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QUARTERLY REPORT

LOW SEVERITY UPGRADING OF F-T WAXES WITH SOLID SUPERACIDS

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Introduction

To avoid methane production in the F-T synthesis on iron catalysts, efforts are currently being directed towards conversion of synthesis gas to high molecular weight hydrocarbons including waxes. Since large amounts of long-chain paraffins are available from F-T synthesis, production of liquid fuels from wax has aroused considerable interest. However, little has been reported on the hydrocracking of n-alkanes with carbon numbers larger than n-C₁₆. Commercial Co-Mo and Pt/Y-zeolite catalysts operate under severe reaction conditions and could deactivate when cracking long-chain paraffins due to coking within the catalyst pores. Solid acids appear superior to conventional hydrocracking in terms of reactivity and resistance to coking. The significant characteristic of this catalyst is its flexibility in treating a variety of feedstocks to produce high-octane gasoline and jet fuels. Low severity upgrading of long-chain paraffins on the present catalyst shows good activity towards light paraffins, not observed on other catalysts reported in prior studies. A most interesting and novel finding, making use of the strong acid properties of sulfated zirconium oxides, ZrO₂/SO₄, is a new approach to pretreating long-chain paraffins with carbon numbers greater than n-C₃₂.

Work Done and Conclusions

Reactivity of Pt/ZrO₂/SO₄ on hydrocracking n-C₃₂

We reported previously that we succeeded in synthesizing a Pt/ZrO₂/SO₄ catalyst which gives high conversions and selectivities for desired products from long-chain paraffins such as n-hexadecane. The catalyst preparation procedure has been carefully worked out and is entirely reproducible.

The hydrocracking activity and selectivity of n-dotriacontane (mp. 70 °C, bp. 467 °C) was conducted with Pt/ZrO₂/SO₄ in a batch horizontal shaking reactor under rather mild conditions

: 170 °C, 350 psig initial hydrogen pressure. As shown in Figure 1, the main products from the hydrocracking of n-C₃₂ range from C₄ to C₁₈ with large amounts in the C₄-C₉ range. High conversion levels and selectivity to isoparaffins in excess of 90% has been achieved. The amount of multibranched paraffins produced is considerable (multi/mono=3). Conversion to light products increases as the reaction proceeds; after 60 minutes, the gasoline fraction exceeds 45%. No methane and ethane were found in the gaseous products; only trace amounts of propane were detected. In addition, no olefinic hydrocarbons or higher molecular weight products were observed.

Profiles shown in Figure 2 demonstrate that, as the reaction proceeds, the weight fraction of iso-C₃₂ drops considerably and that of cracked products increases, indicating that the reaction proceeds through initial isomerization of n-alkanes followed by consecutive β -scission reactions and further isomerization. Evidently, n-alkanes must be isomerized before cracking takes place.

On the other hand, isomerization is favored at short reaction times while the reaction is driven towards deep cracking over long time periods. The high yield of multibranched paraffins can be explained by the tendency to form structural stable intermediates which undergo consecutive isomerization of the carbon cation.

The effect of catalyst loading on hydrocracking of n-C₃₂ is shown in Figure 3. High conversions are achieved with feed/catalyst ratios lower than 3.0. Conversion to light products decreases sharply with increasing feed/catalyst ratios; there was evidence of catalyst deactivation after reaction, obviously caused by coking of unsaturated intermediates. There may be a limitation on mass transfer from the gas phase to the catalyst surface in the present tubing bomb reactor. It is therefore desirable to design a new reaction system to improve hydrocracking efficiency.

Effect of Hydride Donor Solvent on Hydrocracking of n-C₃₂

We have found that the addition of MCP (methylcyclopentane) to the feedstock can give higher selectivity to multibranched paraffins allowing increased control over the product distribution. As shown in Figure 4, product distribution shifts to a higher carbon number range and the typical volcano plot is broadened. Besides donation of hydride ion, MCP improves the diffusion restrictions caused by high viscosity of long-chain paraffins. In the presence of MCP, no evidence of deactivation was observed with a feed/catalyst ratio up to 12, suggesting that the carbon cation which may deactivate the catalyst has been saturated by hydride ions. The viscosity of n-alkanes is decreased because of the solvent effect of MCP. As a result, hydrogen readily penetrates the catalyst surface to generate protonic acid sites. After reaction, more than 95% of MCP was recovered from the products, indicating that MCP acts as a hydride shuttling reagent. Addition of MCP does not influence total conversion, whereas selectivity to isomerized products increases greatly with increasing MCP concentration (Figure 5). This is a promising way to control product selectivity.

Future Work

It will be particularly important to determine the constitution of the Pt/ZrO₂/SO₄ catalysts. XRD, TEM, XPS and TPD will be used in the upcoming work. Activities will be related to measurable properties. A comparison will be made of a Pt/Zr(OH)₄/SO₄ catalyst prepared by impregnating the Pt salt and a Zr(OH)₄/SO₄ catalyst prepared by mechanically mixing the hydroxide with PtO₂. It may be possible to replace the platinum by a cheaper metallic hydrogenation catalyst such as nickel and this will be investigated. The effect of operating conditions on product distribution as well as the effect of olefins on hydrocracking long-chain paraffins will be investigated to achieve insight into the chemistry of these reactions.

Figure 1. Conversion of hydrocracking of n-C₃₂ as a function of time

Figure 2. Cracking and isomerization selectivities of $n\text{-C}_{32}$ as a function of time

Figure 3. Effect of catalyst loading on hydrocracking of n-C₃₂

Figure 4. Distribution of cracking products from isomerization and hydrocracking of $n\text{-C}_{32}$ with $\text{Pt/ZrO}_2/\text{SO}_4$ (Temperature: 433 K; Pressure: 2.5 MPa)

Figure 5. Effect of MCP concentration on hydrocracking of n-tetradecane

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