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PROGRESS REPORT

LOW SEVERITY UPGRADING OF F-T WAXES WITH SOLID SUPERACIDS

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SUMMARY

Experiments conducted in the last quarter have concentrated on investigations of the catalytic hydrocracking of a SASOL wax and characterization of sulfated zirconium oxide catalysts by means of TEM and pore size distribution analysis. The results indicate that catalyst activity depends to a large extent on proper coordination of platinum to strong acid sites as well as on pore size distribution.

Hydroisomerization and Hydrocracking of a SASOL Wax

We have previously reported the isomerization and hydrocracking of n-hexadecane and a n-C_{32} straight chain paraffin with a $Pt/ZrO_2/SO_4$ catalyst at 170°C and 350 psig of hydrogen. This study has now been extended to the treatment of a Fisher-Tropsch wax with a carbon number range from C_{55}-C_{62}. The results reported in Table 1 show that the $Pt/ZrO_2/SO_4$ catalyst is active for the isomerization and hydrocracking of this substrate. At an 88.6 wt% conversion level, an 86.1% selectivity to isoparaffins was achieved. The products consisted mainly of C_4-C_9 and C_{10}-C_{14} fractions, suitable as gasoline and diesel fuels. A feed/catalyst ratio of 6:1 was used; there was no evidence of catalytic deactivation.

The melted wax is viscous and there was a decrease in conversion with time, indicating that diffusion might be a limitation for chains of very high molecular weight.

Characterization of $Pt/ZrO_2/SO_4$ Catalyst

TEM Analysis

Transmission electron microscopy was employed to verify particle size distribution and platinum dispersion. A typical micrograph displays platinum bearing particles finely dispersed on the more transparent background of crystallite ZrO_2. The ZrO_2 particle size is uniform, with the major portion being around 10 nm in size. Electron diffraction of the ZrO_2 background shows a multicrystallite pattern, characteristic of a tetragonal crystallite; this result corresponds well with XRD data. When the electron beam is focused on one of the dark spots, a parallel diffraction matrix appears on the diffraction pattern of ZrO_2. It is likely that the black spot is a characteristic pattern of crystallite PtO_2 supported on ZrO_2/SO_4.

The structure of acid sites has been studied extensively. However, the nature of hydrogenation sites on the surface of the zirconium sulfate is not clear. In order to elucidate the nature of the interaction between PtO_2 and ZrO_2/SO_4, activities of three ZrO_2/SO_2 based catalysts prepared by different methods were compared under the same conditions; n-hexadecane was used as the substrate. The first catalyst, as a base test, was simply ZrO_2/SO_4. As shown in Table 2, this catalyst exhibits poor activity; deactivation due to coking takes place quickly in the absence of platinum. Experiment HC-55 shows that the combination of the two solids, PtO_2 plus ZrO_2/SO_4, is better than ZrO_2/SO_4 but is still a poor catalyst, indicating that physically-doped platinum does not furnish hydrogenation sites. In the third experiment, HC-56, the catalyst was prepared by mixing PtO_2 and $Zr(OH)_2$ with subsequent calcination at 600°C. This catalyst behaved as expected, giving a 72.5 wt% conversion and 84.1% selectivity to isoparaffins. It appears that, to be effective, the platinum must coordinate with the crystallite oxygen to generate hydrogenation sites which during calcination, and which may be adjacent to acid sites.

Pore Size Distribution

One of the properties that has a great influence on catalyst behavior in hydrocracking is the pore size distribution. The pore volume of an effective $Pt/ZrO_2/SO_4$ catalyst is distributed mainly in the region of 20-60 and 300-1000 Å, characteristic of a bifunctional distribution (Figure 1). It may be that initial isomerization of long chain waxes occurs in the large pores, whereas hydrocracking to form gasoline takes place in smaller pores, indicating that hydrocracking activity depends on specific pore volume. Another catalyst prepared by the same method but with a different final pH, showed much lower hydrocracking activity. It may be that too many macropores were present. The pore area distribution analysis shows that most of the BET surface area of the $Pt/ZrO_2/SO_4$ catalyst is concentrated in a narrow mesopore region of 20-50 Å with avery small portion in the macropore region (Figure 2). It is clear that mesopores play an important role in hydrocracking, since they contribute significantly to the BET surface area. On the other hand, from a kinetic point of view, the narrow BET surface area distribution should make this catalyst more effective for hydrocracking of middle to heavy n-alkanes, e.g. C_{10} to C_{32}.

FUTURE WORK

Zirconium superacids with hydrogenation metals other than Pt such as Pd, Ru, Ni, Mo and W will be prepared and tested for hydrocracking of F-T waxes. In addition, the effects of Pt and sulfur content on hydrocracking will be investigated.

A continuous flow reaction system is planned. It will be used to eliminate possible mass transfer limitations associated with the present reactor system.

Table 1. Product Distribution from Hydrocracking of a SASOL Wax

Reaction Conditions	
Temperature, °C	170
Pressure, psig	350
Reaction time, min	60
Feed/Catalyst	2.5
Product Distribution	
Conversion, wt%	88.6
Selectivity to isoparaffins	86.1
C_1-C_3	none
C_4-C_9	34.7
C_{10}-C_{14}	28.4
C_{14}^{+}	12.4
iso-C_{58}*	13.1

* Isomerized SASOL wax.

Table 2. 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_9

a. Prepared by mixing PtO_2 powder with calcined ZrO_2/SO_4.

b. Prepared by mixing PtO_2 powder with $Zr(OH)_4/SO_4$, then calcined at 600°C.

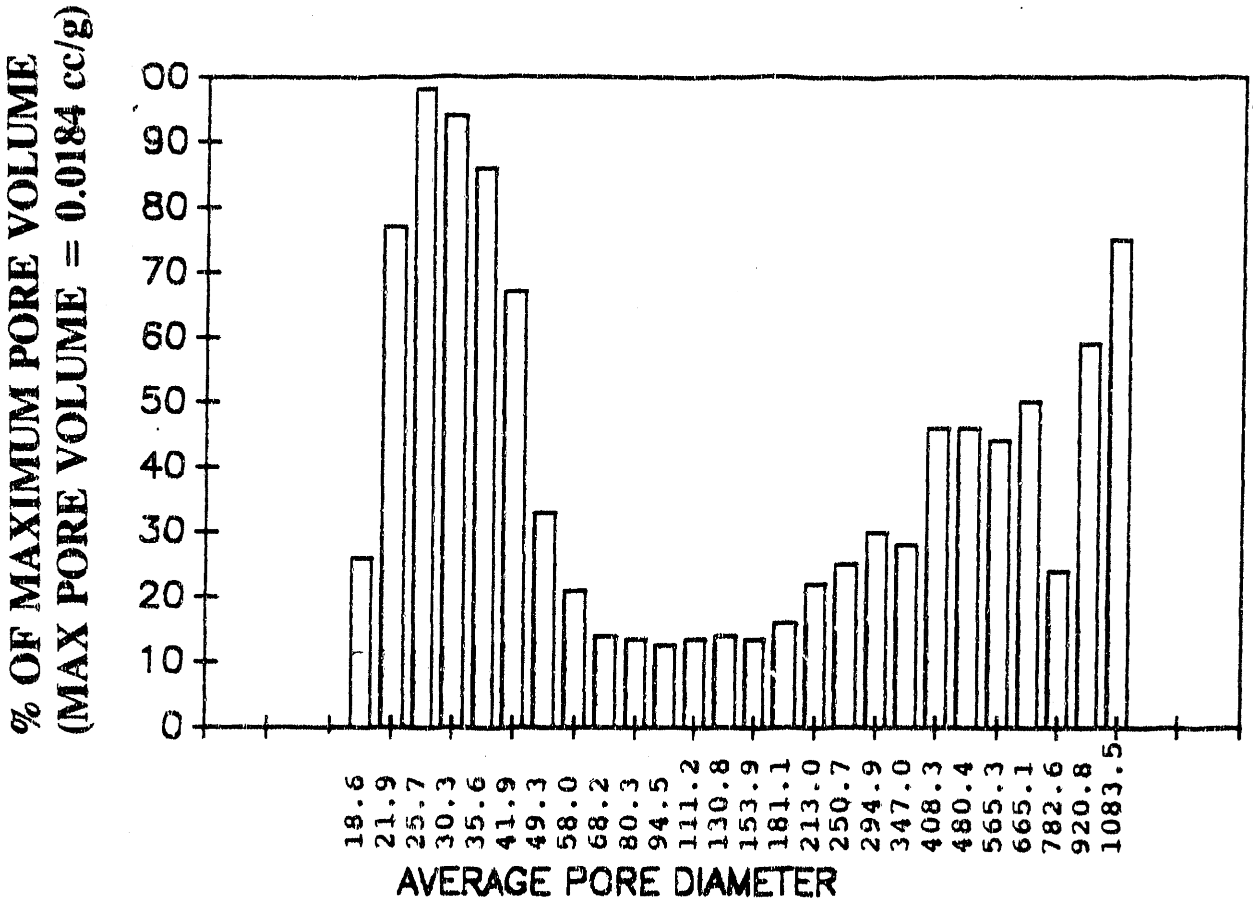

Figure 1. Incremental pore volume distribution of $Pt/ZrO_2/SO_4$ catalyst

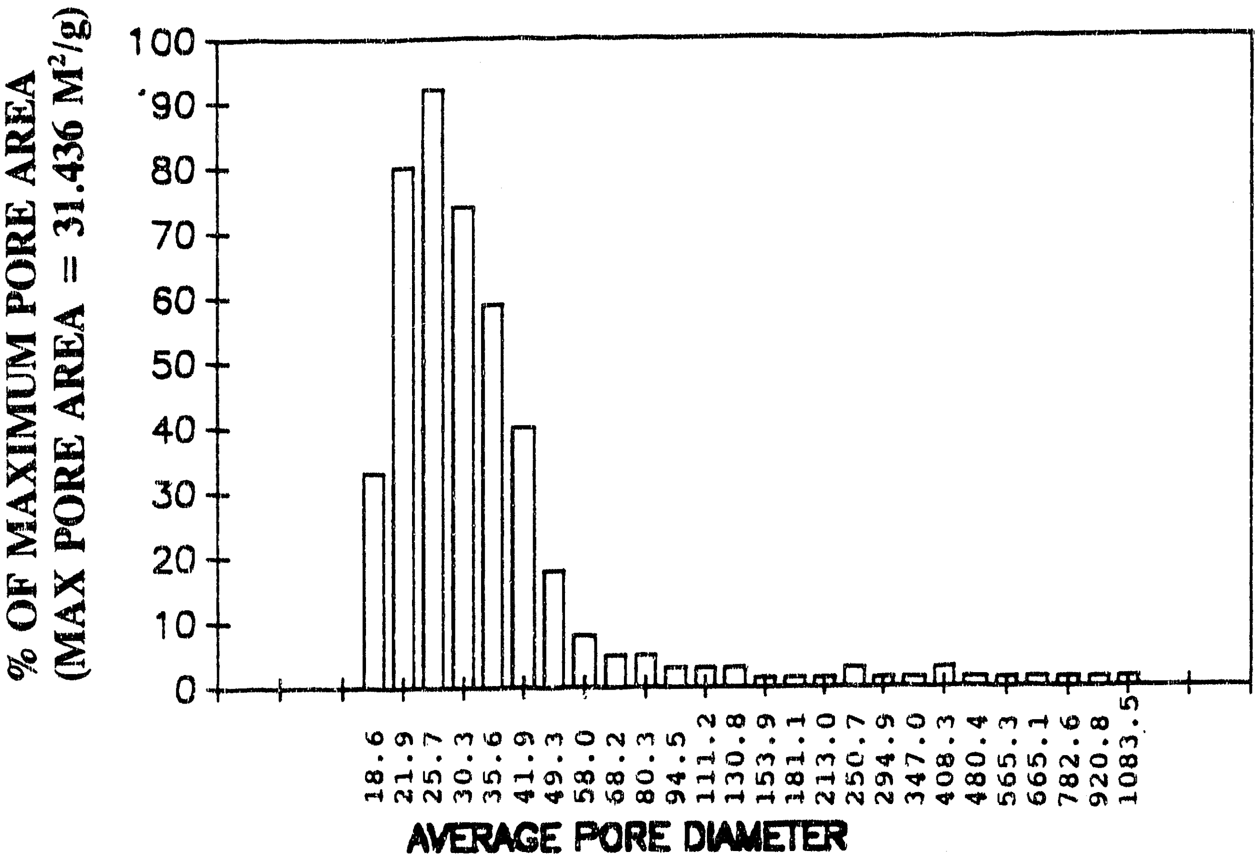

Figure 2. Incremental pore area distribution of $Pt/ZrO_2/SO_4$ catalyst

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