Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 107–108 (2005) 531–536

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Effect of sulfidation on Mo-W-Ni trimetallic catalysts in the HDS of DBT

Y. Gochi [a], C. Ornelas [a], F. Paraguay [a], S. Fuentes [b],
L. Alvarez [a], J.L. Rico [c], G. Alonso-Núñez [a,c,*]

[a] *Centro de Investigación en Materiales Avanzados S.C., Chihuahua, Chih., C.P. 31109, México*
[b] *Centro de Ciencias de la Materia Condensada, UNAM, Ensenada, Baja California, C.P. 22860, México*
[c] *Laboratorio de Catálisis, FIQ, UMSNH, Edif. E, C.U., Morelia, Mich., C.P. 58000, México*

Abstract

This work presents the effect of different sulfiding agents on Mo-W-Ni trimetallic catalysts, such as "NEBULA" catalysts. The materials were prepared by direct precipitation of ammonium molybdate, ammonium tungstate and nickel nitrate, generating a trimetallic precursor designated NH_4-Ni-$Mo_{0.5}W_{0.5}$-O. Hydrogen sulfide (H_2S), dimethyl disulfide (DMDS) and dimethyl sulfide (DMS) in a hydrogen atmosphere were used to sulfide the precursor at 400 °C for 2 h. The NEB_{H_2S}, NEB_{DMDS} and NEB_{DMS} catalysts obtained were evaluated in the hydrodesulphurization (HDS) reaction of dibenzothiophene (DBT). DMDS and DMS are less polluting agents than H_2S, which is indeed a highly toxic compound. The catalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). In addition, textural properties were measured using the BET and BJH methods. NEB_{H_2S} and NEB_{DMDS} catalysts present similar catalytic activities for HDS, higher than NEB_{DMS}. However, the latter catalyst was the most selective towards biphenyl (BF). NEB_{H_2S} and NEB_{DMDS} catalysts were exposed twice to the HDS reaction, they presented an improvement in catalytic activity compared to the first catalytic test.

Keywords: Sulfiding; Trimetallic; NEBULA catalysts; Precipitation; Hydrodesulfurization

---

1. Introduction

In recent years, different processes have been developed to remove the sulfur present in the heavy fractions of petroleum. The most important process is the hydrodesulfurization (HDS) process because it is the most economically feasible, wherein transition metals sulfides (TMS) are the optimal catalysts to carry out the numerous reactions of hydrogenation and hydrogenolysis. Preparation of catalysts with better catalytic activity and stability than commercial ones presents a great challenge for the refining industry and the search of new routes of preparation is an area of current interest. TMS, particularly, molybdenum and tungsten sulfides are catalytically active in hydrotreating [1,2]. In 2001, ExxonMobil, Akzo Nobel and Nippon Ketjen introduced a new unsupported catalyst called NEBULA. It is a Mo-W-Ni trimetallic catalyst with an activity at least three times better than any other hydrotreating catalyst available. It is especially suitable for production of fuels with ultra low sulfur content (~10 ppm) and for nitrogen elimination and saturation of aromatic compounds in diesels. Fig. 1 presents the evolution of catalysts for HDS until NEBULA catalyst [3–5].

Due to the high degree of toxicity of H_2S, different sulfiding agents are used, i.e. carbon disulfide (CS_2), dimethyl disulfide (DMDS), dimethyl sulfide (DMS), tertiarybutyl polysulfide (PSTB) and tertiarynonyl polysulfide (PSTN). In recent advances were reported catalysts sulfided by DMDS showed catalytic activities as high as other catalysts sulfided by H_2S [6–8]. In this work, the trimetallic precursor, NH_4-Ni-$Mo_{0.5}W_{0.5}$-O, was sulfided under H_2S, DMDS or DMS to determine their influence on the catalyst activity and the HDS reaction pathway of dibenzothiophene (DBT) [9].

---

* Corresponding author. Tel.: +52 614 439 1165; fax: +52 614 439 1130.
E-mail address: gabriel.alonso@cimav.edu.mx (G. Alonso-Núñez).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.07.068

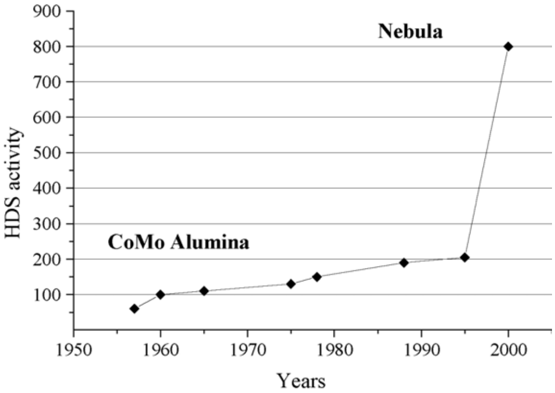

Fig. 1. Development of the HDS catalysts in the last 50 years.

2. Experimental

2.1. Preparation of precursor

The precursor preparation was according to the patent obtained by Soled et al. [4]. Two aqueous solutions were prepared (A and B). Solution A consisted of ammonium heptamolybdate (AHM) and ammonium metatungstate (AMT) dissolved in water at 90 °C under stirring. The pH of this solution was maintained at about 9.8 by adding NH_4OH. Solution B consisted of nickel nitrate dissolved in water at 90 °C, while stirring, solution B was slowly added to solution A at 90 °C, a precipitate was formed, then the solid was filtered, washed with hot water and dried at 120 °C. The molar ratio Mo:W:Ni of precipitate was 1:1:2 and is represented as NH_4-Ni-$Mo_{0.5}W_{0.5}$-O.

2.2. Preparation of catalysts

Sulfidation was carried out in a Thermolyne 21100 tubular furnace at 400 °C for 2 h using H_2S, DMDS or DMS (10 vol% in hydrogen). The catalysts obtained are, hereafter, called NEB_{H_2S}, NEB_{DMDS} and NEB_{DMS}, respectively. NEB_{H_2S} and NEB_{DMDS} catalysts are named as $NEB_{H_2S}(2)$ and $NEB_{DMDS}(2)$ after the second catalytic test.

2.3. Catalytic activity and selectivity

The HDS reaction was carried out in a Parr 4520 batch reactor of 1 l volume. The reactor was loaded with 1 g of catalyst and 150 ml of A decalin solution containing 5 wt% of DBT (6.6 g). A catalyst sieving fraction of 35–50 mesh size was employed to avoid intraparticle transfer resistance. The catalytic activity test was performed at 350 °C, 490 psi, under constant agitation of 600 rpm. The reaction was carried out for 5 h, with sampling being performed every 30 min and analysis with gas chromatography.

The DBT conversion increases linearly with time as expected for a pseudo-zero-order reaction [11]. The main reaction products for the HDS of DBT are biphenyl (BP) formed by direct C–S bond cleavage of DBT (the so-called direct desulphurization pathway, DDS) and phenylcyclohexane (PCH) formed by an initial hydrogenation of one of the aromatic rings of DBT followed by C–S bond rupture (the hydrogenating pathway, HYD). The HYD/DDS selectivity ratio is based on the product concentration ratio (PCH/BP). It should be noted that an intermediate primary hydrogenated product, tetrahydrodibenzothiophene (THDBT) is also formed along the HYD pathway. Its concentration remains low and could be neglected when calculating the HYD/DDS ratio. Moreover, this compound is not an HDS product since it still contains sulfur. The mean standard deviation for catalytic measurements was about 2.5%. After the DBT reaction, the catalysts were separated from the reaction mixture by filtration, washed with isopropanol to remove residual hydrocarbons and dried at room temperature. Finally, the resulted catalysts were stored in inert atmosphere for further characterization.

2.4. Characterization of catalysts

All materials were characterized before and after HDS of DBT. The X-ray diffraction (XRD) studies were carried out with a Philips X Pert MPD diffractometer, equipped with a curved graphite monochromator using a Cu Kα radiation source. The catalysts morphology was studied with a JEOL JSM-58000LV scanning electronic microscope at different magnification settings. A Philips CM200 transmission electronic microscope with LaB_6 filament was also used to observe the microstructure of the materials. The superficial area was measured in a Quantachrome equipment series Nova 1000 by nitrogen adsorption at −196 °C using the BET method. The samples were outgassed in vacuum at 250 °C before adsorption of nitrogen. The pore-size distribution was obtained by nitrogen desorption, following the BJH method.

3. Results and discussion

The results of activity, selectivity, superficial area and the S/W atomic ratio of the catalysts are summarized in Table 1.

Table 1
Reaction rate coefficients (k), DBT conversion at 5 h of reaction, selectivity, atomic ratio S/W and surface area of NEB_{H_2S}, NEB_{DMDS} and NEB_{DMS} catalysts

Catalyst	$k \times 10^7$ (mol/(s g))	DBT conversion (%)	Selectivity (HYD/DDS)	Area before HDS (m^2/g)	Area after HDS (m^2/g)	S/W
NEB_{H_2S}	14.59	68.25	1.25	7.37	17.31	3.0
NEB_{DMDS}	13.11	62.17	0.82	14.87	28.00	3.5
NEB_{DMS}	7.96	37.25	0.56	20.58	21.21	3.4
$NEB_{H_2S}(2)$	17.11	55.98	1.15	17.31	22.65	–
$NEB_{DMDS}(2)$	17.05	48.10	0.97	28.00	50.49	–

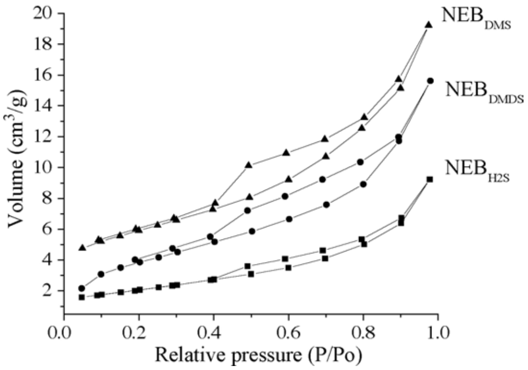

Fig. 2. Adsorption–desorption isotherms of the NEB$_{H_2S}$, NEB$_{DMDS}$ and NEB$_{DMS}$ catalysts before HDS reaction.

The NEB$_{H_2S}$ catalyst presents the highest reaction rate constant compared to NEB$_{DMDS}$ and NEB$_{DMS}$, while the latter presents the lowest one. Moreover, NEB$_{DMS}$ is the most selective towards biphenyl (BF), favoring DDS. The highest surface area before HDS reaction corresponds to the NEB$_{DMS}$ catalyst (20.5 m^2/g) and the lowest to the NEB$_{H_2S}$ catalyst (7.37m^2/g), the same behavior is maintained after the HDS reaction. It is interesting to observe that the surface area of all spent samples increase significantly as a result of surface restructuring throughout the HDS reaction. The surface area of NEB$_{H_2S}$, NEB$_{DMDS}$ and NEB$_{DMS}$ catalysts before reaction showed an inverse relation respect to their reaction rate coefficients**,** indicating a greater concentration of active sites per unit of area in NEB$_{H_2S}$ catalyst. However, when NEB$_{H_2S}$ and NEB$_{DMDS}$ catalysts were again tested in HDS, their surface area increased and their catalytic activity improved. Furthermore, both catalysts show similar reaction rate constants (17×10^{-7} mol/(s g)), indicating that DMDS is as good sulfiding agent as H_2S to generate metal sulfides with high catalytic activity. The different S/W ratios reported in Table 1, obtained by EDS analysis (1% error), suggest that the use of different sulfiding agents influences the sulfidation degree.

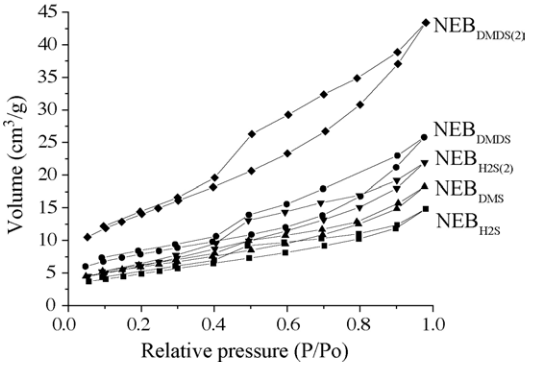

Fig. 3. Adsorption–desorption isotherms of the NEB$_{H_2S}$, NEB$_{DMDS}$ and NEB$_{DMS}$ catalysts after HDS reaction.

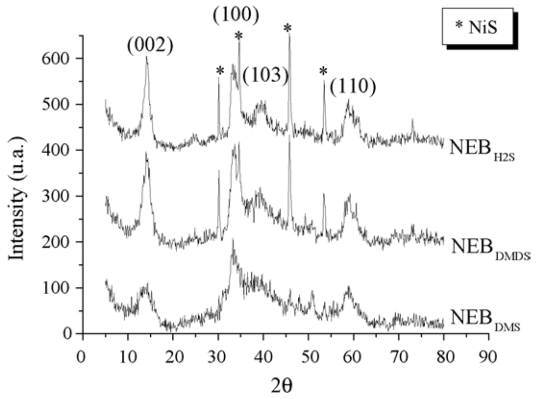

Fig. 4. Diffractograms of the NEB$_{H_2S}$, NEB$_{DMDS}$ and NEB$_{DMS}$ catalysts before HDS reaction.

Fig. 2 presents the adsorption–desorption isotherms of catalysts before the HDS reaction. These samples show type IV isotherms, corresponding to mesoporous materials. In Fig. 3, the adsorption–desorption isotherms after reaction are presented. All isotherms are similar to those for bimetallic catalysts reported previously [10]. This type of isotherm facilitates the determination of superficial areas due to saturation of the monolayer in the relative pressure range between 0.08 and 0.4; from these values, the slope of

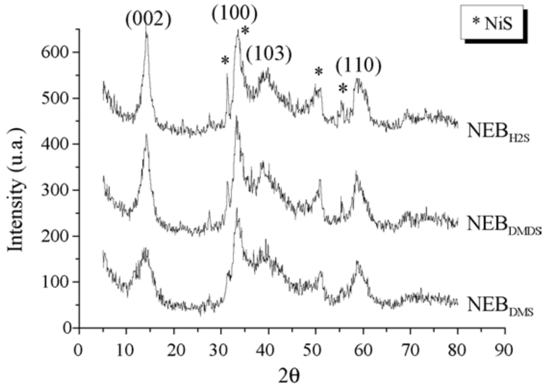

Fig. 5. Diffractograms of the NEB$_{H_2S}$, NEB$_{DMDS}$ and NEB$_{DMS}$ catalysts after HDS reaction.

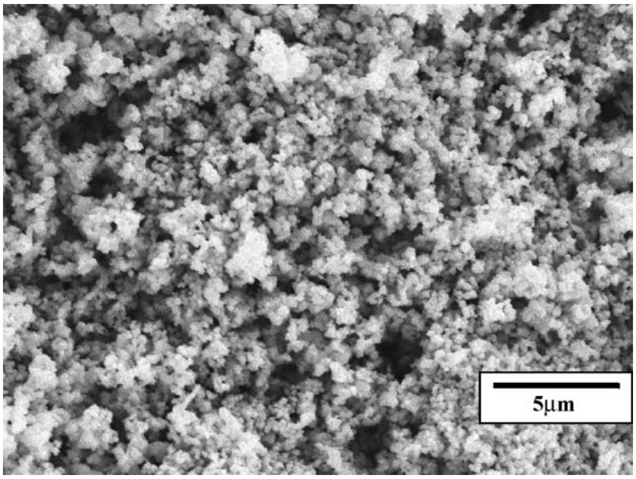

Fig. 6. Scanning electron micrograph of the NEB$_{H_2S}$ catalyst after HDS reaction.

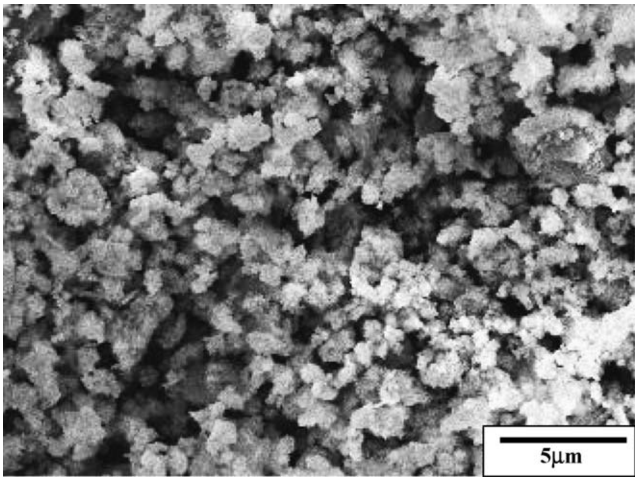

Fig. 7. Scanning electron micrograph of the NEB_{DMDS} catalyst after HDS reaction.

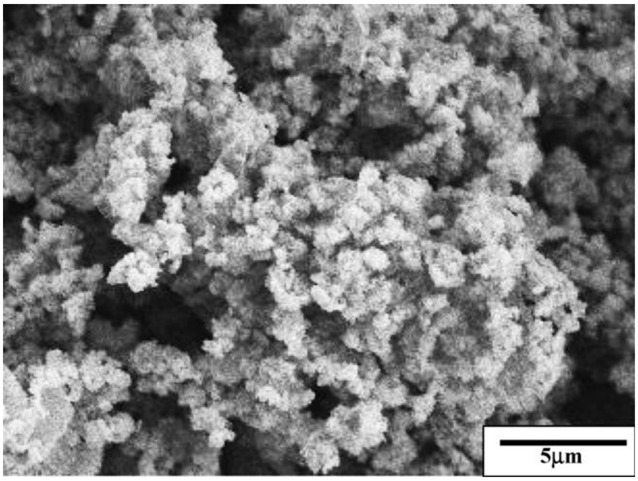

Fig. 8. Scanning electron micrograph of the NEB_{DMS} catalyst after HDS reaction.

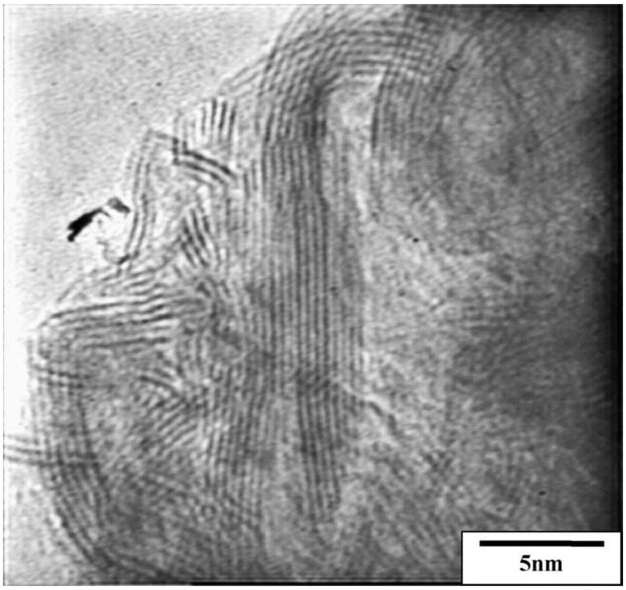

Fig. 9. Transmission electron micrograph of the NEB_{H_2S} catalyst after HDS reaction.

curve changes when capillary condensation begins. At relative pressures greater than 0.8, the curve becomes smoother until complete saturation of pores occurs.

The diffractograms of catalysts before the HDS reaction are presented in Fig. 4. The XRD patterns of these catalysts are in agreement with those reported by Alvarez et al. [10]. In general, the catalysts exhibit poorly crystalline structures of MoS_2 and WS_2. The NiS phase was observed in the NEB_{H_2S} and NEB_{DMDS} catalysts and could be the reason of the low value of surface area in both samples. Recently, Berhault et al. [8] reported the formation of more highly dispersed crystallites after DMS treatment, which is in

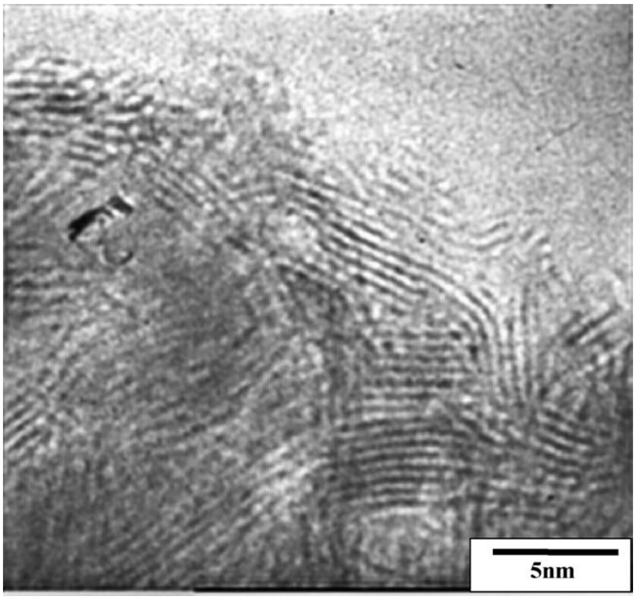

Fig. 10. Transmission electron micrograph of the NEB_{DMDS} catalyst after HDS reaction.

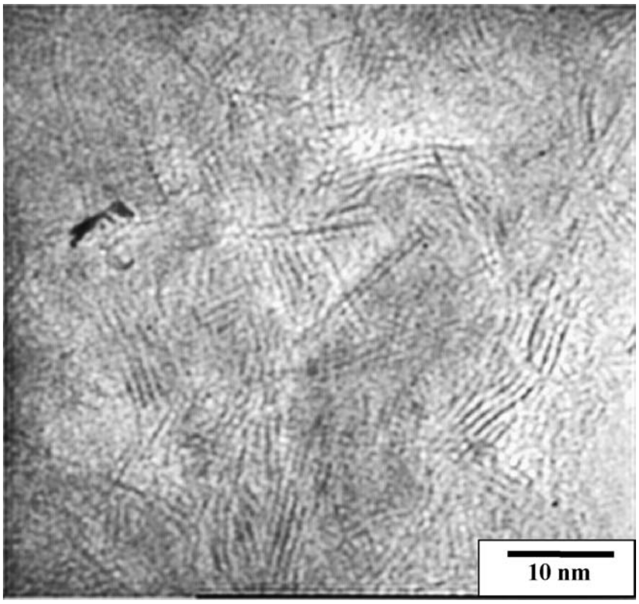

Fig. 11. Transmission electron micrograph of the NEB_{DMS} catalyst after HDS reaction.

agreement with the XRD pattern of the NEB_{DMS} catalyst. Similarly, Fig. 5 presents the XRD patterns of catalysts after reaction; the signals for NEB_{H_2S} and NEB_{DMDS} catalysts are greater, especially in the (0 0 2) direction than for the NEB_{DMS} catalyst. In addition, the NiS phase in these catalysts tends to disappear after the catalytic test, probably due to re-dispersion of nickel.

Figs. 6–8 show the scanning electron micrographs of the catalysts NEB_{H_2S}, NEB_{DMDS} and NEB_{DMS} after the HDS reaction. In general, single agglomerates and spongy particles are observed and the sulfiding agent does not markedly affect the morphology. Although the catalysts in this research work are trimetallic, similar morphology was observed on bimetallic catalysts previously reported [10]. In addition, significant changes in morphology after the HDS reaction were not evident.

Figs. 9–11 present the transmission electron microscopy (TEM) micrographs of NEB_{H_2S}, NEB_{DMDS} and NEB_{DMS} catalysts, respectively, after the HDS reaction. The catalysts revealed the presence of typical structures of the layer like MoS_2 and WS_2 phases. The NEB_{H_2S} catalyst has greater stacking in the (0 0 2) direction and longer layers than the NEB_{DMDS} catalyst. The lattice fringes on NEB_{H_2S} catalyst have a spacing of about 0.61–0.62 nm and stacking of 6–8 layers of average length about 16 nm, which is well ordered in the same direction. Although, NEB_{DMDS} catalyst has layers smaller than NEB_{H_2S}, the stacking is similar. On the other hand, it can be seen that stacking decreases in NEB_{DMS}, showing layer in all directions. The results about stacking in the (0 0 2) direction are in agreement with the XRD patterns.

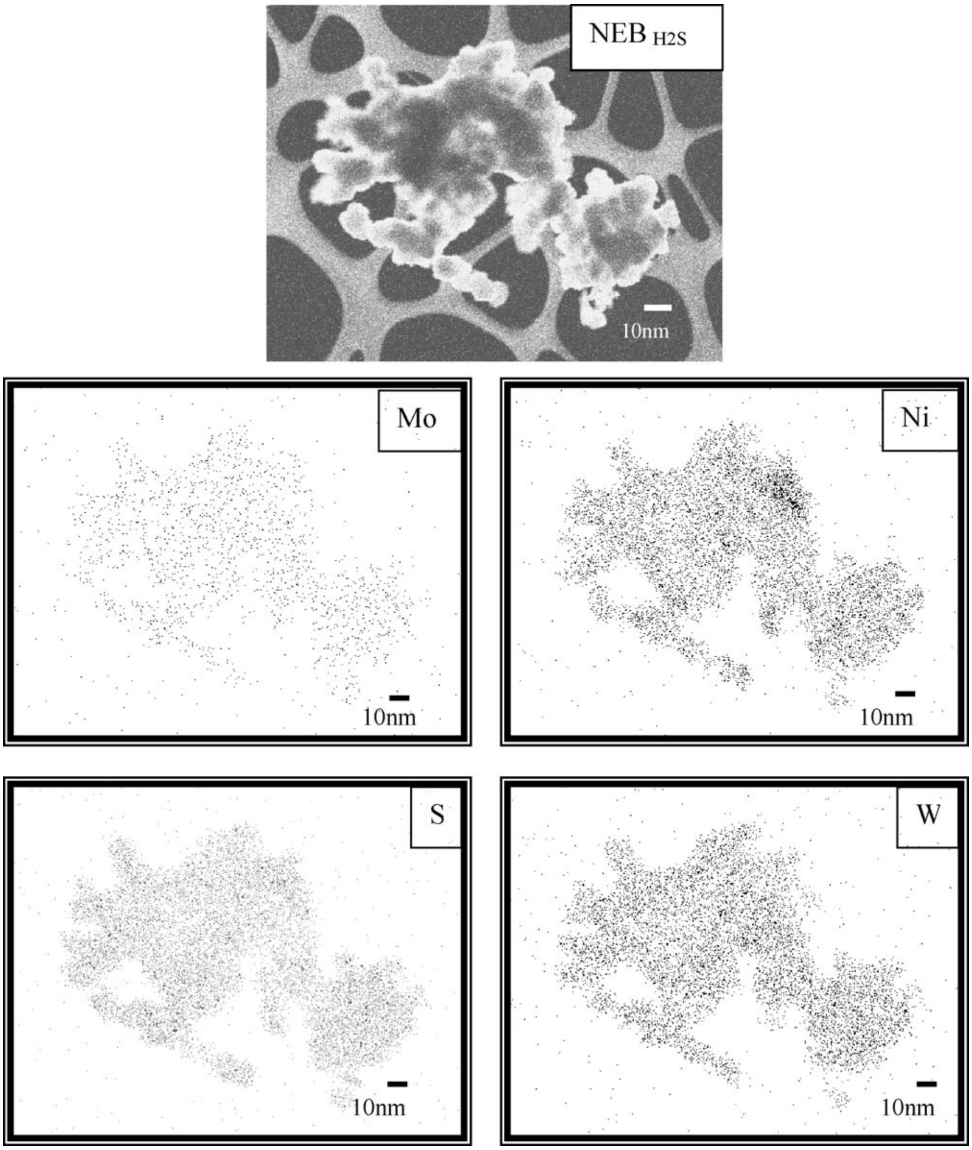

Fig. 12. Elemental mapping of the NEB_{H_2S} catalyst after HDS reaction by transmission electron microscopy.

Fig. 12 shows the TEM mapping of the NEB_{H_2S} catalyst, which exhibits the highest reaction rate coefficient. It is possible to observe a good elemental dispersion in the analyzed superficial zone which improves the catalytic activity in the HDS reaction. The NEB_{H_2S} catalyst presents good dispersion before and after the HDS reaction.

The use of different sulfiding agents does not only influence the degree of sulfidation, but also lead to catalysts of different crystalline phases and surface areas. Indeed, the sulfiding medium plays a very important role in the morphology and activity of the hydrotreating catalysts, as clearly revealed by XRD, scanning electron microscopy (SEM), TEM and BET results.

4. Conclusion

Our results suggest that DMDS can be used as sulfiding agent instead of H_2S to generate catalysts with high activity. The sulfidation with DMDS yields a catalyst (NEB_{DMDS}) with greater superficial area and selectivity towards BF than those for NEB_{H_2S}. A further increase in superficial area and activity was observed exposing the $NEB_{H_2S}(2)$ and $NEB_{DMDS}(2)$ catalysts to a second catalytic test. Both samples behaved similarly and exhibited a reaction rate constant of 17×10^{-7}mol/(s g). Elemental mapping showed that all elements (Mo-W-Ni) are homogeneously distributed. The sulfiding medium influences the morphology, activity and selectivity of catalysts in the HDS of DBT.

Acknowledgements

The authors greatly appreciate the valuable technical assistance of A. Reyes, E. Torres, W. Antúnez and D. Lardizabal. We are grateful to UMSNH for a sabbatical year and also to CONACYT for financial support (Project No. 40118-Y).

References

[1] R.R. Chianelli, Catal. Rev. Eng. 26 (1984) 361.
[2] H. Topsoe, B.S. Clausen, F.E. Massoth, Hydrotreating Catalysis, Science and Technology, Springer-Verlag, Berlin, Hiedelberg, 1996.
[3] F.L. Plantenga, R. Cefortain, S. Eijsbouts, F. van Houtert, S.L. Soled, S. Miseo, R. Krycak, G. Anderson, K. Fujita, NEBULA: a hydroprocessing catalysts with breakthrough activity (2002), Stud. Surf. Sci. Catal. 145 (2003) 407–410.
[4] S.L. Soled, S. Miseo, R. Krycak, H. Vroman, T.C. Ho, K. Riley, United States Patent 6,299,760 to Exxonmobil.
[5] L.A. Gerritsen, A new star is born: the next step in ultralow-sulfur diesel, Catal. Courier (2001).
[6] C. Glasson, C. Geantet, M. Lacroix, F. Labruyere, P. Dufresne, J. Catal. 212 (2002) 76.
[7] G. Berhault, L. Cota, A. Duarte, A. Mehta, R.R. Chianelli, Catal. Lett. 78 (2002) 81.
[8] G. Berhault, A. Mehta, A.C. Pavel, J. Yang, L. Rendon, M.J. Yacaman, L. Cota, A. Duarte, R.R. Chianelli, J. Catal. 198 (1) (2001) 9.
[9] M. Daage, R.R. Chianelli, J. Catal. 149 (1994) 414.
[10] L. Alvarez, J. Espino, C. Ornelas, J.L. Rico, M.T. Cortez, G. Berhault, G. Alonso, J. Mol. Catal. A Chem. 210 (2004) 105.
[11] T.A. Pecoraro, R.R. Chianelli, J. Catal. 67 (1981) 430.