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PROGRESS REPORT

LOW SEVERITY UPGRADING OF F-T WAXES WITH SOLID SUPERACIDS

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INTRODUCTION

The Fischer-Tropsch (F-T) reaction, as practiced at SASOL using Lurgi reactors and an iron catalyst, produces large amounts of methane, most of which is reformed to synthesis gas for further F-T synthesis. To avoid this large production of methane, the new directions in F-T synthesis are directed toward the conversion of synthesis gas to high molecular weight hydrocarbons including waxes. This is being done by varying temperatures and pressures of the reaction and by using cobalt-based catalysts. The waxes have a good market, and the high molecular weight products are then hydrocracked to diesel fuel and gas oil as well as to some lighter products. However, the hydrocracking catalysts used are usually based on Y zeolite catalysts which do not provide high selectivity to isoparaffins, desirable products for high octane gasoline, jet fuels and lubricating oils.

We have discovered that the isomerization and hydrocracking of a long chain paraffin, n-hexadecane, with a solid superacid such as ZrO_2/SO_4 gives very high selectivities, (i.e., > 90% to hydrocracked isoparaffins, C_4-C_{13}) in the presence of platinum and a low pressure of hydrogen[1]. Undesirable light gases (methane and ethane) are not produced during these reactions. In addition, a high multi-branched to monobranched ratio of long chain hydrocarbons is produced.

We have written the formula for this catalyst as $Pt/ZrO_2/SO_4$.[1] Early attempts during this first quarter to reproduce this catalyst for the hydrocracking and isomerization of n-hexadecane gave results which were not reproducible, conversion varying from a few percent to 70%. It was, therefore, of utmost importance to devise a procedure that could be depended upon to synthesize a reproducible catalyst which would give high conversions and high selectivities to cracked and isomerized products of high fuel and lubricating oil values. The catalysts should be active under mild conditions, i.e., below 170°C and hydrogen pressures below 350 psi. Conventional heavy end cracking catalysts (modified zeolites) are active at 300-400°C.

SYNTHESIS OF $Pt/ZrO_2/SO_4$

We have succeeded in synthesizing a $Pt/ZrO_2/SO_4$ catalyst which gives high conversions and selectivies for desired products from n-hexadecane. The catalyst preparation procedure has been carefully worked out and is entirely reproducible.

The selection of starting salts was made based on their solubilities and the catalyst structure desired. The starting materials reported in the literature are $ZrOCl_2$ and $ZrO(NO_3)_2$. Removal of the anion part of these salts is a crucial step in preparing the catalyst. We found that a catalyst prepared from $ZrOSO_4$ exhibits higher activity than that prepared from $ZrOCl_2$ or from $ZrO(NO_3)_2$; use of $ZrOSO_4$ gives a precipitated zirconium hydroxide which already contains sulfate ions and no washing to remove Cl^- or NO_3^- is necessary. $ZrOSO_4$ obtained from two different suppliers (Pfaltz & Bauer, Inc. and Strem Chemical Co.) gave equally effective catalysts.

a) Hydrolysis of $ZrOSO_4$

Fifty grams of this material are dissolved in 560 ml of distilled water to give a 0.25 M solution. The solution is stirred at a constant rate for one hour in order to dissolve the material completely. Hydrolysis is then carried out with 29.8% NH_4OH at room temperature. The rate of addition of the hydroxide is adjusted to about 10 drops/min. The initial pH of the solution is about 1.2. A slow titration rate should be used until the pH reaches 4.0. The solution pH is sensitive to the rate of addition of NH_4OH in the 6.0 to 8.0 range; but above of 8.5 the addition of NH_4OH only changes the pH value slowly.

The titration rate can be increased to 18 drops/min until a final pH of 9.5 is reached. Total time is three hours. The solution is allowed to stir for an additional five minutes, and then allowed to stand overnight.

b) Washing and Drying of Precipitates

The washing of precipitates is carried out to remove undesired anions. For each washing, the precipitate is first filtered, mixed with 600 ml of distilled water, stirred for 10 minutes and allowed to settle for five minutes. The supernatant liquid is decanted and the washing is repeated. After the second washing, the solution is filtered and the precipitates put into an oven at 110°C for 24 hrs to remove physically adsorbed moisture.

c) Sulfation of Precipitates

The precipitate is powdered to -100 mesh and then sulfated using 10 ml of 1.0 N H_2SO_4 per gram of precipitate. The sulfation time is one hr with one minute stirring for every 10 minute period. The precipitate is filtered, kept as dry as possible on the filter, and then dried in an oven at 110°C overnight.

d) <u>Impregnation and Calcination</u>

After overnight drying, the precipitate, $Zr(OH)_4$, is screened to -60 mesh. The total weight of solids is about 20 grams. Impregnation is a key step in preparation of $Pt/ZrO_2/SO_4^{2-}$. The platinum is added to the hydroxide by first preparing a solution of $H_2PtCl_6 \cdot 6H_2O$ in distilled water sufficient to give 0.005 gram of Pt per gram of $Zr(OH)_4$. The amount of Pt salt is 0.0115 gram/gram of $Zr(OH)_4$. After adding the Pt salt to water, the solution is slowly added to the solids while grinding in a mortar. The mixture is then ground for five minutes and dried in an oven at 110°C for about 30 minutes. After impregnation the catalyst is dried at 110°C for an additional five hours, then rescreened to -60 mesh. The catalyst is subsequently calcined in air at 600°C for three hours, then allowed to cool to 400°C. It is immediately transferred into hot vials (110°). Calcining for longer times or at temperature over 650°C might decrease the activity.

HYDROISOMERIZATION AND HYDROCRACKING OF n-HEXADECANE

Hydrocracking experiments were conducted using horizontal shaking tubing bombs. Before reaction, the catalyst was activated in an oven at 450°C for an hour. It was then transferred immediately to the hot tubing bomb, closed, and the bomb quickly cooled to room temperature. After addition of n-hexadecane, the reactor was twice purged with hydrogen.

The hydrocracking of n-hexadecane was carried out at about 160°C with an initial hydrogen pressure of 350 psig, a catalyst to feed ratio of 6.0, and a reaction time of one hour.

A typical product distribution for hydrocracking of n-hexadecane is shown in Table 1. At a 69.3 wt% conversion level, an 84.9% selectivity to isoparaffins was observed. Among the products, 45.5% of paraffins in the C_4-C_9 region were produced. Methane and ethane were not found in the gaseous products. It is also worthy of note that no olefinic hydrocarbons or higher molecular weight products were found. This is believed to be due to the high hydrogenation ability of platinum in the presence of hydrogen.

FUTURE WORK

Samples of n-tetracosane ($C_{24}H_{50}$) and normal $C_{32}H_{66}$ have been purchased. Hydrocracking and isomerization of these high molecular weight straight-chain hydrocarbons using the $Pt/ZrO_2/SO_4$ catalyst will be studied under the mildest conditions necessary to furnish high selectivities to gasoline, diesel fuel and lubricating oils.

Three waxes prepared by SASOL have been obtained for future work with actual F-T waxes. Their melting points are 87°C, 99°C, and 107°C, respectively. The physicochemical properties of these F-T waxes will be furnished when they are used in hydrocracking and isomerization experiments.

It will be particularly important to determine the constitution of the $Pt/ZrO_2/SO_4$ catalyst(s). XRD and TEM measurements will be made during the next quarter. A comparison

Table 1. Product Distribution from Hydroconversion of n-Hexadecane

Reaction Conditions	
Temperature, °C	160
Hydrogen pressure, psig	350
Reaction time, hr	1
Feed/Catalyst, by weight	6
Conversion, wt%	69.3
Selectivity of isoparaffins,%	84.9
Product Distribution, %	
C_4	
iso-	3.17
n-	0.89
C_5-C_9	
iso-	39.28
n-	2.18
C_{10}-C_{12}	
iso	11.43
n-	0.55
C_{13}-C_{15}	6.83
Iso-hexadecane	
multibranched	3.32
monobranched	1.62
Hexadecane	30.7
Total	100

will be made of a $Pt/Zr(OH)_4/SO_4$ catalyst prepared by impregnating the Pt salt and a $Zr(OH)_4/SO_4$ catalyst prepared by mechanically mixing the hydroxide with PtO_2.

It may be possible to replace the platinum by a cheaper metallic hydrogenation catalyst such as nickel, and this will be investigated.

REFERENCES CITED

1. Wen, Michael Y., Irving Wender, and John W. Tierney, "Hydroisomerization and Hydrocracking of n-Heptane and n-Hexadecane on Solid Superacids," *Energy and Fuels*, **4**, 372 (1990).

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