

Effect of Nickel and Cobalt Promoters on SBA-15-supported MoS₂ Catalysts for Deep Hydrodesulfurization

Diego Valencia¹, Oliver Y. Gutiérrez¹, Lilia Lizama¹, Isidoro García-Cruz², Tatiana Klimova^{1*}

¹Facultad de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, Coyoacán, México D.F., 04510, México

²Programa de Ingeniería Molecular, Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, Colonia San Bartolo Atepehuacán, México D. F. 07730, 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 (HDS) is driven by the new environmental legislation regarding fuel specifications [1]. Many efforts are aimed to design more active or selective HDS catalysts, depending on their particular application. It is known that the active phases in HDS catalysts are MoS₂ or WS₂ nanocrystallites promoted by cobalt or nickel atoms, deposited on high specific surface area supports. Since catalytic behavior of HDS catalysts depends in a complex manner on a series of factors and their combinations (active phase, promoter and support)[2], in the present work we tried to get a deeper insight into the effect of the promoter used on the development of Mo catalysts supported on SBA-15-type materials in deep HDS. For this aim, simultaneous HDS of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) was performed over NiMo and CoMo/SBA-15 catalysts.

Materials and Methods

Synthesis of SBA-15 was carried out by the method reported by Zhao et al. [3]. Before catalyst preparation, the support was characterized by N₂ physisorption and small-angle XRD. Mo, NiMo and CoMo/SBA-15 catalysts were prepared by a standard incipient wetness impregnation technique using aqueous solutions of (NH₄)₆Mo₇O₂₄·4H₂O and Ni (or Co)(NO₃)₂·6H₂O. Mo was impregnated first. Catalysts were characterized by N₂ physisorption, powder XRD, HRTEM and TPR, and tested in simultaneous HDS of DBT and 4,6-DMDBT in a batch reactor at 300 °C and 7.3 MPa total pressure for 8 h.

Results and Discussion

Calcined catalysts showed the same form of N₂ adsorption-desorption isotherm and small-angle XRD pattern as the parent SBA-15 support. Formation of crystalline phases in oxide catalysts was detected only in CoMo/SBA-15 sample, where a new phase identified as β-CoMoO₄ was observed. This result is in line with the previous report [4].

TPR profiles of Mo catalysts promoted by Ni or Co also showed significant differences (curve (c), Figure 1 A and B). The nickel promoter significantly decreased the temperature of the reduction of Mo oxide species, while the effect of cobalt addition was relatively small. In addition, the Ni-promoted sample showed a high proportion of dispersed octahedral Mo species easy to reduce (T_{max} about 400 °C). The nature of the promoter also affected the morphology of the MoS₂ active phase.

In the HDS of DBT, both Ni and Co-promoted MoS₂ catalysts showed an increase in the DBT conversions and the rate constant values in comparison with their unpromoted

Mo/SBA-15 counterpart (Table 1). Nickel promoter effect was much higher than that of cobalt. However, in the HDS of 4,6-DMDBT, we obtained an unexpected result, namely, the activity of the CoMo/SBA-15 sample resulted to be lower than that of the starting Mo/SBA-15 catalyst. This result can be attributed to the formation of large particles of β-CoMoO₄ crystalline phase in the corresponding oxide precursor and to the well-known fact that Co addition to Mo HDS catalysts in general results in an increase of the direct desulfurization (DDS) pathway of the reaction, which is sterically hampered in the case of the 4,6-DMDBT molecule.

Table 1. Activity of Mo, NiMo and CoMo/SBA-15 in HDS of DBT and 4,6-DMDBT

Catalyst	Conversion at 8 h (%)		Pseudo-first-order rate constant (L s ⁻¹ g _{cat} ⁻¹)	
	DBT	4,6-DMDBT	DBT	4,6-DMDBT
Mo/SBA-15	35	38	2.8 × 10 ⁻⁶	3.2 × 10 ⁻⁶
NiMo/SBA-15	79	64	8.9 × 10 ⁻⁶	6.1 × 10 ⁻⁶
CoMo/SBA-15	44	25	3.7 × 10 ⁻⁶	2.1 × 10 ⁻⁶

Significance

It was shown that the promoter nature has an important effect on the behavior of Mo/SBA-15 catalysts in deep HDS of refractory compounds, especially in the case of 4,6-DMDBT. The Ni-promoted catalyst is able to desulfurize both DBT and 4,6-DMDBT, whereas the Co-promoted one is active only in DBT HDS. This should be taken into account in the development of the catalysts for deep HDS for industrial implementation.

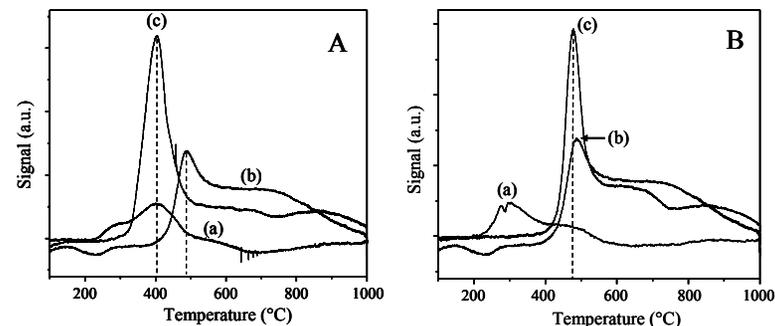


Figure 1. TPR profiles of (A): Ni/SBA-15 (a), Mo/SBA-15 (b) and NiMo/SBA-15 (c); and (B): Co/SBA-15 (a), Mo/SBA-15 (b) and CoMo/SBA-15 (c).

References

- Knudsen, K.G., Cooper, B.H., and Topsøe, H. *Appl. Catal. A: General* 189, 205 (1999).
- Prins, R., de Beer, V.H.J., Somarjai, G.A.. *Catal. Rev. Sci. Eng.* 31, 1 (1989).
- Zhao, D., Huo, Q., Feng, J., Chmelka, B. F., Stucky, G. D. *J. Am. Chem. Soc.* 120, 6024 (1998).
- Zepeda, T. A., Fierro, J. L. G., Pawelec, B., Nava, R., Klimova, T., Fuentes, G. A., Halachev, T. *Chem. Mater.* 17, 4062 (2005).