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de96005562
DOE/PC/91304--T14

FINAL REPORT ORIGINAL

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 Pt/ZrO_2/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 Pt/ZrO_2/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 Pt/ZrO_2/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 Pt/ZrO_2/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 Pt/ZrO_2/SO_4 but also increased selectivity to long chain isoparaffins.

Product distribution of hydrocracking and hydroisomerization of n-hexadecane catalyzed

by Pt/ZrO_2/SO_4 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_o	Initial hydrogen pressure, atm.
P_{H2}	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_{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 ($CO+H_2$), 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 C1 to over C200. 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, $Pt/ZrO_2/SO_4$, 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 $Pt/ZrO_2/SO_4$ 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(16). 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 SiO_2-Al_2O_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 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. SiO_2-Al_2O_3(38) or ReHX zeolite(39), as well as bifunctional catalysts with a weak hydrogenation component, e.g. nickel sulfide(29) or WS_2/SiO_2-Al_2O_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/SiO_2-Al_2O_3(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 Brõnsted 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. $AlCl_3$-$CuCl_2$, $AlCl_3$-$CuSO_4$); (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_o, which is associated with the ability of an acid to protonate a basic indicator. For dilute aqueous solutions, H_o 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 Brõnsted and Lewis types in terms of the IR structures.