New NiMo/ZrO_2-SBA-15 catalysts highly active in simultaneous hydrodesulfurization of DBT and 4,6-DMDBT

Oliver Gutiérrez[1], Alejandro Soriano[1], Diego Valencia[1], Gustavo Fuentes[2] and Tatiana Klimova[1]*

[1]*Facultad de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, Coyoacán, México D.F 04510 (México)*

[2]*Área de Ingeniería Química, Universidad Autónoma Metropolitana-Iztapalapa, Av.Michoacán y Purísima, Iztapalapa, México D.F 09340 (México)*

*klimova@servidor.unam.mx

Introduction

Hydrodesulfurization (HDS) is a key process for producing clean engine fuels. Nowadays, many efforts are made to improve the HDS catalysts by using new materials as catalytic supports. Among them, mesoporous molecular sieve SBA-15 has attracted much interest in the last two years. Thus, Mo and W catalysts supported on purely siliceous SBA-15 were found to be more active than γ-alumina supported ones in thiophene and dibenzothiophene HDS, and cyclohexene and toluene hydrogenation [1-3]. Further increase in HDS activity was reached when SBA-15 supports were modified by the incorporation of heteroatoms (Al, Ti, and Zr) [4,5]. In the present work, with the aim of searching for new, highly effective HDS catalysts, SBA-15 materials modified with different amounts of ZrO_2 (from 25 to 50 wt. %) were prepared and tested as supports for NiMo catalysts. The catalysts were evaluated in simultaneous HDS of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in order to characterize their performance in HDS of the sulfur-containing molecules with different reactivity towards sulfur elimination.

Materials and Methods

SBA-15 was synthesized according to the well-known procedure [6]. ZrO_2-containing SBA-15 supports (Zr(*x*)SBA-15 samples, where *x* is the wt. % of ZrO_2) were prepared by incipient wetness impregnation of zirconium (IV) propoxide in n-propanol on pure siliceous parent SBA-15. NiMo catalysts (12 wt % of MoO_3, 3 wt % of NiO) were prepared by successive impregnation of aqueous solutions of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ on the supports. Additionally two catalysts supported on mechanical mixtures of SBA-15 and ZrO_2 were prepared for comparison purposes. Supports and catalysts were characterized by N_2 physisorption, XRD, UV-Vis DRS, isoelectric point, TPR, SEM-EDX and HRTEM. The HDS activity tests were performed in a batch reactor at 300 °C and 7.3 MPa total pressure for 8 h using a hexadecane solution of DBT (1300 ppm of S) and 4,6-DMDBT (500 ppm of S). Prior to the activity tests, the catalysts were sulfided *ex-situ* at 400°C for 4 h in a stream of H_2S-H_2.

Results and Discussion

The results from textural characterization of the supports indicate that zirconia incorporation on the SBA-15 surface produces a decrease in the SBA-15 textural properties, which is more pronounced at high ZrO_2 loading. However, the characteristic shape of N_2 adsorption-desorption isotherms and small-angle XRD patterns of SBA-15 are still maintained after ZrO_2 incorporation. The formation of tetragonal and monoclinic ZrO_2 crystalline phases was detected in the samples with ZrO_2 loading higher than 25 wt. % (XRD). In line with XRD results, UV-Vis DRS spectra of the supports show a progressive increase in the agglomeration of ZrO_2 species with increasing zirconia content. For the catalysts, the dispersion of Ni and Mo oxidic and sulfided species increases with ZrO_2 loading in the SBA-15 support.

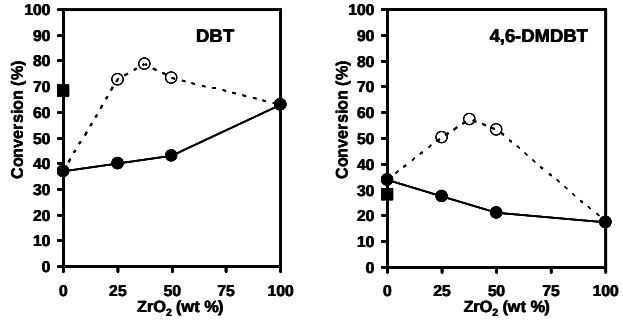

Figure 1. DBT and 4,6-DMDBT conversions at 4 h reaction time for NiMo catalysts supported on: Zr(*x*)SBA-15 materials (○), ZrO_2 and SBA-15 mechanical mixtures (●); and Al_2O_3 (■).

All NiMo catalysts supported on Zr(*x*)SBA-15 materials showed high activity in HDS of both DBT and 4,6-DMDBT (Figure 1). Their activities were slightly higher than that of conventional NiMo/Al_2O_3 catalyst in DBT HDS and significantly higher in 4,6-DMDBT elimination. DBT conversion of 97 % and 4,6-DMDBT of 91 % was reached at 8 h reaction time with the most active catalyst, NiMo/Zr(37)SBA-15.

Significance

High-performance NiMo catalysts were prepared using ZrO_2-modified SBA-15 supports, which showed high activity for simultaneous HDS of both, DBT and 4,6-DMDBT.

Acknowledgments

Financial support by CONACYT-Mexico (grant 46354) is gratefully acknowledged. The authors wish to thank M. Aguilar Franco, I. Puente and C. Salcedo for technical assistance.

References

1. Vradman, L., Landau, M.V., Herskowitz, M., Ezersky, V., Talianker, M., Nikitenko, S., Koltypin, Y., and Gedanken, A. *J. Catal.* 213, 163 (2003).
2. Sampieri, A., Pronier, S., Blanchard, J., Breysse, M., Brunet, S., Fajerwerg, K., Louis, C., and Pérot, G. *Catal. Today* 107-108, 537 (2005).
3. Dhar, G.M., Kumaran, G.M., Kumar, M., Rawat, K.S., Sharma, L.D., Raju, B.D., and Rao, K.S.R. *Catal. Today* 99, 309 (2005).
4. Kumaran, G.M., Garg, S., Soni, K., Kumar, M., Sharma, L.D., Dhar, G.M., and Rao, K.S.R. *Appl. Catal. A: General* 305, 123 (2006).
5. Gutiérrez, O., Fuentes, G., Salcedo, C., and Klimova, T. *Catal. Today* 116, 485 (2006).
6. Zhao, D., Huo, Q., Feng, J., Chmelka, B.F., and Stucky, G.D., *J. Am. Chem. Soc.* 120, 6024 (1998).