

## **SURFACE PASSIVATION AND SHAPE SELECTIVITY IN HYDROCRACKING OVER ZSM-5**

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The shape selectivity of ZSM-5 has been enhanced by passivating its external surface area by silation. This passivated zeolite is found to be superior for the selective removal of waxy material from a lubricating oil fraction by hydrocracking.

### **1. Introduction**

The shape-selective hydrocracking of the waxy fraction (normal and slightly branched alkanes) in petroleum oils is called hydrodewaxing. These molecules need to be removed to improve the low temperature fluidity (lower the pour points [1]) of the oils. Apart from low pour points, lubricating oils are also expected to possess a low temperature coefficient of viscosity defined by an empirical quantity called viscosity index (VI) [2,3]. During the dewaxing process the normal alkanes should be removed with minimum destruction of the branched and cyclic alkanes as the latter have low pour points and high VI values. An elegant way of achieving this objective is the use of highly shape-selective catalysts.

ZSM-5 zeolites are used, at present, as dewaxing catalysts [4]. In ZSM-5, only those acid sites located within the pore system possess shape selective cracking properties; and the selectivity of ZSM-5 to crack only the normal paraffins can be enhanced by selectively passivating (or poisoning) the acid sites on the external surface of the zeolite crystals [5]. The present report describes the consequence of such a modification on the catalytic properties of ZSM-5 in the dewaxing process.

### **2. Experimental**

Three types ZSM-5 sample were used. Sample A was a small crystallite size material (0.2  $\mu$ m average size) with a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 82. Sample A(S) was prepared from A by passivating its external surface with silica. The passivation was done by adding 50 g of sample A to a solution of di-trimethyl silylamine

(20.87 g) in n-hexane and decomposing the silicon compound at 773 K to deposit the silica (15 wt%) on the external surface. The preferential deposition of the  $\text{SiO}_2$  on the surface was ascertained by XPS measurements. The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of the samples estimated by XPS of the surfaces of A and A(S) were 70.6 and 128.6 while the chemical analysis of the samples gave values of 82 and 90.8 for the samples A and A(S). The larger of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio observed for sample A(S) by XPS measurements shows that  $\text{SiO}_2$  is deposited preferentially on the surface of the zeolite crystallites. Further, adsorption experiments gave similar values for adsorption of n-hexane on both the samples (11.3 wt% and 10.9 wt% for A and A(S) at  $p/p_0 = 0.5$ ) confirming that  $\text{SiO}_2$  did not enter the pores of the zeolites. Sample B was a large crystallite size material (2.0  $\mu\text{m}$  size) with a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 84. The dewaxing catalysts were prepared from these samples by blending them with alumina hydrate in the ratio 65:35 (wt/wt), extruding the mixtures and calcining them at 773 K. The extrudates were then loaded with 1.5 wt% NiO by impregnation of  $\text{Ni}(\text{NO}_3)_2$  and calcination.

The feed used in these studies was a Bright Stock raffinate obtained from a Persian Gulf Crude with the following properties.

Distillation: 5 wt% at 756 K and 95 wt% at 1028 K

Sulfur (wt%): 1.5

Pour point (K): 60.

The dewaxing reaction was carried out in a high pressure down flow fixed bed reactor (Géomécanique, France). The product characterization was carried out by gas chromatographic analysis (Hewlett Packard 5880 A), distillation procedures, Pour point and VI measurements.

### 3. Results and discussions

Table 1 presents the results of the dewaxing of a Bright Stock raffinate over the three catalysts A, A(S) and B to obtain a dewaxed oil with a pour point of 267 K. The temperature required to dewax the feed stock to obtain the dewaxed oil (DWO) with a pour point of 267 K is lower (578–581 K) over the small crystallite samples A and A(S) than over the larger crystallite sample B (603 K). This is attributed to the larger activity of catalysts A and A(S) because of the greater accessibility of their internal surface area (to the reacting molecules) than the large crystallite catalyst B [6]. The VI of the DWO obtained from catalyst A is found to be lower (90.3 for A) than from the larger crystallite catalyst (91.9 for B). In the case of catalyst A (small crystallites) the naphthenic molecules which are too large to enter the zeolite pores and which have large VI values are cracked away by the large external surface leading to a loss in VI of the DWO. The loss of the high VI naphthenic fraction is less on large crystallites with lower external area and the product has a higher VI. The pour point of the DWO is dependent only on the amount of the high melting paraffinic fraction (normal and slightly

Table 1

Shape selectivity in the dewaxing of Bright Stock raffinate over ZSM-5

Conditions: Pressure: 4.5 M Pa; WHSV: 0.8 h<sup>-1</sup>H<sub>2</sub>/oil : 400 v/v; Time on stream: 50–100 h.

| Catalyst/<br>zeolite | Zeolite<br>crystallite<br>size ( ) | Temp. of<br>reaction <sup>2</sup><br>(K) | Prod. distribution (wt.%)      |                     |                  | Viscosity<br>index of<br>DWO <sup>4</sup> |
|----------------------|------------------------------------|--|--------------------------------|---------------------|------------------|---|
|                      |                                    |  | C <sub>1</sub> –C <sub>4</sub> | C <sub>5</sub> –DWO | DWO <sup>3</sup> |   |
| A                    | 0.2                                | 581                                      | 8.8                            | 7.4                 | 83.2             | 90.3                                      |
| A (S) <sup>1</sup>   | 0.2                                | 578                                      | 8.1                            | 7.2                 | 84.7             | 92.0                                      |
| B                    | 2.0                                | 603                                      | 11.5                           | 5.1                 | 84.4             | 91.9                                      |

<sup>1</sup> External surface passivated by silation.<sup>2</sup> Average temperature required to obtain a DWO pour point of 267 K.<sup>3</sup> Dewaxed oil pour point: 267 K.<sup>4</sup> Values accurate to  $\pm 0.4$  units.

Note: Deviations in massbalance from 100% are due to errors in estimation of the lighter fractions.

The DWO yield itself is accurate to  $\pm 0.2$  wt.%.

branched) destroyed by the catalysts. At constant product pour point, the larger crystallites being more shape selective destroy less naphthenes than smaller crystallites thereby producing DWO with higher VI. This is also reflected in the larger yield of DWO (84.4 wt%) obtained on the sample B than on sample A (83.8 wt%).

Though larger crystallites are preferred due to higher DWO yields and larger VI values, these suffer from lower activity (discussed earlier) and larger gas yields due to greater secondary cracking [6]. The gas (C<sub>1</sub>–C<sub>4</sub>) yield is 11.5 wt% for B while it is only 8.8 wt% for A. If the external surface of A is passivated (sample A(S)), the yield and VI of the DWO are both increased (84.7 wt% and 92.0) to the same level of the large crystallite sample B. At the same time the gas yields are low (8.1 wt%) and the activity is higher (same as A). Thus increasing the shape selectivity of small crystallite ZSM-5 by passivating its external surface leads to a superior catalyst for dewaxing purposes.

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