

Quarterly Report

**LOW SEVERITY UPGRADING OF F-T WAXES WITH
SOLID SUPERACIDS**

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SUMMARY

In this quarter we studied the effect of hydrogen pressure, and of sulfur and nitrogen-containing compounds on the isomerization and hydrocracking of n-hexadecane using a Pt/ZrO₂/SO₄ catalyst. The reactions were carried out at 300°C and hydrogen pressures between 50 and 500 psig. Increasing hydrogen pressure resulted in increased conversion and increased hydrocracking. Nitrogen containing compounds had a greater inhibiting effect on the conversion of n-hexadecane than sulfur-containing compounds. The reaction of diphenylmethane in air at 25°C and in the presence of sulfated zirconia was studied as a possible means to characterize the protonic acidity of solid superacids.

RESULTS AND CONCLUSION

Effect of Hydrogen Pressure on the Conversion of n-Hexadecane over Pt/ZrO₂/SO₄ Catalyst

We have previously reported that, at 160°C, an increase in hydrogen pressure results in a significant increase in reaction rate for hydrocracking of n-hexadecane. The product distribution shifts to low molecular weights on raising the hydrogen pressure. It is believed that the increase in reaction rate is due to an enhancement in the number of protonic acid sites generated from dissociation of molecular hydrogen. We have recently found that Pt/ZrO₂/SO₄ catalyst is active for hydrocracking of long-chain paraffins at higher temperatures (300°C). No evidence of deactivation at high temperature was observed. We wondered if hydrogen pressure would affect product distribution and catalytic activity at high temperature. The reactions were carried out at 300°C in a microreactor for 20 minutes. A reactions time of 20 minutes was selected to avoid extensive hydrocracking which would be expected at longer reaction times and would generate

large amounts of gases.

As shown in Table 1, at 50 psig (120-140 psig during reaction) low conversion (21.5 wt%) of n-hexadecane is observed. However, the product is rich in iso-hexadecane (46.5%), indicating that the hydrocracking activity of the catalyst is not high at low pressure. Under these conditions insufficient hydrogen is available to generate enough protonic acid sites, responsible for the hydrocracking reactions. On raising the pressure to 150 psig (185-280 psig during reaction), the total conversion of n-hexadecane increased and the product distribution shifted to lower molecular weight, indicating increased hydrocracking. When the hydrogen pressure was increased to 500 psig (400-700 psig during reaction), extensive hydrocracking of n-hexadecane took place. The yield of iso-hexadecane dropped to 8.1 wt% while the amount of C₄-C₉ increased to 81.1 wt%.

Effect of Nitrogen and Sulfur-Containing Compounds on the Conversion of n-Hexadecane

Metal-promoted solid superacids, such as Pt/ZrO₂/SO₄, possess a bifunctional character. They contain an acid site generated from ZrO₂/SO₄ and a metal center that has a hydrogenation function. It is known that nitrogen-containing compounds inhibit acid catalyzed reactions because basic nitrogen blocks the acid sites. Sulfur-containing compounds interact with the metal center causing the deactivation of metal-promoted solid acids. It is therefore important to know the critical concentration of nitrogen and sulfur that the metal-promoted solid superacids can tolerate.

Hydrocracking of n-hexadecane in the presence of sulfur or nitrogen-containing compounds was carried out at 300°C and 500 psig (600-700 psig during reaction) for 20 min. Thiophene and pyridine were chosen as sulfur and nitrogen-containing compounds. As shown in Table 2, the presence of 200 ppm of sulfur in the hexadecane does not affect the activity of the Pt/ZrO₂/SO₄

catalyst. When the concentration of sulfur was increased to 500 ppm, the conversion of n-hexadecane dropped from 76.2 wt% to 46.3 wt%. The product distributions from conversion of n-hexadecane in the presence of sulfur are similar to those obtained in the absence of sulfur. The inhibiting effect of sulfur-containing compounds on conversion of n-hexadecane increases on raising the sulfur concentration. At 1000 ppm, 21.7 wt% conversion of n-hexadecane was obtained, and the catalyst was not completely deactivated. At a sulfur concentration of 1000 ppm, the number of sulfur molecules is sufficient to cover the metal centers.

Pyridine shows a greater inhibiting effect than thiophene on conversion of n-hexadecane. As with sulfur, the presence of 50 ppm nitrogen does not affect the conversion of n-hexadecane (Table 3). However, when the concentration of nitrogen was raised to 100 ppm, a significant decrease in conversion of n-hexadecane was observed. At a nitrogen concentration of 200 ppm, only 10 wt% conversion was obtained.

Cracking of Diphenylmethane (DPM) over Pt/ZrO₂/SO₄ Catalyst at Room Temperature

Certain anion-modified metal oxides such as ZrO₂/SO₄ are acid catalysts but there is some controversy as to their superacidic strength, and there is doubt about the validity of using Hamett indicators to characterize their strengths^[1]. It appears that a more reliable measure of their acid strength is needed. We are investigating the cleavage of DPM at ambient conditions, known to proceed via protolysis, as a convenient qualitative way to compare the relative protonic acid strength of these solid acids.

Some preliminary results are shown in Table 4 where the product distribution obtained from the reaction of DPM over ZrO₂/SO₄ catalyst at 25°C and atmospheric pressure is presented. A DPM conversion of 18.9 wt% was obtained after 22 hours. Benzene was formed in larger

amounts than toluene, most likely because the benzyl cation ($\text{C}_6\text{H}_5\text{CH}_2^+$), formed from the protolytic cleavage of the $\text{C}_{\text{alkyl}}-\text{C}_{\text{aryl}}$ bond in DPM, reacts rapidly with excess DPM in the reaction mixture to form ortho-, meta- and para-substituted benzyldiphenylmethanes. It is less likely for the benzyl cation to form toluene by reaction with a hydride ion. To the best of our knowledge, high DPM conversions at room temperature over a solid acid catalyst such as ZrO_2/SO_4 are hitherto unreported. The result indicates that strong protonic acid sites are present on the surface of ZrO_2/SO_4 .

FUTURE WORK

The effect of anions other than SO_4^{2-} on the acidity and activity of metal promoted solid acid catalyst will be studied. SO_4^{2-} will be replaced by MoO_4^{2-} and WO_4^{2-} and their activity in conversion of n-hexadecane will be compared. The structures and acidities of these catalysts will be characterized by FT-IR, TEM and SEM in an effort to relate the catalytic activity to the structural properties. Work will continue on the use of DPM as a test reaction for measuring protonic acid strength, and preparation of the final report will begin..

Table 1. Effect of Hydrogen Pressure on the Conversion of n-Hexadecane over $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ Catalysts (300°C, 20 minutes microreactor)

	Initial hydrogen pressure and pressure during reaction(psig)			
	50 (120-140)	150(185-280)	240(170-350)	500(400-700)
Conversion, wt%	21.5	35.0	52.8	76.2
Product distribution, wt%				
$\text{C}_4\text{-C}_9$	47.8	80.3	68.7	81.1
$\text{C}_{10}\text{-C}_{13}$	5.7	4.2	11.2	10.8
iso- C_{16}	46.5	15.5	20.1	8.1

Table 2. Effect of a Sulfur-Containing Compound (Thiophene) on the Conversion of n-Hexadecane (Pt/ZrO₂/SO₄ catalyst, 300°C, 500 psig of H₂, 20 minutes in a microreactor)

	Concentration of sulfur (ppm of S)			
	none	200	500	1000
Conversion (wt%)	76.2	76.0	46.3	21.7
Product distribution, wt%				
C ₄ -C ₉	81.1	88.0	71.6	59.2
C ₁₀ -C ₁₃	10.8	10.6	15.2	24.4
iso-C ₁₆	8.1	1.4	13.2	16.4

Table 3. Effect of a Nitrogen-Containing Compound (Pyridine) on the Conversion of n-Hexadecane (Pt/ZrO₂/SO₄ catalyst, 300°C, 500 psig of H₂, 20 minutes in a microreactor)

	Concentration of nitrogen (ppm of N)			
	none	50	100	200
Conversion (wt%)	76.2	77.0	17.0	10.3
Product distribution, wt%				
C ₄ -C ₉	81.1	82.5	33.4	77.8
C ₁₀ -C ₁₃	10.8	10.8	36.2	10.7
iso-C ₁₆	8.1	6.7	30.4	11.5

Table 4. Product Distribution Obtained from the Reaction of DPM over a ZrO_2/SO_4 Catalyst at 25°C and Atmospheric Pressure for 22 Hours.

DPM/ ZrO_2 mol ratio	2.2	1.1
DPM conversion (wt%)	18.9	27.1
Product Distribution (wt%)		
benzene	20.8	42.4
toluene	0.12	0.11
benzyl diphenylmethane	18.4	30.7
dibenzyl diphenylmethane	7.3	20.1
unidentified	53.4	6.7

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