pt/ZrO₂/SO₄ Catalyst

Run No.	Feed	Hydride transfer agent	Conversion (wt. %)	Selectivity (wt. %)		
				C5-C9	C10-Cm ^a	i-C16 or i-C32
R014	n-C16	none	70.5	54.5	22.3	23.2
R015	n-C16	adamantane (0.5 wt. %)	70.8	61.8	18.0	20.2
R016	n-C16	adamantane (7.7 wt. %)	83.6	42.2	19.7	38.1
R017	n-C32	none	80.5	67.0	30.0	2.3
R018	n-C32	MCP (50 wt. %)	86.7	37.7	57.7	3.9

a: m = 13 in the case of n-C16 and 15 in the case of n-C32

Reaction conditions: (i) n-C16: cat./feed: 1/6, 433 K, 360 psig H₂ (cold) and 60 min;
(ii) n-C32: cat./feed: 1/3, 443 K, 460 psig H₂ (cold) and 60 min.

The conversions of n-heptane and n-hexadecane decreased when an olefin was added. The decrease was much more significant in the case of n-heptane in the presence of 1-heptene: addition of 0.6 wt. % of 1-heptene reduced the conversion of n-heptane from 75.0 to 3.0 wt. %; when 50.0 wt. % of 1-heptene was added, the conversion was undetectable. Also, when an olefin was present

Figure 18. Hydride Transfer Mechanism of Adamantane in the Acid-Catalyzed Hydrocracking of n-Hexadecane

in n-hexadecane, the selectivity to C5-C9 decreased with a concomitant increase in selectivity to C10-C13 and i-C16. In all cases, olefins were hydrogenated rapidly and completely to their corresponding paraffins. In the case of n-heptane with added 1-heptene, the catalyst appeared to be deactivated after reaction (its color was changed from grey to yellow). The presence of an olefin reduces the catalytic activity of the Pt/ZrO₂/SO₄ catalyst.

The negative effect of the presence of olefins can be understood as follows: olefins are comparatively rich in electrons so that they compete with n-alkanes for active acid sites, adsorbing strongly on the sites of high acid strength, slowing down the reaction rate. In the hydrocracking and hydroisomerization of n-hexadecane, the negative effect of 1-hexadecene on the activity of the Pt/ZrO₂/SO₄ catalyst was greater than that of 5-decene, indicating that the location of the double bond in an olefin affects its interaction with the acid sites on the catalyst surface. Olefins with a terminal double bond are more reactive towards acid sites than those with an internal

double bond mainly because the former have a higher electron density and lower steric hindrance

Table 15 Effect of Addition of Olefins on the Hydrocracking and Hydroisomerization of n-Heptane and n-Hexadecane Catalyzed by Pt/ZrO₂/SO₄

Run No.	Feed	Olefin	Conversion (wt. %)	Selectivity (wt. %)		
				C5 -C9	C10 - C13	i-C16
R019	n-C7	none	75	NA		
R020	n-C7	1-heptene (0.6 wt. %)	3.0			
R021	n-C7	1-heptene (50.0 wt. %)	0.0			
R022	n-C16	none	69	58.2	19.2	22.6
R023	n-C16	1-hexadecene (1.5 wt. %)	59.9	52.3	21.4	26.3
R024	n-C16	5-decene (1.5 wt. %)	52.7	53.9	22.4	23.7
R025	n-C16	5-decene (10.0 wt. %)	43.0	43.2	26.7	30.1

Reaction conditions: i) n-heptane: cat./feed: 1/10, 423 K, 350 psig H₂ (cold) and 60 min
 ii) n-hexadecane: cat./feed: 1/6, 433 K, 360 psig H₂ (cold) and 60min

7.4.3 Further Comments on the Mechanism of Hydrocracking and Hydroisomerization

The mechanism of hydrocracking and hydroisomerization of n-alkanes catalyzed by a bifunctional catalyst remains controversial. According to the classic bifunctional mechanism proposed by Coonradt and Garwood,⁽³⁰⁾ the initial carbocation intermediates are generated from direct protonation of olefins, which result from the dehydrogenation of their corresponding paraffins on metal sites. It was then expected that a minor amount of olefins, introduced as

impurities or formed in-situ by cracking or dehydrogenation of paraffins, could act as initiators to form carbocation intermediates. Hydrogen pressure was perhaps expected to have an inhibitive effect on reaction rate because it was unfavorable for formation of olefins in the dehydrogenation step. However, our experimental findings showed that addition of olefins (on the order of several percent) had a strong inhibitive effect on the acid-catalyzed reactions of n-alkanes, and that an increase in hydrogen pressure significantly enhanced the catalytic activity of the Pt/ZrO₂/SO₄ in the hydrocracking and hydroisomerization of n-alkanes. It implies that dehydrogenation of paraffins might not occur in our reacting systems and the Pt/ZrO₄/SO₄ catalyst in the hydrocracking and hydroisomerization of n-alkanes did not act as conventional bifunctional catalysts. Carbocation intermediates, however, could be generated in the following ways: hydride abstraction by Lewis sites, carbon-hydrogen bond attack by the protons of Brønsted acid sites, and/or intermolecular hydride transfer.

7.5 Summary

It has been found in this work that the Pt/ZrO₂/SO₄ catalyst is active for the conversion of heavy waxes to liquid fuels by hydrocracking and hydroisomerization under relatively mild reaction conditions. Reaction conditions such as hydrogen pressure, reaction temperature and catalyst loading have strong effects on catalytic activity and product selectivity. With increasing hydrogen pressure, the conversion of n-hexadecane increases greatly. We have demonstrated that the Pt/ZrO₂/SO₄ catalyst is also active at 1600 psig of hydrogen pressure without deactivation. The long-term performance of the Pt/ZrO₂/SO₄ catalyst evidently showed that the activity of this catalyst did not change after 96 hours of reaction. Addition of a hydride transfer agent such as adamantane or methylcyclopentane enhances the catalytic activity for conversion of alkanes and increases the selectivity to long chain products. The activity of the Pt/ZrO₂/SO₄ catalyst for conversion of n-hexadecane and n-heptane was reduced greatly upon addition of olefins due to their ability to compete with paraffins for active acid sites.

8.0 KINETIC MODELING OF HYDROCRACKING AND HYDROISOMERIZATION OF n-HEXADECANE

8.1 Objectives

(1) To develop a simplified reaction network using lumped components for describing hydrocracking and hydroisomerization of n-hexadecane as a function of reaction time in a batch reactor.

(2) To estimate the model parameters and predict the effect of Pt loading as well as hydrogen pressure on the yield of product fractions with respect to reaction time.

8.2 Background

Hydrocracking and hydroisomerization of paraffins catalyzed by bifunctional catalysts have been widely used in the petroleum refining industry. Kinetic modeling of this process has been undertaken to investigate the reaction mechanism and predict product distributions. Froment et al.⁽¹³⁴⁾ developed a kinetic model for describing hydrocracking and hydroisomerization of n-decane and n-dodecane over zeolite catalysts in a continuously stirred reactor (CSTR). The products were lumped into monobranched and multibranched isomers of the initial reactants, and cracked products. They found that models incorporating physical adsorption of the initial reactants and their isomers in the zeolite pores could adequately fit the experimental data. The same reaction network and lumping structure used for n-decane and n-dodecane were also found to be applicable to n-octane.⁽¹³⁵⁾ However, in the case of a low boiling point hydrocarbon such as n-octane, besides considering physical adsorption of the initial reactants and their isomers, adsorption of cracked products must be taken into account. Kennedy et al.⁽¹³⁶⁾ developed a kinetic model to describe the hydroisomerization of n-heptane over Pt/zeolite catalyst. This model was used to reveal the effect of the balance between acid and metal activities on product selectivities. The kinetic models mentioned above were based on the classic bifunctional reaction mechanism proposed by Weisz and Coonradt⁽³⁰⁾, in which the first step involves dehydrogenation of

n-alkanes to form olefins. This model is inconsistent with our experimental findings for the hydrocracking and hydroisomerization of n-hexadecane over the Pt/ZrO₂/SO₄ catalyst as described in the preceding chapters. The initial attempt in the kinetic modeling of the hydrocracking and hydroisomerization of n-hexadecane catalyzed by Pt/ZrO₂/SO₄ was to propose a simplified reaction network with regard to lumped components (n-C16, i-C16 and cracked products). A kinetic model based on this reaction network was developed and then used for predicting the overall conversion of n-hexadecane and selectivity of isohexadecanes and cracked products.

8.3 Experimental

In order to validate the kinetic model, reactions of n-hexadecane were carried out in the tubing bomb microreactor shown in **Figure 2** following the procedure described in **Section 6.3.1**. For all reactions, six grams of n-hexadecane and one gram of Pt/ZrO₂/SO₄ catalyst (**SZD1**) were charged to the reactor. A summary of these reactions is given in **Table 16**.

8.4 Results and Discussion

8.4.1 Kinetic Model

Conversion of a normal hydrocarbon into isomerized and cracked products by hydrocracking and hydroisomerization in the presence of Pt/ZrO₂/SO₄ involves both series and parallel reaction pathways. In the case of n-hexadecane, the reaction network is simplified as shown in **Figure 19**.

This reaction network involves the following experimental facts or assumptions:

- (1) The lumped liquid products obtained from the hydrocracking and hydroisomerization are unreacted hexadecane, isohexadecanes and cracking products (C5-C13). The gas products lighter than C4 are not considered. Typically, the gas products were less than 2 wt%, mainly in C4. This observation was also confirmed by others^(9,128)
- (2) All reactions are irreversible and pseudo-first order.
- (3) Secondary cracking is considered unimportant to simplify the kinetic model.

(4) The ideal gas law can be used. The gas phase was about 99% H_2 , and the compressibility factor (Z) of hydrogen is about 1.02 under our reaction conditions (440 psig and 433K).⁽¹³⁷⁾

Table 16 Reaction Conditions and Product Yields for the Kinetic Modeling Studies (n-C16: 0.0256 mole; Catalyst: Pt/ZrO₂/SO₄; Temperature: 433 K)

Run No.	Pt loading (wt. %)	Pressure (psig)	Time (min)	Product yield (mole)		
				n-C16	i-C16	C5-C13
R029	0.5	360	20	0.0169	0.0031	0.0130
R030	0.5	360	40	0.0101	0.0041	0.0258
R031	0.5	360	60	0.0075	0.0034	0.0331
R042	0.5	460	20	0.0110	0.0300	0.0258
R043	0.5	460	40	0.0058	0.0037	0.0320
R044	0.5	460	60	0.0040	0.0027	0.0395
R045	0.5	700	20	0.0095	0.0047	0.0254
R046	0.5	700	30	0.0045	0.0028	0.0455
R047	0.5	700	40	0.0015	0.0012	0.0543
R036	1.0	360	30	0.0079	0.0044	0.0288
R037	1.0	360	60	0.0057	0.0043	0.0320
R038	2.0	360	10	0.0134	0.0041	0.0187
R039	2.0	360	20	0.0059	0.0030	0.0389

(5) The apparent rate constants (k_1 , k_2 and k_3) depend only on reaction temperature, and not on hydrogen pressure and Pt loading.

(6) Hydrogen pressure and Pt loading affect the rate of cracking, but not the rate of isomerization because isomerization does not consume hydrogen and Pt plays a role to saturate

Figure 19. Simplified Reaction Network Used for Hydrocracking and Isomerization of n-Hexadecane.

cracked products by hydrogenation. Preliminary analysis of the data indicated that the power for hydrogen pressure was not significantly different from 1.0 but that the power for platinum loading was significantly different from one. Formation of two moles of cracked products consumes one mole of hydrogen.

(7) No thermal reactions occurred at these reaction conditions

Using the experimental facts or assumptions mentioned above, the molar changes in n-hexadecanes, isohexadecanes and cracked products can be written as:

$$\frac{dY_1}{w_{cat} dt} = -(k_1 + k_2 w_{Pt}^n P_{H_2}) Y_1 \quad (8-1)$$

$$\frac{dY_2}{w_{cat} dt} = k_1 Y_1 - k_3 w_{Pt}^n P_{H_2} Y_2 \quad (8-2)$$

$$\frac{dY_3}{w_{cat} dt} = 2(k_2 Y_1 + k_3 Y_2) w_{Pt}^n P_{H_2} \quad (8-3)$$

The initial conditions are:

for $t=0$: $Y_1=0.0256$, $Y_2 = Y_3 = 0.0$ where

Y_1 = unreacted n-C16	[mole]
Y_2 = i-C16	[mole]
Y_3 = cracked products, C5-C13	[mole]
k_1 = apparent rate constant for isomerization of n-C16	[(gcat·min) ⁻¹]
k_2 = apparent rate constant for hydrocracking of n-C16	[(gcat) ⁿ⁻¹ ·(gPt ⁿ ·atm·min) ⁻¹]
k_3 = apparent rate constant for hydrocracking of i-C16	[(gcat) ⁿ⁻¹ ·(gPt ⁿ ·atm·min) ⁻¹]
w_{cat} = amount of catalyst	[g]
w_{Pt} = weight percentage of Pt	[gPt/gcat]
n = reaction order with respect to Pt	
P_{H_2} = hydrogen pressure during reaction	[atm]

The hydrogen pressure during the batch runs was not constant, and it is given by:

$$P_{H_2} = P_0 - \frac{n'RT}{V} = P_0 - \frac{Y_3 RT}{2V}$$

where P_0 = initial hydrogen pressure	[atm]
T = reaction temperature	[K]
V = gas volume (39)	[cm ³]
n' = molar number of hydrogen consumed	[mole]

8.4.2 Kinetic Parameter Estimation

A total of 13 experimental runs were made at 433 K (Table 19). For each run, the amounts of unreacted n-hexadecanes, isohexadecanes and cracked products were determined. The kinetic parameters (k_1 , k_2 , k_3 and n) were obtained by minimizing the following objective function:

$$f = \sum_{i=1}^N [w_n(Y_{1,i} - \hat{Y}_{1,i})^2 + w_i(Y_{2,i} - \hat{Y}_{2,i})^2 + w_c(Y_{3,i} - \hat{Y}_{3,i})^2] \quad (8-5)$$

where: f = objective function,

w_n , w_i , w_c = weighting factors for n-C16, i-C16 and cracked products,

N = number of experiments,

$\hat{Y}_{1,i}$, $\hat{Y}_{2,i}$, $\hat{Y}_{3,i}$ = moles of unreacted n-C16, i-C16 and cracked products C5-C13 for run i given by the model, respectively.

$Y_{1,i}$, $Y_{2,i}$, $Y_{3,i}$ = moles of unreacted n-C16, i-C16 and cracked products C5-C13 measured experimentally for run i , respectively.

The w_n , w_i and w_c in equation 8-5 were set to unity for all three products because the accuracy of measurements for these three products were equal. For a given set of kinetic parameters, equations 8-1 through 8-3 can be used to predict the yield of cracked products and i-C16. The calculated and experimental data are then used to determine f . The desired set of parameters is that which gives the lowest value of f . This was done using a standard statistical routine: a derivative free nonlinear regression program AR from the BMDP library.⁽¹³⁸⁾

Equations 8-1 to 8-4 contain the four parameters which are to be determined, three rate constants and one reaction order with respect to Pt loading. The equations are nonlinear because of equation 8-4, and must be solved numerically. This can be done using an integration routine in AR. For each run, $\hat{Y}_{1,i}$, $\hat{Y}_{2,i}$, and $\hat{Y}_{3,i}$ were calculated using a set of assumed parameters and substituted into equation 8-5. The assumed parameters were then corrected in AR using a pseudo-Gauss-Newton iterative algorithm to reduce f . The minimum f obtained was 1.319897E-3. The corresponding kinetic parameters are given in Table 17 together with the standard deviations. The pseudo R^2 , a scale-free measure of approximately how much of the variation of the dependent variable is accounted for by the model was 0.87.

Four starting estimates of these four parameters were used. Since these parameters are highly correlated, the computed values were not identical, but a similar value of f was obtained for each initial set of estimates.

Table 17 Kinetic Parameters and Asymptotic Standard Deviations in the Kinetic Model

Parameter	Computed Value	Asymptotic standard deviation
k_1	0.022	0.017
k_2	0.044 (0.015) ^a	0.024
k_3	0.058 (0.020) ^a	0.0092
n	0.84	0.078

a: the data in the brackets are calculated values of $k_2 w_{pt}^{0.84} P_{H_2}$ and $k_3 w_{pt}^{0.84} P_{H_2}$ using initial value of P_{H_2} (30 atm at 433 K) and 0.5 wt. % of Pt loading.

The solution given above was selected because all calculated parameters had small estimated standard deviations. The apparent rate constant for isomerization of n-C16 (k_1) has different units than the apparent rate constant for hydrocracking of n-C16 (k_2) or i-C16 (k_3). In equations 8-1 and 8-2, k_2 or k_3 must be multiplied by Pt loading (w_{pt}^n) and hydrogen pressure (P_{H_2}) to be comparable to k_1 . Values are shown in Table 17 in brackets. The calculated value of $k_2 w_{pt}^{0.84} P_{H_2}$ was 68% of k_1 . This indicates that, under these conditions, isomerization of n-C16 does not necessarily precede hydrocracking; cracked products from n-C16 can be obtained by either isomerization of n-C16 to form i-C16 followed by hydrocracking or direct hydrocracking of n-C16. With increasing conversion of n-C16, P_{H_2} decreases with a concomitant decrease in $k_2 w_{pt}^{0.84} P_{H_2}$ and $k_3 w_{pt}^{0.84} P_{H_2}$. The rate of isomerization may further increase. The apparent rate constant for hydrocracking of isohexadecanes (k_3) was 33% greater than that for cracking of n-hexadecanes (k_2), in agreement with the experimental finding⁽¹³⁹⁾ that isoparaffins were more easily cracked than n-paraffins because they form stable tertiary carbonium ion intermediates more easily.

8.4.3 Application of the Kinetic Model

The kinetic model was used to predict the effects of hydrogen pressure and Pt loading on the reactivity and product selectivities in hydrocracking and hydroisomerization of n-hexadecane.

Using the four kinetic parameters obtained above in equations 8-1 to 8-4, the yields of unreacted n-C16 (Y_1), i-C16 (Y_2) and cracked products (Y_3) were calculated using the IVPAG program from the IMSL library⁽¹⁴⁰⁾ for solving a system of differential equations. The average relative error between experimental and calculated data points for four sets of hydrogen pressures (cold) and Pt loadings was about 25 %, which was acceptable considering the simplified reaction network employed. Nevertheless, at high conversions of n-hexadecane, the calculated cracked fractions are visibly lower than the experimental ones likely due to secondary cracking.

Using the kinetic model, the yields of cracked fractions and isohexadecanes with respect to reaction time can be calculated for different hydrogen pressures (cold) and Pt loadings. The yield of isohexadecanes increases with increasing reaction time at the initial stage of reaction. It reaches a maximum and then decreases with a further increase in time. The yield of cracked fractions increases with increasing reaction time. An increase in hydrogen pressure or Pt loading increases the yield of cracked products significantly, with however a concomitant decrease in the yield of isohexadecanes. These results indicate that product yields can be controlled by reaction variables such as reaction time, hydrogen pressure or the composition of Pt/ZrO₂/SO₄. Low hydrogen pressures, low Pt loadings or short reaction times favor the formation of isohexadecanes. Conversely, high hydrogen pressures, high Pt loadings or long reaction times are favorable for the formation of cracked products.

To check the predictability of the kinetic model, reactions were carried out under different conditions from those used for generating the kinetic parameters. The predicted and experimental yields are compared in Table 18. The results show that the model predicts the yield of cracked products better than that of isohexadecanes under all conditions. The yield of isomerized products should not be extrapolated using this model. The predicted yields at high Pt loading (5 wt. %, R040) or hydrogen pressure (300 psig, R041) were close to the experimental ones. However, at

low Pt loadings (0.2 wt. %, R035), the predicted yields of i-C16 and cracked C5-C13 were much higher than the experimental ones. The higher yields at low Pt loadings may be due to the fact that when Pt was low, olefinic products obtained from cracking could not be hydrogenated to a sufficient extent so that some of active sites might be blocked, decreasing catalytic activity. At high hydrogen pressures (1600 psig, R048), the predicted yield of cracked products C5-C13 was much lower than the experimental one, probably due to severe secondary cracking occurring at high conversions of n-C16. Based on these results, the kinetic model can be used to predict product fractions at intermediate conversion levels of n-C16 (<70 wt. %) if catalyst deactivation does not occur.

Table 18. Experimental Yields vs. Predicted Yields Using the Kinetic Model (n-C16: 0.0256 mole; Catalyst: Pt/ZrO₂/SO₄; Temperature: 433 K)

Run No.	Pt (wt. %)	Time (min)	P _{H₂} (psig)	n-C16		i-C16		C5 - C13	
				Expt.	Pred.	Expt.	Pred.	Expt.	Pred.
R035	0.2	60	360	0.015	0.0043	0.0037	0.011	0.015	0.022
R040	5.0	10	360	0.0069	0.0076	0.0042	0.0017	0.034	0.034
R041	0.5	50	300	0.0088	0.0045	0.0040	0.0083	0.030	0.027
R048	0.5	30	1600	0.00011	0.0012	0.00010	0.00079	0.065	0.049

The results show that the model predicts the yield of cracked products better than that of isohexadecanes under all conditions. The yield of isomerized products should not be extrapolated using this model. The predicted yields at high Pt loading (5 wt. %, R040) or hydrogen pressure (300 psig, R041) were close to the experimental ones. However, at low Pt loadings (0.2 wt. %, R035), the predicted yields of i-C16 and cracked C5-C13 were much higher than the experimental ones. The higher yields at low Pt loadings may be due to the fact that when Pt was low, olefinic products obtained from cracking could not be hydrogenated to a sufficient extent so that some of active sites might be blocked, decreasing catalytic activity. At high hydrogen pressures (1600 psig,

R048), the predicted yield of cracked products C5-C13 was much lower than the experimental one, probably due to severe secondary cracking occurring at high conversions of n-C16. Based on these results, the kinetic model can be used to predict product fractions at intermediate conversion levels of n-C16 (<70 wt. %) if catalyst deactivation does not occur.

8.5 Summary

A kinetic model for the hydrocracking and hydroisomerization of a long chain n-alkane (n-hexadecane) over Pt/ZrO₂/SO₄ based on a simplified reaction network was developed in this work to describe the amounts of lumped n-C16, i-C16 and cracked products as a function of reaction time. A derivative free nonlinear regression program, AR, from the BMDP library was successfully employed to optimize the nonlinear differential equations. The predicted product fractions obtained under various hydrogen pressures or platinum loadings agreed with the experimental data with an average relative error 25%. The model can be used to predict the effect of initial hydrogen pressure or platinum loading on the reactivity and product distributions for the hydrocracking and hydroisomerization of n-hexadecane. It should also provide quantitative guidance for control of product selectivities by varying reaction parameters.

9.0 CONCLUSIONS

The primary objective of this work was to explore the use of sulfated metal oxides in general, and zirconium oxide in particular, as a catalyst for the hydrocracking and hydroisomerization of long chain hydrocarbons including FT waxes. The main conclusions from this work are listed as follows:

(1) The $\text{Pt/ZrO}_2/\text{SO}_4$ exhibits a high activity for the hydrocracking and hydroisomerization of long chain paraffins (n-C16 and n-C32) as well for Sasol waxes under relatively mild reaction conditions ($< 453 \text{ K}$ and 360 psig hydrogen pressure) to yield liquid products. No methane, ethane or olefins are detected in the cracked products.

(2) Addition of a hydrogenation metal greatly modifies the catalytic activity and acid properties of sulfate promoted zirconium oxide. Three hydrogenation metals (platinum, palladium and nickel) were used. $\text{Pt/ZrO}_2/\text{SO}_4$ gave 30% higher conversion of n-hexadecane than $\text{Pd/ZrO}_2/\text{SO}_4$. $\text{Ni/ZrO}_2/\text{SO}_4$ was inactive for the conversion of n-hexadecane due to the poor hydrogenation capability of Ni under given reaction conditions (433 K and 360 psig of H_2 (cold)).

(3) In hydrocracking and hydroisomerization of n-hexadecane catalyzed by $\text{Pt/ZrO}_2/\text{SO}_4$ catalyst, at a given hydrogen pressure and reaction temperature, the conversion of n-hexadecane increases significantly with increasing Pt loading with a concomitant increase in selectivity to cracked products and a decrease in selectivity to isohexadecanes. The cracked product distribution shifts to shorter chain hydrocarbons.

(4) In hydrocracking and hydroisomerization of n-hexadecane catalyzed by $\text{Pt/ZrO}_2/\text{SO}_4$ catalyst, an increase in hydrogen pressure results in an increase in the conversion of n-hexadecane at given reaction temperature (433 K). Selectivity to cracked products also increases with a concomitant decrease in selectivity to isohexadecanes. The distribution of cracked products is not affected greatly by hydrogen pressure.

(5) In hydrocracking and hydroisomerization of n-heptane and n-hexadecane catalyzed by $\text{Pt/ZrO}_2/\text{SO}_4$ catalyst, addition of an olefin (1-heptene, 5-decene or 1-hexadecene) reduces the

conversions of n-heptane and n-hexadecane. The negative effect of olefins with a terminal double bond on the catalytic activity is greater than that of olefins with an internal double bond.

(6) Addition of a hydride transfer agent (adamantane or methylcyclopentane) increases the conversions of n-hexadecane and n-dotriacontane. Selectivity to cracked products decreases and selectivity to isomerized hexadecane or dotriacontane increases

(7) The Pt/HfO₂/SO₄ catalyst showed a much lower activity than Pt/ZrO₂/SO₄ prepared at the same conditions due to a lower number of acid sites and acid strength. A sulfate-promoted and Pt doped mixture of zirconium and hafnium oxides, Pt/ZrO₂·HfO₂/SO₄ with a molar ratio of Zr to Hf of one, had an activity higher than the Pt/ZrO₂/SO₄ catalyst. An increase in the molar fraction of HfO₂ reduced the selectivity to cracked products and increased selectivity to isomerized products.

(8) The long-term performance of Pt/ZrO₂/SO₄ (0.5 wt.% of Pt) catalyst for the hydrocracking and hydroisomerization of n-hexadecane in a continuous fixed-bed reactor was good: this catalyst maintained its initial activity after 96 hours. It was also very active at high hydrogen pressures (1600 psig) at 433 K and the sulfate group was not reduced.

(9) A novel zirconia precursor Zr(SO₄)₂·4H₂O, instead of conventional materials such as ZrOCl₂ and ZrO(NO₃)₂, was used successfully to prepare the Pt/ZrO₂/SO₄ catalyst. The main advantage is that this zirconia precursor eliminates the need to thoroughly wash the precipitates to remove undesirable ions such as Cl⁻ and NO₃⁻.

(10) The catalytic activity and acidic properties of the Pt/ZrO₂/SO₄ catalyst were similar regardless of the nature of zirconia precursor employed (Zr(SO₄)₂·4H₂O, ZrOCl₂ or ZrO(NO₃)₂). They were affected by preparation procedures such as the precipitation method, the concentration of the sulfuric acid solution used, and the calcination temperature. A Pt/ZrO₂/SO₄ catalyst sample prepared by heterogeneous precipitation with addition of 1 N of sulfuric acid for sulfation and calcination for three hours at 873 K gave the highest activity for hydrocracking and hydroisomerization of n-hexadecane.

(11) Sulfate, tungstate and molybdate groups were used to treat zirconium oxides which

were then doped with platinum. The number of acid sites, acid strength and catalytic activity of the sulfate-promoted zirconium oxides were much greater than those promoted by either of the other two groups.

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