

# Highly Active Deep HDS Catalysts Prepared Using Mo and W Heteropolyacids Supported on SBA-15

Lilia Lizama and Tatiana Klimova\*

Facultad de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, Coyoacán, Mexico D.F. 04510 (México)

\*klimova@servidor.unam.mx

## Introduction

Nowadays, the need to improve the removal of sulfur from gasoline and diesel oil by means of deep hydrodesulfurization is driven by the new environmental legislation regarding fuel specifications. Many efforts are aimed to design more active HDS catalysts by either using new catalytic supports or changing the active phase. To date, there have been very few reports on the application of heteropolyacids (HPAs) in the preparation of HDS catalysts [1]. Different carriers have been used to support HPAs. It was found that when HPAs are deposited on alumina their characteristic heteropolyanion structure is destroyed, and the catalytic behavior of these catalysts is similar to that of the conventional Mo/W ones [2]. New mesoporous molecular sieves such as SBA-15 [3], highly stable and with better textural properties compared to  $\gamma$ -alumina, seem to be suitable for depositing HPA precursors. The aim of the present work is to demonstrate that SBA-15-supported HPAs are good oxidic precursors for the preparation of highly active catalysts for deep HDS.

## Materials and Methods

SBA-15 was prepared according to [3], using Pluronic P123 as structure-directing agent and TEOS as the silica source. Mo/W were incorporated to the SBA-15 support by impregnation of methanol solutions of Keggin-type HPAs ( $H_3PM_{12}O_{40}$ , M= Mo or W). Nickel nitrate was used as promoter source. After each impregnation, the samples were calcined for 2 h at 350°C in air. The composition of the catalysts was 12 wt % of  $MO_3$  and 3 wt % of NiO. The samples were designated as HPM/SBA for unpromoted catalysts and NiPM/SBA, for promoted catalysts. Reference catalysts were prepared from conventional precursors ( $(NH_4)_6Mo_7O_{24}$  and  $(NH_4)_6H_2W_{12}O_{40}$ ) and were designated as M/SBA and NiM/SBA. The support and catalysts were characterized by  $N_2$  physisorption, small- and wide-angle XRD, UV-Vis DRS,  $^{31}P$  MAS-NMR, FT-IR and TPR. Catalysts' activation was carried out *ex situ* in a tubular reactor at 400 °C for 4 h in a stream of  $H_2S/H_2$  (15 vol. %). The 4,6-DMDBT HDS activity tests were performed in a batch reactor at 300 °C and 7.3 MPa total pressure for 8 h.

## Results and Discussion

The nitrogen adsorption-desorption isotherms (Figure 1), as well as the small-angle XRD patterns show that W and Mo heteropolycompounds can be supported on SBA-15 without substantial loss of the support characteristics. In the  $^{31}P$  MAS-NMR spectra of Mo catalysts, the peak at -3.5 ppm characteristic of the Keggin structure of the parent HPMo, can be observed. Similar results were obtained for the catalysts of the W series, where the signal of HPW structure was observed at -15 ppm (Figure 2). These results, as well as the absence of a signal at 0 ppm (a phosphate formed from HPA decomposition), indicate that the characteristic Keggin structure was preserved in the oxidic precursors supported on SBA-15.

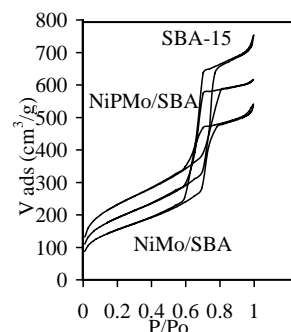


Figure 1.  $N_2$  adsorption-desorption isotherms for SBA-15 support and Mo catalysts.

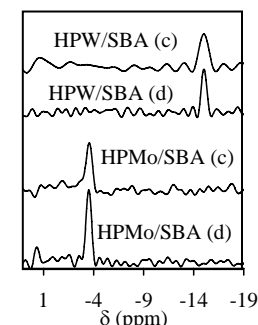


Figure 2.  $^{31}P$  MAS-NMR spectra of Mo and W dried (d) and calcined (c) catalysts.

Table 1. Catalytic activity and selectivity in 4,6-DMDBT HDS

Catalyst	$k_1$ L/(s gcat)	$k_1$ L/(s mol $MO_3$ )	HYD/DDS (at 40% 4,6-DMDBT conversion)
NiMo/SBA	$8.0 \times 10^{-6}$	$9.6 \times 10^{-3}$	6.4
NiPMo/SBA	$1.3 \times 10^{-5}$	$1.6 \times 10^{-2}$	7.1
NiW/SBA	$7.6 \times 10^{-6}$	$1.5 \times 10^{-2}$	2.4
NiPW/SBA	$1.9 \times 10^{-5}$	$3.7 \times 10^{-2}$	5.5

Both, Mo and W catalysts prepared from HPA precursors showed higher activity in 4,6-DMDBT HDS than their conventionally prepared analogs probably due to an enhancement of the HYD route.

## Significance

The use of SBA-15 materials as supports together with HPAs as catalyst precursors show promising features for the preparation of Mo and W-based Ni-promoted catalysts, active for HDS of hindered dibenzothiophenes.

## Acknowledgements

Financial support by DGAPA-UNAM (grant IN-104106) is acknowledged. The authors wish to thank M. Aguilar, I. Puente and C. Salcedo for technical assistance.

## References

- Pawelec, B., Damyanova, S., Mariscal, R., Fierro, J.L.G., Sobrados, I., Sanz, J., and Petrov, L. *J. Catal.* 223, 86 (2004).
- Griboval, A., Blanchard, P., Payen, E., Fournier, M., and Dubois, J.L. *Catal. Today* 45, 277 (1998).
- Zhao, D., Huo, Q., Feng, J., Chmelka, B.F., and Stucky, G.D. *J. Am. Chem. Soc.* 120, 6024 (1998).