

# Palladium Effect Over Mo/NiMo Alumina-Titania Catalysts on the 4,6-Dimethyldibenzothiophene Hydrodesulfurization Reaction

A. Aguirre<sup>1</sup>; J. A. Montoya<sup>1\*</sup>, P. del Angel<sup>1</sup> and J. A. de los Reyes<sup>2</sup>

<sup>1</sup> Instituto Mexicano del Petróleo, Investigación y Posgrado, Eje Central Lázaro Cárdenas 152, 07730 San Bartolo Atepehuacán, México, D.F.

<sup>2</sup> Universidad Autónoma Metropolitana-Iztapalapa Area de Ingeniería Química, Av. R. Atlixco 189, 09340 México, D.F.

\*[amontoya@imp.uam.mx](mailto:amontoya@imp.uam.mx)

## Introduction

Industrial hydrotreating (HDT) catalysts are composed of MoS<sub>2</sub> (or WS<sub>2</sub>) phase promoted by Co or Ni supported on alumina. The origin of the almost exclusive use of alumina as support has to be ascribed to its outstanding textural and mechanical properties and its relatively low cost. However, Mo or W-based catalysts supported on Al<sub>2</sub>O<sub>3</sub> modified by TiO<sub>2</sub> have attracted attention due to their high catalytic activity for HDT reactions [1]. Previous work in our laboratory has been devoted to synthesize Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> mixed oxides by using the sol-gel method, exhibiting textural properties adapted to HDT typical reaction conditions [2]. Besides, it is well known that precious metals are highly active in the HDT reactions. For instance, Ru has been used as a dopant for NiMo/Al<sub>2</sub>O<sub>3</sub> systems, exhibiting a promoting effect for hydrodesulfurization (HDS) and hydrogenation (HYD) reactions [3]. Pd has been reported to have significant resistance against H<sub>2</sub>S, high activity for the elimination of sulfur and high selectivity towards hydrogenated products [4]. Therefore, the aim of this paper was to study the effect of the addition of Pd on the HDS catalytic properties of NiMo sulfided catalysts supported on an alumina carrier modified by titania.

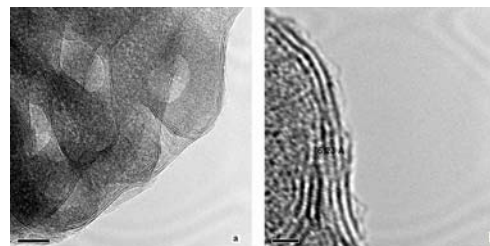
## Materials and Methods

A series of Mo, Ni, Pd/alumina-titania (4 wt%) (AT) catalysts were prepared using successive incipient wetness impregnation. The theoretical Mo loading was of 9 wt% and Ni/(Ni+Mo)=0.3 atomic ratio, and the palladium loading was 0.3% wt. (Table 1). The catalysts were calcined at 673K and sulfided under a flow of H<sub>2</sub>S(10% mole) /H<sub>2</sub> at 673 K. The materials were characterized by N<sub>2</sub> physisorption, XRD, DRS-Uv-Vis, Raman Spectroscopy, XPS, HRTEM. The catalytic activity tests were performed in a batch reactor at 593K and 800 psi using 100 mL of n-dodecane as solvent and 200 mg of 4,6-dimethyldibenzothiophene (4,6-DMDBT) model molecule.

## Results and Discussion

Figure 1 shows a typical high resolution HRTEM image of the molybdenum mesoporous material which was formed during the catalysts preparation. It is also observed the formation of three layers MoS<sub>2</sub> active phase surrounding the mesoporous material and forming pores with diameters of about 15nm. The MoS<sub>2</sub> is a discontinuous phase showing that the material has several layer and stacking faults. The MoS<sub>2</sub> active phase was identified with its characteristic 6.23Å atomic distance [5]. Significant differences in the textural and structural features for the MoOx and MoS<sub>2</sub> phases supported on TiO<sub>2</sub>-modified Al<sub>2</sub>O<sub>3</sub> were found after characterization by XRD, DRS and XPS with respect to the same phases supported on Al<sub>2</sub>O<sub>3</sub>.

In regard to the catalytic activity, the highest 4,6-DMDBT rate corresponded to the AT/MoPdNi catalysts showing that the presence of Pd increased this value. The selectivities [expressed as DDS (direct desulfurization)/HYD (hydrogenation) ratios] values for the different catalysts were calculated from the product distribution for the transformation of 4,6-DMDBT. It can be observed that this value increased when adding Pd, Ni and Ni and Pd. Since the reaction scheme is recognized to be complex [6], no direct conclusions can be drawn and selectivity results will be discussed carefully. The morphology of this new pore system and the presence of the palladium in the catalysts seems to be responsible for the high HDS activity.



**Figure 1.** MoS<sub>2</sub> active phase TEM micrographs. (a) High resolution micrograph, the MoS<sub>2</sub> surrounds the material and the pores, (b) High resolution micrograph of the MoS<sub>2</sub> measuring 6.23Å.

**Table 1. Metal loadings and HDS activity results**

Catalyst	%Mo	%Ni	%Pd	R <sub>0</sub> E-06 mol/s g <sub>metal</sub>	S <sub>DDS/HYD</sub> <sup>a</sup>
AT/Mo	9	--	--	0.25	0.17
AT/MoPd	9	--	0.3	0.25	0.28
AT/MoNi	9	1.5	--	1.82	0.38
AT/MoNiPd	9	1.5	0.3	2.30	0.48

<sup>a</sup>calculated at 10% of 4,6 DMDBT conversion

## Significance

The development of new catalytic systems with high catalytic activity in HDS could contribute to reduce the sulfur levels required by the legislations of different countries.

## References

1. J. Ramírez, G. Macías, L. Cedeño, A. Gutiérrez-Alejandre, R. Cuevas, P. Castillo, *Catal. Today*, 98, 19 (2004).
2. J. Escobar, J.A. de los Reyes, T. Viveros, *Ind. Eng. Chem. Res.*, 3, 666 (2002).
3. M. Cattenot, C. Geantet, M. Breyse, *Appl. Catal. A. Gen.*, 213, 217 (2001).
4. A.Röthlisberger, R.Prins, *J. Catal.*, 235, 229 (2005).
5. H. Shimada, *Catal. Today*, 86, 17 (2003).
6. F. Bataille, J.L. Lemberton, P. Michaud, G. Perot, M. Vrinat, M. Lemaire, E. Schulz, M. Breyse, S. Kasztelan, *J. Catal.*, 191, 409 (2000).