QUARTERLY REPORT

LOW SEVERITY UPGRADING OF F-T WAXES WITH SOLID SUPERACIDS

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SUMMARY:

In the past year, we synthesized a Pt/ZrO₂/SO₄ catalyst which exhibits high conversions and selectivity for desirable products from long-chain paraffins, such as n-hexadecane, n-dotriacontane(n-C₃₂) and a SASOL wax(C₅₈-C₆₄). The catalyst preparation procedure has been carefully worked out and is reproducible. Isomerization and hydrocracking activities of long-chain paraffins and selectivities to various products were examined under mild conditions: 443 K and 2.5 MPa initial hydrogen pressure. The influence of temperature, pressure, catalyst loading and Pt concentration on n-alkane conversions was studied to obtain an understanding of the mechanism occurring on the acid catalyst surface. Upgrading of the alkanes proceeds through initial isomerization followed by β -scission reactions and further isomerizations. Isomerization is favored at low temperature and short reaction times whereas cracking is favored at higher temperatures or pressures. The hydrogen pressure has a considerable influence on the product distribution. It is likely that hydrogen transfer proceeds through dissociation of molecular hydrogen to generate protonic acid sites which are responsible for cleavage of C-C bonds. The effect of increasing Pt loadings shows a trend similar to that of increasing hydrogen pressure. Characterization of the present catalyst demonstrates that catalytic activity depends to a large extent on proper coordination of finely dispersed platinum to strong acid sites as well as on pore size distribution.

WORK DONE AND CONCLUSIONS:

Activity and selectivity of Pt/ZrO₂/SO₄

The Pt/ZrO₂/SO₄ catalyst exhibits high activity towards cracking of long-chain n-alkanes. A similar product distribution, from C₄ to C₁₄, was observed in hydrocracking of hexadecane, n-

dotriacontane($n\text{-C}_{32}$), and a SASOL wax. Results summarized in Table 1 demonstrate the high cracking and isomerization activity of the catalyst. It is noteworthy that no methane and ethane are found in the gaseous products. In addition, no olefinic hydrocarbons or higher molecular weight products are formed, believed due to the high hydrogenation ability of platinum in the presence of hydrogen. Reactions were carried out in a 27 ml microreactor at a feed/catalyst ratio of 6:1; no evidence of catalytic deactivation was observed at the end of the reaction. The melted SASOL wax is viscous and there was a decrease in conversion with time, indicating that diffusion might be a limitation for chains of high molecular weight.

Effects of reaction variables on hydrocracking of long-chain alkanes

Temperature: The effect of temperature on the catalytic activity of $\text{Pt/ZrO}_2/\text{SO}_4$ was studied using $n\text{-C}_{32}$ as a substrate under a pressure of 2.5 MPa and 60 minutes reaction time. Total conversion increased from 60.1% to 98.1% on raising the temperature from 383 K to 463 K (Figure 1). At lower temperatures, the product distribution shifts towards longer chains ($> \text{C}_9$). The formation of isomeric products is favored at higher temperatures, with the ratio of multi/mono(methyl)branched paraffins increasing from 2.6 to 3.5. It is known that protonic acid sites are responsible for skeletal isomerization and cracking. The high conversion and selectivity achieved with the increase in temperature may be explained by greater dissociation of H_2 at higher temperature to generate protonic acid sites.

Hydrogen pressure: The $\text{Pt/ZrO}_2/\text{SO}_4$ catalyst is characterized by high activity for long periods of time in the presence of molecular hydrogen. Hydrogen prevents formation of coke with subsequent catalyst deactivation. The response of the activity to the initial hydrogen pressure is shown in Figure 2; conversion increases significantly as the pressure rises from 2.5

MPa to 5.0 MPa. We can thus control the activities for this acid-catalyzed reaction by varying the hydrogen pressure and the temperature.

Catalyst loading: The ratio of catalyst/feed was varied by changing the amount of substrate. For hydrocracking of hexadecane, total conversion decreased from 78% to 60% with increase of feed/catalyst ratio from 6 to 12. However, for cracking of $n\text{-C}_{32}$, total conversion dropped more sharply with increasing feed/catalyst ratio. It is likely that catalyst activity is inhibited by poor mass transfer from gaseous hydrogen to acid sites due to the high viscosity of $n\text{-C}_{32}$.

Platinum concentration: It has been reported that addition of platinum enhances the activity of ZrO_2/SO_4 because of its inhibiting effect on coking^[2]. It is generally accepted that the function of platinum in hydrocracking catalysts involves dehydrogenation followed by hydrogenation^[3]. We have recently found that the amount of platinum used has a strong influence on the catalyst activity of the solid superacids. Raising the Pt concentration increases conversion(Figure 3a). The initial reaction rate on a 1.0% Pt doped catalyst is twice as high as that on a 0.5% Pt doped catalyst(Figure 3b). It seems plausible that increasing of Pt results in formation of more active sites. This coincides with recent findings^[1] by in-situ XPS, where it was indicated that the most important effect of platinum is to dissociate molecular hydrogen to generate protonic acid sites.

Hydride donors : A well known hydride donor, methylcyclopentane(MCP) was added with $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ and $n\text{-C}_{32}$. As shown in Figure 4, addition of MCP has a marked effect. In the absence of MCP, products are mainly in the C_4 to C_9 gasoline region. The presence of MCP drives the product distribution towards longer-chain paraffins because of instantaneous saturation

of surface carbenium ions, thus inhibiting cracking activity. We were able to recover the MCP quantitatively after reaction.

Characterization of the Pt/ZrO₂/SO₄ Catalyst

Transmission electron microscopy was employed to determine particle size distribution and platinum dispersion. A typical micrograph displays platinum particles finely dispersed on the more transparent background of crystallite ZrO₂. The ZrO₂/SO₄ particle size is uniform with the major portion being about 10 nm in size, corresponding well with XRD data. It appears that platinum is finely dispersed as PtO₂ on ZrO₂/SO₄.

To elucidate the nature of the interaction between PtO₂ and ZrO₂/SO₄, activities of three ZrO₂/SO₄ based catalysts were compared under the same conditions; n-hexadecane was used as substrate. A first catalyst, ZrO₂/SO₄ exhibits poor activity; deactivation due to coking takes place quickly in the absence of platinum. A second catalyst, consisting of physically-doped platinum (simply mixing PtO₂ and ZrO₂/SO₄), slightly improves the activity but is still a poor catalyst. In situ IR indicated that this catalyst did not generate many protonic acid sites^[2]. A third catalyst was prepared by mixing PtO₂ and Zr(OH)₄ with subsequent calcination at 873 K. This catalyst behaved as expected, giving a 72.5 wt% conversion and 84.1% selectivity to isoparaffins (Table 2). It is evident that the platinum must coordinate with the ZrO₂/SO₄ to generate active sites responsible for dissociation of molecular hydrogen.

Pore size distribution has a great influence on catalyst behavior in hydrocracking. The pore volume of an active Pt/ZrO₂/SO₄ is distributed mainly in the region of 20-60 and 300-1000 Å, characteristic of a bifunctional distribution (Figure 5a). It may be that initial isomerization of long chain paraffins occurs in the large pores, whereas hydrocracking to form gasoline takes

place in the smaller pores. The pore area distribution analysis shows that most of the BET surface area of this Pt/ZrO₂/SO₄ catalyst is concentrated in a narrow mesopore region of 20-50 Å (Figure 5b). It is clear that mesopores play an important role in hydrocracking, since they contribute significantly to the BET surface area. We obtained evidence that proper pore size distribution of the Pt/ZrO₂/SO₄ may be more important than particle size for hydrocracking long-chain paraffins.

FUTURE WORK:

Sulfated zirconium, hafnium and titanium acids as well as their mixtures will be prepared and tested for hydrocracking of F-T waxes. In addition, these catalysts will be characterized and results related to their hydrocracking activity. Surface properties of these catalysts will be examined by TPD-IR to help elucidate hydrocracking mechanisms and the structure of acid sites.

A fixed-bed continuous flow reaction system is being designed. It will be employed to eliminate possible mass transfer limitations associated with the present microreactor system and improve the reactivity of the present catalysts. A kinetic model expression based on this system will be developed in an attempt to optimize the reaction.

References

1. Ebitani, K.; Konno, H.; Tanaka, T.; Hattori, H., *J. of Catal.*, 135, 60-67(1992)
2. Ebitani, K.; Tsuji, J.; Hattori, H.; Kita, H., *J. of Catal.*, 135, 609-617(1992)
3. Mohanty, S.; Kunzru, D.; Saraf, D.N., *FUEL*, 169, 1467-1472(1990)

Table 1. Product Distribution from Hydrocracking of Long-chain Paraffins

Reaction Conditions			
Temperature,K	433		
Pressure, MPa	2.5		
Reaction time, min	60		
Product Distribution			
Feed :	n-C ₁₆	n-C ₃₂	SASOL wax(C ₅₈ -C ₆₄)
Conversion, wt%	79.2	90.2	88.6
Selectivity to iso	83.6	88.7	86.1
C ₁ -C ₃	none	none	none
C ₄ -C ₉	51.2	52.2	34.7
C ₁₀ -C ₁₄	14.8	18.9	28.4
C ₁₄ ⁺	7.13	14.2	12.4
iso-C _n	6.07	4.9	13.1

Table 2. Comparison of Hydroconversion of n-Hexadecane on Different Catalysts

Run No	Catalyst	Conv. wt%	Selectivity to isoparaffins, %	Product Distribution
HC-54	ZrO ₂ /SO ₄	3.0	100	iso-C ₁₆
HC-55	PtO ₂ +ZrO ₂ /SO ₄ ^a	11.0	90	iso-C ₁₆
HC-56	PtO ₂ /ZrO ₂ /SO ₄ ^b	72.5	84.1	C ₄ -C ₁₃

a. Prepared by mixing PtO₂ powder with calcined ZrO₂/SO₄.

b. Prepared by mixing PtO₂ powder with Zr(OH)₄/SO₄, then calcined at 873 K.

Figure 1. Conversions and product yields of n-C₃₂ as a function of time with a Pt/ZrO₂/SO₄ catalyst(2.5 MPa, 60 min reactime)

Figure 2. The effect of hydrogen pressure on catalytic activity of $\text{Pt/ZrO}_2/\text{SO}_4$ for hydrocracking of n-hexadecane (Temperature : 433 K)

Figure 3a. Effect of Pt concentration on isomerization and hydrocracking of n-hexadecane with Pt/ZrO₂/SO₄ (Temperature: 433 K; Pressure: 2.6 MPa; Reaction time: 60 min)

Figure 3b. Effect of Pt concentration on reaction rate for isomerization and hydrocracking of n-hexadecane with Pt/ZrO₂/SO₄ (Temperature: 434 K; Pressure: 2.6MPa)

CRACKING PRODUCTS, g/100g FEED REACTED

Figure 4. Distribution of cracking products from isomerization and hydrocracking of n-C₃₂ with Pt/ZrO₂/SO₄ (Temperature: 433 K; Pressure: 2.5 MPa)

Figure 5a. Incremental pore volume distribution of a Pt/ZrO₂/SO₄ catalyst

Figure 5b. Incremental pore area distribution of a Pt/ZrO₂/SO₄ catalyst

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