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MILD HYDROTREATING OVER NiMo/SEPIOLITE CATALYST

Nancy Martín^{a*} and Francisco Melo^b

^aUAM-I, Depto. Química, Av. San Rafael Atlixco, 186, 09340 México, D. F., Mexico.

^bUPV-ITQ, Av. De los Naranjos s/n, Valencia, España

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Abstract

In order to introduce an alternative catalyst for hydrotreating (HDT) reaction a study of NiMo supported on natural sepiolite catalysts is presented. The sepiolite catalyst has been prepared in this laboratory and a NiMo/Al₂O₃ commercial catalyst is used as a reference. The textural properties of the materials and their catalytic activity in hydrotreating (HDT) and hydrodesulfuration (HDS) using an FCC feed at 400–475°C and 50 MPa total pressure, have been evaluated. The support of the commercial catalyst is alumina containing mesopores. The sepiolite support is a hydrated magnesium phyllosilicate containing micropores but with an open structure that confers the possibility to use it as a catalyst. The hydrotreating conversion (wt.% HDT) is defined here as the net hydrotreating conversion into products boiling below 380°C. For the commercial catalyst the wt.% HDT was only 5% higher than for the catalyst supported on sepiolite and the product selectivity was very similar. HDS conversion was 20% lower for the sepiolite supported catalyst. Taking into account these results the sepiolite is a suitable support of HDS catalysts.

Keywords: Sepiolite, hydrodesulfuration, hydrotreating

*Corresponding author. Fax: (52)(55)58044666; E-mail: mgnc@xanum.uam.mx

INTRODUCTION

Crude oil supplied today throughout the world has a comparatively high API gravity and high levels of sulfur. At the same time demand for distillate products is increasing with no change in the demand for heavy oil. These trends have emphasized the importance of processes that convert the heavier oil fractions into lighter and more valuable clean products, processes like hydrotreating and hydrocracking [1].

Catalysts for such hydrotreating processes are chosen on the basis of activity, selectivity, and life time. New types of catalysts with significantly improved catalytic performance must be developed to satisfy future environmental legislation.

Sepiolite is a good candidate as support of catalysts for hydrotreating of heavy feeds particularly in the vacuum bottom conversion catalysts. This is based on their favorable characteristics for similar reactions.

Sepiolite is a clay mineral having the formula $\text{Si}_{12}\text{Mg}_8\text{O}_{30}(\text{OH})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$ [2] formed by bidimensional layers of tetrahedral silica and octahedral magnesia in a 2:1 proportion, sharing oxygen in the apical borders of the layers in such a way that a permanent microporosity $10.8 \times 4.0 \text{ \AA}$ in size is generated imparting a fiber-like morphology to the material made up of cylindrical pores among the fibers. The sepiolite texture, with an open porous network, free from constrictions, is quite suitable to retain sulfur compounds.

Studies on hydrotreating reactions catalyzed by NiMo sepiolite using untreated and acid-treated sepiolite have been reported [3]. The authors showed that the best performance was obtained for the first one, indicating that basic sites are preferred for anchoring the MoO_3 particles compared to acidic sites.

The advantage of using sepiolite as support instead of alumina is that this material does not require any treatment after its extraction due to its high purity, and is a natural very abundant cheap material.

In this contribution, we present the behavior of a sepiolite supported Ni-Mo catalyst for hydrotreating and hydrodesulfurization of an FCC feed under mild conditions. The performance of the NiMo/sepiolite catalyst in terms of HDS and hydrotreating activities is compared with that of a commercial NiMo/alumina having similar Ni and Mo contents.

EXPERIMENTAL

The sepiolite used as support comes from Vallecas (Madrid) and was provided by TOLSA S.A. (Spain). It is an aluminated sepiolite with more than 95% sepiolite content. The catalyst was prepared by simultaneous impregnation of the support with an appropriate solution of ammonium heptamolybdate and nickel nitrate (Merck) to obtain of 4 wt.% NiO and 20 wt.% MoO_3 . The impregnated samples (NiMo/SE) were dried in air at 373 K overnight and

calcined in air at 773 K for 3 h with a temperature rate of 2 K/min. A commercial NiMo/Al₂O₃ catalyst (TK-525 by Haldor Topsoe A/S) (NiMo/A) was used as a reference catalyst. The metal oxide contents of these two catalysts were measured by atomic absorption spectroscopy in a Spectra A 10 Plus Varian spectrometer. Textural properties were determined from the N₂ adsorption isotherms at 77 K in an ASAP-2000 Micromeritics apparatus. The acidity of catalysts was measured in a FTIR Nicolet 710 Spectrometer with adsorption and desorption of pyridine at 423 K.

Table 1

Properties of FCC feed

Sulfur content (wt.%)	1.487
Nitrogen content (ppm)	1690
Vanadium content (ppm)	1.6
Specific gravity, 15°C (g cm ⁻³)	0.931
Distillation range ASTM 1160 (°C)	
5 wt.%	364
10 wt.%	395
30 wt.%	432
50 wt.%	456
70 wt.%	493
90 wt.%	562
VABP (°C)	468
380°C ⁺ (wt.%)	88.1

The liquid feed used in this study was an FCC provided by a Huelva refinery of CEPSA, Spain. The main physicochemical properties of the feed are listed in Table 1. Hydrotreating of a FCC feed was performed in a fixed bed stainless steel tubular reactor having 2.54 cm ID and 65 cm length. The reactor was loaded with 6 g of 0.25-0.42 mm particles, diluted with SiC to reach a constant bed volume of 11 cm³. Then the catalysts were presulfided at atmospheric pressure and 673 K for 3 h using a mixture of 10 vol. % H₂S in H₂. The reactions were carried out at 5 MPa total pressure, 673-748 K temperature, and H₂/feed ratio of 1000 Nm³/m³. The weight hourly space velocity, WHSV, was 5 h⁻¹. In all cases the catalytic data reported here correspond to the stationary behavior which was obtained after a period of operation of 5 h. The hydrotreating (HDT) conversion (%C_{380°C⁺}) is defined here as total yield of products boiling below 653 K (380°C) and has been calculated as follows:

$$\text{wt.\% HDT} = \frac{(\text{wt.\% of } 380^{\circ}\text{C}^{+} \text{ in feed}) - (\text{wt.\% of } 380^{\circ}\text{C}^{+} \text{ in products})}{(\text{wt.\% of } 380^{\circ}\text{C}^{+} \text{ in feed})} \times 100$$

The distillation curve of the liquid products was determined by simulated distillation (SIMDIS, ASTM D-2887) in a Varian GC 3400 equipped with a FID and a capillary column. The gases in the reaction products were analyzed in a HP-GC 5890 Series II with a TCD and a capillary column. The sulfur content of the feed and liquid products were determined by X-ray fluorescence in a Philips MiniPal EDX spectrometer.

RESULTS AND DISCUSSION

The chemical composition and the textural properties of the sepiolite support (SE) and the catalysts derived from the N₂ adsorption-desorption experiments are given in Table 2. The sepiolite catalyst shows lower surface area and pore volume than the alumina catalyst with most of its pores belonging to the mesopore range, although some mesoporosity could be created during the thermal treatments. The surface area in the impregnated sepiolite decreases by 28% due to the deposition of metals (NiMo) and subsequent calcination at 873 K. This is due to blocking of the micropores of sepiolite during the impregnation process [4].

Table 2
Textural properties and acidity of catalysts.

Catalysts	Composition ^a (wt.%)		Acidity ^d		Area BET	Volume pore	Average pore diameter
	MoO ₃	NiO	Bronsted	Lewis	(m ² /g)	(cm ³ .g ⁻¹)	(nm)
SE	0.0	0.0	3.0	27.5	206.2	0.272	7.4
NiMo/SE ^b	3.4	14.3	3.3	35.6	172.7	0.245	5.7
NiMo/A ^c	3.9	18.0	2.9	25.0	213.9	0.457	8.2

^a Obtained by Absorption Atomic Spectroscopy

^b Supported on sepiolite

^c Commercial catalyst, supported on alumina

^d μmol of pyridine/g of catalyst obtained at 423 K

Pyridine adsorption was used to titrate Brönsted and Lewis acid sites. Acid sites at 423 K obtained from the FTIR spectra are given in Table 2. There are no

apparent differences in acidity between the two catalysts. Experiments at higher temperatures indicated that most of the acids sites in our catalysts are of weak or medium strength.

In this study we have measured the steady-state activities of the NiMo/alumina and NiMo/sepiolite catalysts for the HDS and HDT of an FCC feed under mild conditions. Figure 1 shows the activity for HDT and HDS reactions as a function of reaction temperature. The catalyst NiMo/SE displays a HDS activity slightly lower to that obtained for the commercial catalyst. However, it can be seen a similar behavior is observed for both samples, *i.e.*, HDT and HDS conversions increases with temperature.

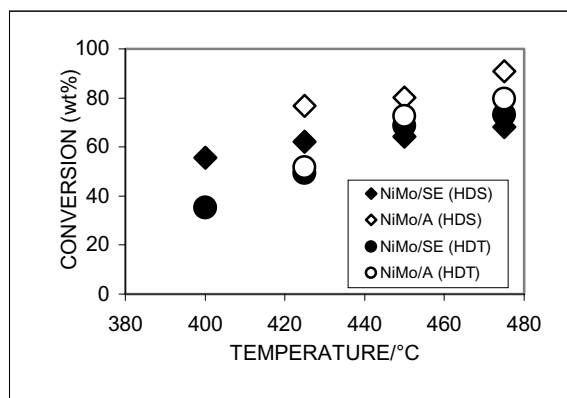


Fig. 1. Hydrodesulfurization (HDS) and hydrotreating (HDT) conversion of FCC feed as a function of reaction temperature.
Reaction conditions: $P = 5 \text{ MPa}$; $\text{WHSV} = 5 \text{ h}^{-1}$; $\text{H}_2/\text{feed ratio} = 1000 \text{ Nm}^3\text{m}^{-3}$

The HDT conversions ($\%\text{C}_{380}^{+}$) obtained at 723 K are given in Table 3. These are similar for the two catalysts. While HDS and hydrogenation activities are related to supported MoS_2 phase, the hydrocracking activity is correlate with the support proton acidity [1]. Commercial and sepiolite supported catalysts showed similar Bronsted acid sites (Table 2). In accordance with the similar acidity of both catalysts it can be inferred that similar Ni-Mo-OH groups are on the alumina and sepiolite surfaces, and therefore we obtained similar HDT activity for both catalysts.

Regarding the selectivity, commercial and sepiolite supported catalysts showed very similar fractions distribution at 723 K (Table 3). The highest yield is obtained for middle distillates (MD) and gas oil fractions, and the lowest one, for gases and naphtha fractions. This distribution may be explained considering the low acidity of these supports which results in a lower gas oil cracking activity producing fewer gases and naphtha. Also the trend for a low proportion of gases and naphtha is accentuated at higher temperatures and for the highest level of metal in the feed, as has been reported in the literature [5].

Table 3

wt.% HDS, wt.% HDT, and product distribution, obtained in the mild hydrotreating of FCC feed.
Reaction conditions: T = 723 K; P = 5 MPa; WHSV = 5 h⁻¹; H₂/feed ratio = 1000 Nm³m⁻³

Catalysts	wt.%HDT ^a	Gases ^b	Naphtha ^c	MD ^d	Gas oil ^e	wt.% S	wt.% HDS
FCC feed	88.1	0	0.3	0.9	10.7	1.487	0
NiMo/SE	68.6	1.2	13.8	28.3	57.7	0.530	64.3
NiMo/A	72.6	1.2	9.0	26.9	62.9	0.295	80.2

^a wt.% HDT Conversion defined as the net hydrotreating conversion into products boiling below 380°C = %C_{380°}⁺.

^b Gases < 150°C bp; ^cNaphtha: 150-250°C bp; ^dMiddle Distillates: 250-380 °C bp; ^eGas oil: >380°C

On the other hand, as can be seen in Table 3, the HDS activity at 723 K for the commercial catalyst is 20 % higher than for NiMo/SE catalyst. This is probably due to a higher active surface area and porosity in the former catalyst which would favour a better catalytic performance while increasing the accessibility of the large molecules of the feed containing the heteroatoms to the catalyst active sites.

Massoth and Muralidhar [6] showed the existence of two different kinds of MoS₂ in Mo/Al₂O₃. One type is active for HDS while the other one is active for hydrogenation reactions. This suggests that NiMo/A catalyst could have a greater proportion of HDS active sites than NiMo/SE catalysts. The interaction of hydroxyl groups with the molybdenum oxide on different types of support is expected to be similar in nature but the number and strength of them may vary from support to support [7]. These Mo species would show a strong interaction with hydroxyl groups in sepiolite [4, 8]. Therefore, the formation of less reducible, and possibly less sulfidable Mo species in sepiolite could explain the lower HDS activity. These results of HDS activity point to a combination of different numbers of available sites together with the surface area of both substrates.

CONCLUSIONS

NiMo/Sepiolite catalyst show similar performance (HDT activity and product selectivity) to NiMo/alumina commercial catalyst for a mild HDT of FCC feed. However, HDS activity was slightly less for the sepiolite supported catalyst (20% lower). This lower HDS activity on the sepiolite catalysts could be explained by their surface area and porosity, properties that can be optimized.

Therefore sepiolite is suitable as support of HDS catalysts due to an open porous network free of constrictions. This important feature, together with a HDS activity only slightly different than that of alumina and its lower cost make this material quite appropriate as an alternative for the more conventional catalysts in HDS reactions.

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