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Hydrocracking of Vacuum Gasoil on the Novel Mesoporous MCM-41 Aluminosilicate Catalyst

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The performance of NiMo (12 wt% MoO_3, 3 wt% NiO) supported on the mesoporous crystalline MCM-41 aluminosilicate for mild hydrotreating of a vacuum gasoil has been compared with that of an amorphous silica–alumina and a USY zeolite with the same Ni and Mo loadings. The MCM-41-based catalyst was seen to give superior HDS, HDN, and HC activities to the latter two catalysts in a one-stage operation using an untreated gasoil. The better performance of the former catalyst is explained by its higher surface area, the presence of uniform pores in the mesopore range, mild acidity, and stability. In the case of a two-stage operation using a pretreated feed, the MCM-41 catalyst showed a lower HC activity than USY, but higher than the amorphous silica–alumina while preserving its better selectivity to middle distillates. © 1995 Academic Press, Inc.

INTRODUCTION

Hydrotreating of petroleum fractions has become a key process in the modern refining industry due to increasing environmental concerns, which has increased the demand for cleaner distillates (1). Catalytic hydrotreating is also commonly used to upgrade the quality of feedstocks in order to increase the performance and product specifications in downstream deep conversion units, such as catalytic cracking and hydrocracking. The term hydrotreating is commonly used to refer to a mild operation in which the primary purpose is to remove heteroatoms, mainly sulfur and nitrogen (HDS and HDN operations, respectively), without altering too much the boiling range of the feed. By contrast, hydrocracking refers to the process in which the main objective is to convert the heavy fractions of the feed into more valuable lighter products, such as naphtha, kerosene, and middle distillates (2). Hydrocracking is characterized by its high flexibility in processing a wide variety of feedstocks and obtaining a wide range of products ranging from LPG to lube base oils (2), and is carried out under more severe conditions, in terms of hydrogen pressure and temperature, than conventional hydrotreating. There is, however, a relatively new process known as "mild hydrocracking" (MHC) that can be considered as intermediate between hydrotreating and conventional hydrocracking (3). MHC is performed at much lower hydrogen pressures ($\leq$50 bar) than conventional high-pressure hydrocracking, and requires temperatures slightly higher than hydrotreating. Under these conditions the fraction of feedstock converted to lighter products is relatively low (typically less than 50%) as compared to more severe hydrocracking, and thus MHC is mainly directed to the production of low-sulfur fuel oil and middle distillates (3). As a consequence of the relatively low hydrogen pressures used in MHC, hydrogenation of aromatic compounds present in the feed occurs at a lower extent, and therefore, the quality of the diesel oil produced, in terms of cetane index, is not so high even though in some cases it can meet market specifications. Nevertheless, the steady increase in demand for middle distillates expected for the next years (3), and the low investment costs required for MHC operation (4), since it can be well carried out on existing hydrotreating units after proper revamping, makes MHC a very attractive and inexpensive way to convert vacuum gasoil into more valuable products.

Typical catalysts used in MHC include a hydrogenating–dehydrogenating function supplied by the combination of two nonnoble metals, usually Co (or Ni) and Mo (or W), supported on an acidic carrier, such as halogen-doped alumina, silica–alumina, or zeolites, which allow conversion of heavy hydrocarbons via carbenium ion cracking. The zeolite containing catalysts are now used extensively in MHC. The amorphous-based hydrocracking catalysts are more sensitive to deactivation by coking and by organic nitrogen compounds and ammonia, formed in the hydrodenitrogenation (HDN) reactions, than zeolite-based catalysts (2). However, because of their very high cracking activity, zeolite-based hydrocracking catalysts show a higher selectivity to LPG, gasoline, and low to middle distillates than the amorphous systems (5).

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Moreover, an important aspect of hydrocracking catalysts which takes special relevance when processing heavy feedstocks is the pore distribution of the support, not only to favor an optimum dispersion of the metals on its surface, but also to facilitate the diffusion of the voluminous feed molecules through the pores to the acid sites where cracking will occur. This is a serious problem for zeolite-based hydrocracking catalysts, even if a large pore Y-type zeolite with enhanced mesoporosity is used (5). Thus, it appears that there is still room for searching for new MHC catalysts with improved activity and stability while preserving the good middle distillates selectivity of current amorphous or zeolitic catalysts.

In this respect, the synthesis of a novel mesoporous aluminosilicate, MCM-41, having a uniform system of channels ranging from 16 to 100 Å in diameter (6), has been recently described. MCM-41 can be synthesized in a wide range of Si/Al ratios, and it has been shown to have, after elimination of the template by calcination, acidic OH groups of lower acid strength than those of zeolites (7).

In this paper we have investigated using the mesoporous MCM-41 material as a support in the preparation of bifunctional NiMo-based catalysts suitable for hydrocracking a vacuum gasoil (VGO) under mild operating conditions. For this study we have used three different feedstocks. The first one is an untreated VGO, and the other two are VGO hydrotreated at two different severities to obtain feeds with different S and N content and distillation range. For the MHC of untreated VGO, the performance of the NiMO/MCM-41 catalyst, in terms of HDS, HDN, and MHC activities, is compared with that of amorphous silica–alumina and an ultraestable low unit cell size Y zeolite (USY) having the same Ni and Mo contents. The same reference catalysts were used to compare the hydrocracking activity of the NiMo/MCM-41 sample using the two hydrotreated feeds.

EXPERIMENTAL

Preparation of Catalysts

The MCM-41 aluminosilicate sample was synthesized from Aerosil and $Al_2O_3 \cdot 4H_2O$ as silica and alumina sources, respectively, using hexadecyltrimethylammonium (CTMA) as a template following the procedure described in Ref. (8). The molar composition of the resulting gel can be expressed as

$$SiO_2/Al_2O_3 = 28; \quad OH/SiO_2 = 0.174; \quad H_2O/(CTMA)_2 = 343.$$

The crystalline solid obtained showed a broad XRD band at low angles ($\Theta \sim 2°$) characteristic of MCM-41 material (6). Then, the as-synthesized material was calcined in a N_2 atmosphere at 540°C during 1 h followed by a 6-h calcination in air at the same temperature. This activation procedure has been shown to produce more crystalline and acidic samples as compared to the direct calcination in air (7).

NiMo/MCM-41 catalyst was then prepared by the incipient wetness impregnation technique, with the required amount of an aqueous solution of ammonium heptamolybdate (AHM) and nickel nitrate (NN) to obtain catalysts of 12 wt% MoO_3 and 3 wt% NiO. After impregnation with AHM, the sample was calcined at 500°C for 3 h then impregnated with NN and finally calcined again as above.

NiMo impregnated on amorphous silica–alumina (25 wt% Al_2O_3, Crossfield) and zeolite Y with a unit cell of 24.24 Å, 0.4–0.6 μm crystal size and 0.03 wt% Na_2O (CBV760, PQ Corp.) were prepared in the same way as described for MCM-41. The metal oxide contents of these two catalysts were also 12 wt% MoO_3 and 3 wt% NiO.

Characterization of Catalysts

X-ray powder diffraction (XRD) was carried out on a Phillips PW equipment using the Cu$K\alpha$ radiation, and was used to evaluate the peak position of the as-synthesized MCM-41 sample, as well as the crystallinity of MCM-41 and USY catalysts after the different treatments.

Surface area, pore volume, and average pore diameter were calculated from the adsorption–desorption isotherms of N_2 at 77 K on a ASAP-2000 apparatus.

The acidity of the supports and final NiMo catalysts was measured by IR spectroscopy with adsorption and

TABLE 1

Properties of Untreated (A) and Hydrotreated (B and C) Gasoil Feedstocks

Feedstocks	A	B	C
Sulfur content (wt%)	2.53	0.15	0.035
Nitrogen content (ppm)	2900	2000	1500
Carbon Conradson (wt%)	0.39	0.19	0.10
Density, g/cm^3 (60°C)	0.917	0.879	0.867
Refraction index (67°C)	1.519	1.498	1.498
Distillation range (°C)			
IBP	181	124	85
5%	336	230	160
10%	364	289	195
30%	404	369	292
50%	429	405	349
70%	453	436	389
90%	488	475	435
95%	505	493	454
FBP	559	542	490
360°C+ (wt%)	91.0	73.8	44.9

TABLE 2

Textural Properties of Unsupported and NiMo-Supported Catalysts

Sample	BET surface area ($m^2 \cdot g^{-1}$) Micropore	BET surface area ($m^2 \cdot g^{-1}$) Total	Pore volume ($cm^{-3} \cdot g^{-1}$) Micropore	Pore volume ($cm^{-3} \cdot g^{-1}$) Total	APD[a] (nm)
MCM-41	0	648	0	0.54	3.3
NiMo/MCM-41	0	519	0	0.60	4.6
SiO_2–Al_2O_3	21	268	0.01	0.31	4.6
NiMo/SiO_2–Al_2O_3	15	171	<0.01	0.29	6.8
USY	362	551[b]	0.18	0.41	2.1
NiMo/USY	179	283	0.09	0.29	2.9

[a] Average pore diameter.

[b] The PQ data specifies a surface area of 720 $m^2 \cdot g^{-1}$.

desorption of pyridine at different temperatures. A more detailed description of the procedure was given elsewhere (9).

Reaction System and Procedure

Catalytic experiments were performed in a fixed bed stainless steel tubular reactor having 2.54 cm internal diameter and 65 cm length. Catalyst particles of 0.59–0.84 mm in size were diluted with CSi (diluent/catalyst ratio of 5.5–6.5 by weight) until a constant volume of 40 cm^3 before being introduced into the reactor. The hydrocracking experiments on the different NiMo catalyst were carried out using three different feedstocks (A, B, and C) whose physicochemical characteristics are given in Table 1. Feed A is a vacuum gasoil containing 2.5 wt% sulfur and 2800 ppm nitrogen and was used to evaluate the HDS, HDN, and HC activities of the catalysts in a single stage MHC operation. Feeds B and C were obtained by hydrotreating feed A with a commercial CoMo/alumina catalyst (TK-525, Tøpsoe) under two different conditions. Feed B was obtained at 320°C reaction temperature, 4.0 MPa, WHSV = 0.75 h^{-1}, H_2/feed ratio of 600 Nm^3/m^3, and the conditions for obtaining feed C were 450°C, 3.0 MPa, WHSV = 1.5 h^{-1}, and H_2/feed ratio of 600 Nm^3/m^3. Both feeds differ in the S and N content, as well as in the distillation range (see Table 1). Then, feeds B and C were used to evaluate the HC activity of the catalysts in a hypothetical two-stage operation.

The catalysts were presulfided before starting a reaction run by using a mixture of H_2S/H_2 (10 vol% H_2S) at atmospheric pressure and 400°C for 3 h. The reaction conditions for the hydrocracking experiments were 350–450°C reaction temperature, total pressure of 3.0–4.0 MPa, H_2/feed ratio of 1000–3000 Nm^3/m^3, and WHSV = 1–2 h^{-1}.

The activities reported were obtained after a period of 6–10 h operation, for which steady state behavior was observed.

The distillation curve of the liquid products was determined by SIMDIS (ASTM D-2887) in a Varian GC 3400. The amount of S in the liquids products was measured by X-ray fluorescence (XRF) in an Outokumpu X-MET 840, and the N content was determined by chemiluminiscence in a elemental analyzer (Antek 7000 NS).

RESULTS AND DISCUSSION

The textural properties of unsupported and NiMo containing catalysts derived from the N_2 adsorption–desorption experiments are given in Table 2. For the metal-free samples, it can be seen that MCM-41 presents the highest surface area and pore volume, with all pores being in the

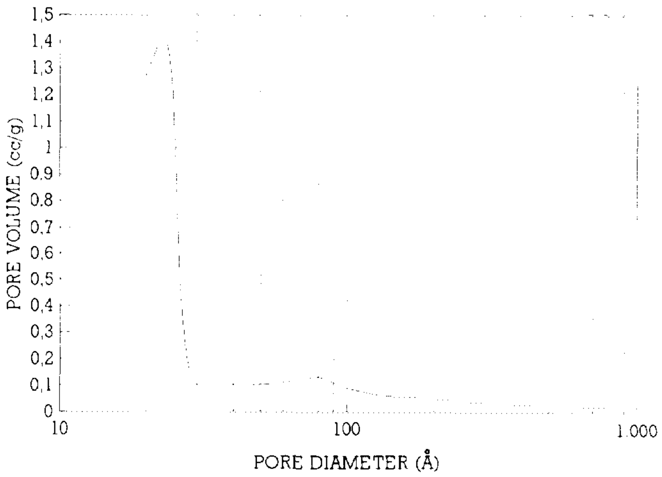

FIG. 1. Pore size distribution of calcined MCM-41 sample.

TABLE 3

Acidity (μmol Py/g Catalyst) of Supports and Final NiMo Catalysts as Measured by IR-Pyridine Experiments at Different Desorption Temperatures

	Brønsted			Lewis		
Sample	150°C	250°C	350°C	150°C	250°C	350°C
MCM-41	23	9	4	83	58	34
NiMo/MCM-41	13	0	0	66	29	10
SiO_2–Al_2O_3	22	10	2	60	38	22
NiMo/SiO_2–Al_2O_3	10	0	0	15	6	0
USY	—	37	15	—	20	13
NiMo/USY	—	15	4	—	19	10

Note. Calculated using the extintion coefficients given by Hughes and White (10).

mesopore range. The pore size distribution of calcined MCM-41 shows a unique peak centered at about 25 Å diameter (Fig. 1). By contrast, most of the pores present in the USY zeolite belong to the micropore range, although some mesoporosity created during the thermal–hydrothermal treatments is also observed. The amorphous silica–alumina sample shows lower surface area and pore volume than the above two catalysts, with most of its pores belonging to the mesopore range. After impregnation of Mo and Ni, a decrease in the surface area is observed in all three catalysts, the relative decrease being much more pronounced in the USY sample. Moreover, the total pore volume of the mesoporous MCM-41 and amorphous silica–alumina remains practically constant after impregnation, while strongly decreasing for the zeolite catalysts.

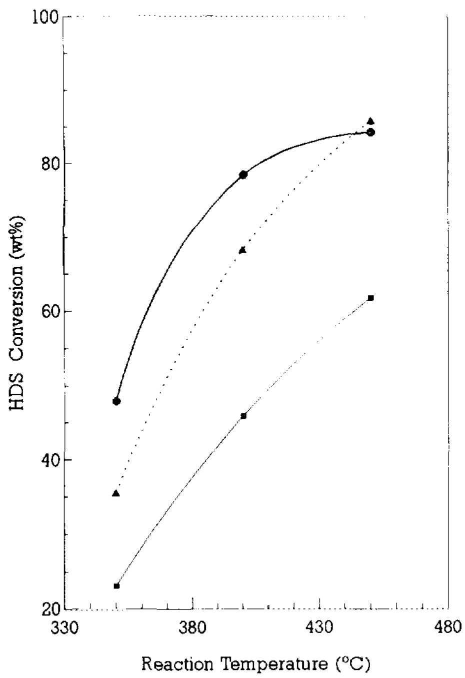

FIG. 2. Hydrodesulfurization (HDS) conversion of feed A as a function of reaction temperature for (●) NiMo/MCM-41, (▲) NiMo/SiO_2–Al_2O_3, (■) NiMO/USY catalysts.

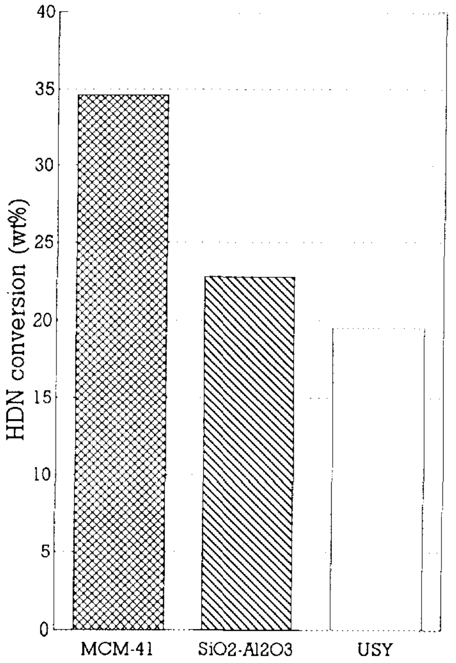

FIG. 3. Hydrodenitrogenation (HDN) conversion of feed A obtained at 400°C reaction temperature on the different supported catalysts.

On the other hand, the acidity results of the supports and final NiMo catalysts are presented in Table 3. For the unsupported samples, USY zeolite shows the highest amount of Brønsted acid sites, most of them being of medium–strong acidity. Table 3 also shows that the acid-

TABLE 4

First-Order Kinetic Rate Constants Obtained for the HDS and HDN of Untreated Feed A at 400°C

	Rate constants ($cm^3/g \cdot h$)	
Catalyst	K_{HDS}	K_{HDN}
NiMo/MCM-41	3.34	0.93
NiMo/SiO_2–Al_2O_3	2.51	0.56
NiMo/USY	1.34	0.48

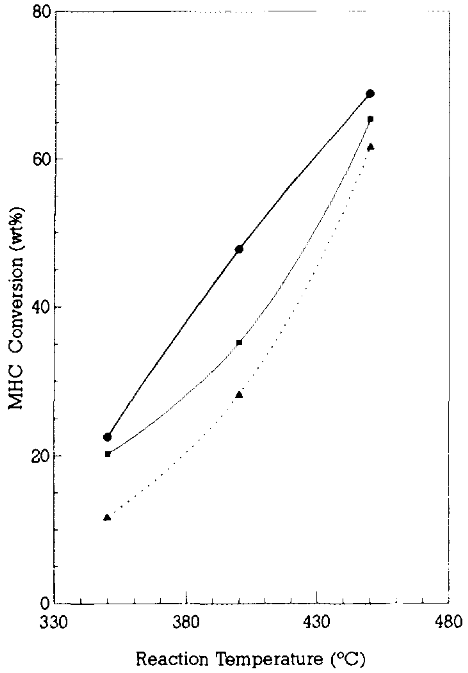

FIG. 4. Hydrocracking (MHC) conversion of feed A as a function of reaction temperature. Same symbols as in Fig. 2.

ity of the mesoporus MCM-41 sample is similar to that of amorphous silica–alumina, both in number and acid strength distribution. Moreover, most of the Brønsted acid sites in the two latter catalysts are of weak–medium strength. It should also be noticed that the amount of Lewis acid sites in the MCM-41 sample is very high, which can be associated with the presence of extraframework aluminum released during the activation treatments, as was demonstrated by ^{27}Al MAS NMR experiments (11). After impregnation of molybdenum and nickel, the Brønsted and Lewis acidity of the catalysts decreases. The decrease in the concentration of Brønsted sites is thought to be due to interaction of the Mo species present during impregnation step with both surface and internal, in the case of zeolites, OH groups of the support (12). This interaction takes place mainly with the strongest Brønsted acid sites, as can be observed from the strong decrease in the amount of pyridine desorbed at the highest temperature (350°C) in the NiMo-containing samples. Thus, practically all the strong Brønsted acid sites on the MCM-41 and amorphous silica–alumina samples disappear after impregnation.

One-Stage Mild Hydrocracking (MHC) of Vacuum Gasoil

Although the main objective of mild hydrocracking (MHC) is the partial conversion of the feed molecules into more valuable lighter products, heteroatom removal (HDS/HDN) is also an important aspect of MHC. In this study we have measured the steady-state activities of the different NiMo catalysts for the HDS, HDN, and MHC of a vacuum gasoil (feed A in Table 1) under the following conditions: 3 MPa total pressure, H_2/feed ratio of 1000 Nm^3/m^3, WHSV of 2 h^{-1}, and temperatures ranging from 350 to 450°C. Figure 2 shows the HDS activity as a function of reaction temperature. For all the three catalysts an increase in the HDS conversion is observed when increasing reaction temperature. It is seen in Fig. 2 that the MCM-41 based catalyst is the most active for the HDS in this range of temperatures, although at 450°C the amorphous silica–alumina gives a similar HDS conversion, indicating a higher activation energy for HDS on the latter catalyst. On the other hand, the zeolite-based catalyst is the less active in the whole range of temperatures. The HDN conversions obtained at 400°C are given in Fig. 3. In general, the HDN conversions are relatively low as compared to HDS under the experimental conditions used, which is in agreement with the much higher severity, in terms of hydrogen pressure, known to be required to perform HDN adequately. The reason for this is that the hydrogenolysis of the C–N bond in polyaromatic molecules requires the previous hydrogenation of the aromatic ring containing the heteroatom, to which its extent is limited by the relatively low H_2 pressure used in this study. Nevertheless, it can be clearly observed in Fig. 3 that the MCM-41-based catalyst is, by far, the most active catalyst toward hydrodenitrogenation (HDN).

The pseudo-first order kinetic rate constants for both HDS and HDN obtained at 400°C reaction temperature on the NiMo-supported catalysts are compared in Table 4.

The relatively high HDS and HDN activities obtained on the NiMo/MCM-41 catalyst can be related, in principle, to its very high surface area (Table 2) and to the mesoporous structure of the MCM-41 aluminosilicate,

TABLE 5

Product Distribution Obtained in the Mild Hydrocracking of Vacuum Gasoil (Feed A) at about 50 wt% Hydrocracking Conversion to Products Boiling below 360°C on the Different NiMo Catalysts

	Distribution of products boiling below 360°C (wt%)		
Catalyst	C_1–C_4	Naphtha[a]	Middle distillates[b]
NiMo/MCM-41	16.2	25.8	58.0
NiMo/SiO_2–Al_2O_3	18.9	23.1	57.9
NiMo/USY	19.7	27.3	52.0

[a] Naphtha: C_5-195°C bp.

[b] Middle distillates: 195–360°C bp.

TABLE 6

Results of Two-Stage Hydrocracking of Feed B

Catalyst	Temperature (°C)	Hydrocracking conversion (wt%)	Product distribution (wt%)			
			C_1–C_4	Naphtha	MDs[a]	360°C+
NiMo/MCM41	400	30.1	4.6	10.8	33.0	51.6
	450	77.8	10.8	31.5	41.3	16.4
NiMo/SiO_2–Al_2O_3	400	20.2	4.1	6.6	30.4	58.9
	450	71.5	12.6	24.4	42.0	21.0
NiMo/USY	400	30.8	7.0	11.9	30.0	51.1
	450	82.8	13.3	34.7	39.3	12.7

[a] MDs = middle distillates.

which would favor a high dispersion of the active species while increasing the accessibility of the large molecules of the gasoil feed containing the heteroatoms to the catalyst active sites. On the other hand, it has been shown by NMR that MCM-41 undergoes a deep dealumination upon calcination (11), giving rise to the formation of aluminum-type species which are well dispersed on the surface, and this could cause interactions of Mo and Ni with the dispersed alumina to form Ni—Mo species similar to those present in the γ-Al_2O_3 based catalysts, which are known to be very active for HDS and HDN.

Finally, the MHC conversions obtained at steady state for the untreated gasoil are presented in Fig. 4 as a function of reaction temperature. The net hydrocracking conversion into products boiling below 360°C has been calculated as follows:

$$\%\text{MHC} = \frac{\begin{array}{c}(\text{wt\% of } 360^\circ\text{C+ in feed})\\ -\ (\text{wt\% of } 360^\circ\text{C+ in products})\end{array}}{(\text{wt\% of } 360^\circ\text{C+ in feed})} \times 100$$

It can be seen in Fig. 4 that the MCM-41-based catalyst gives the highest hydrocracking conversion in the whole range of temperatures studied. In principle, one would expect the hydrocracking activity to correlate with the acidity of the different catalysts. However, the results of Fig. 4 do not show such a correlation, but the most acidic USY-based catalyst, according to the IR-pyridine experiments (Table 3), is less active for MHC than the catalyst based on MCM-41. These results would suggest that the accessibility of the large feed molecules to the Brønsted acid sites of the support should play an important role in the observed hydrocracking activity. Thus, the fraction of active sites accessible to the feed molecules will be larger on the mesoporous MCM-41 aluminosilicate than on the microporous system of the USY zeolite.

On the other hand, it has to be considered that the acidic hydrocracking catalysts used in a first-stage operation, as is the case under study, are readily poisoned by strong adsorption of organonitrogen compounds and ammonia formed during hydrodenitrogenation, and this has a direct effect on the final hydrocracking activity. Indeed, it has been shown that there is a close relationship between the HDN and the HC activities of amorphous and crystalline (zeolite) aluminosilicates (13). Then, it becomes clear from this that the higher HDN activity observed for the MCM-41 catalyst should contribute to its higher cracking activity. Moreover, the results of Table 5 show that at

TABLE 7

Results of Two-Stage Hydrocracking of Feed C

Catalyst	Temperature (°C)	Hydrocracking conversion (wt%)	Product distribution (wt%)			
			C_1–C_4	Naphtha	MDs[a]	360°C+
NiMo/MCM41	350	18.7	2.1	14.3	47.1	36.5
	400	27.8	12.8	15.6	39.2	32.4
NiMo/SiO_2–Al_2O_3	350	12.9	2.3	13.9	44.7	39.1
	400	22.7	5.2	14.5	45.6	34.7
NiMo/USY	350	31.0	4.9	21.9	42.2	31.0
	400	39.2	14.4	25.4	32.9	27.3

[a] MDs = middle distillates.

about 50 wt% hydrocracking conversion, which is the conversion typically achieved in one-stage mild hydrocracking, MCM-41 is more selective for middle distillates (195–360°C bp) and less selective for gases (C_1–C_4) and naphtha (C_5-195°C) than USY. When compared to the amorphous silica–alumina catalyst, MCM-41 gives practically the same selectivity to middle distillates while being more selective for naphtha. Then, it would appear that less recracking occurs on MCM-41. Since acidities are very similar on the two mesoporous catalysts (Table 3) it appears that the higher selectivity to naphtha of MCM-41 than SiO_2–Al_2O_3 could be due to its porosity formed by monodirectional tubes of 35 Å which will cause a higher recracking of the large distillate molecules when diffusing out of the pores, while the less voluminous naphtha molecules should have less problems to diffuse and will suffer a lower recracking.

Simulated Two-Stage Hydrocracking Operation

This part of the study was performed using the previously described hydrotreated feeds B and C (Table 1). Then, these feeds were hydrocracked at 4.0 MPa, 3000 Nm^3/m^2 H_2/feed ratio, and WHSV of 1 h^{-1} on the sulfided NiMo catalysts discussed above. Tables 6 and 7 summarize the hydrocracking results for feeds B and C, respectively, at two different reaction temperatures. The hydrocracking conversions given in Tables 6 and 7 have been calculated taking into account the amount of 360°C+ products present in feeds B and C (Table 1) and using the same equation as for one-stage operation. It can be observed that the MCM-41-based catalyst gives a HC activity similar to that of the USY sample for hydrocracking feed B, which still contains a significant amount of 360°C+ compounds (Table 1). However, the USY sample is the most active for hydrocracking feed C, which has a substantial amount of lighter products (55.1 wt% of 360°C–, Table 1). The higher HC activity obtained for the hydrotreated feeds, in contrast to what was observed for untreated gasoil, with the USY zeolite catalyst can be ascribed, on the one hand, to the lower organic nitrogen content of the hydrotreated feedstocks which would decrease poisoning of the most acidic Brønsted sites of the zeolite, and on the other hand, to the higher content of partially cracked molecules formed after hydrotreating, especially in feed C. The smaller molecules left can easily penetrate into the channels of the zeolite structure and then access the acid sites. However, as can be observed in Tables 6 and 7, the MCM-41 catalyst produces a more selective cracking toward middle distillates than USY, provided by the milder acid strength of the former. It has to be considered that the higher recracking produced in the zeolite is also due to the larger number of stronger acid sites and lower diffusion rate of products in the micropores of the zeolite-based catalyst. Moreover, the MCM-41 catalyst is more active for hydrocracking both feeds B and C than the amorpous silica–alumina while preserving a good selectivity toward middle distillates.

CONCLUSIONS

A crystalline mesoporous aluminosilicate such as MCM-41 is a good catalyst for carrying out MHC of vacuum gasoil. A combination of large surface area, uniform pore size distribution, large enough to allow diffusion of large molecules, together with the presence of mild acidity and high stability, produces a superior HDS, HDN, and hydrocracking performance than either amorphous silica–alumina or a low unit cell size USY zeolite. However, in a hypothetical two-stage operation using a pretreated feed with lower sulfur and nitrogen contents, and with a boiling range shifted to lower boiling point products, the USY-based catalyst shows its superior hydrocracking activity. Nevertheless, the MCM-41 catalyst is more selective toward middle distillates (MDs) than the zeolite. When compared to an amorphous silica–alumina, MCM-41 gives similar selectivity to MDs while giving a higher hydrocracking conversion at a given reaction temperature.

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