

Structure and Catalytic Characterization of Molybdenum Sulfide Nanoplatelets

Nora Elizondo-Villarreal^{1,2*}, Rodrigo Velázquez-Castillo^{1,3}, A. Camacho¹, Miguel José Yacamán^{1*}

¹ Department of Chemical Engineering and Texas Materials Institute, University of Texas at Austin, TX 78712, USA

² Department of Physics, Universidad Autonoma de Nuevo Leon, San Nicolas de los Garza, N. L., CP 66451, Mexico

³ Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de México, Santiago de Querétaro, Qro., C. P. 76000, México

*norae@che.utexas.edu (Nora Eizondo-Villarreal), yacaman@che.utexas.edu (Miguel Jose Yacaman).

Introduction

The new environmental regulations in most of the countries impose the reduction of the sulfur compounds (SO_x) produced upon fuel combustion [1]. This will imply the production of cleaner fuels and thereby an improvement of the efficiency of the hydrodesulfurization (HDS) of the petroleum feedstock. This reaction is performed industrially on CoMo/Al₂O₃ or NiMo/Al₂O₃ catalyst. Their active phase consists of MoS₂ nanocrystallites well dispersed on a high-surface-specific alumina and promoted by cobalt or nickel atoms [2, 3 and 4].

HRTEM is very useful to determinate the distribution of the nanoparticles on surface, and shape of layers of MoS₂ catalyst. It is found that HAADF-STEM, in contrast to HRTEM, enables ready observation of all the transition metal sulfide nanoclusters and gives direct insight into their morphology [5-7].

It is important to determinate the catalytically stabilized phases under operating hydrotreating conditions as a basis for understanding the activity and selectivity of this class of catalysts[8].

Materials and Methods

A self-standing film of α -MoO₃ nanoribbons was prepared by a hydrothermal process. The procedure consisted of adding dropwise a 4 M solution of HCl to a saturated solution of sodium molybdate. The mixture is placed in a Teflon-lined autoclave and left at 423 K for 6 h (precursor of sample A)[9]. Once the reaction time was completed, the product was filtered and dried. Sections of these films were reacted with a stream of H₂S gas mixed with 90 % inert gas N₂ and 10% H₂ in a 9/1 volume ratio at 723 K for 2 h, in order to produce the corresponding sulfide formed at high-temperature sulfidation of molybdenum. Their morphology was studied by scanning electron microscopy (SEM) in a Hitachi S-4500 field emission SEM operating at 5 kV. For crystal structure identification we used a Phillips automated vertical scanning powder diffractometer. The spectra were obtained between 10 and 90 2 θ degrees. We used X-ray photoelectron spectroscopy XPS to surface analysis of the optimized model catalyst A.

Transmission electron microscopy (TEM) and associated techniques such as energy dispersive X-ray spectroscopy (EDS), high-resolution electron microscopy (HREM), and high-angle annular dark field (HAADF) were applied to determine the subnanometer structure, chemical composition, and homogeneity of the sulfides. TEM analysis was carried out in a JEOL 2010 F microscope equipped with a Schottky-type field emission gun, an ultra-high-

resolution pole piece, and a scanning-transmission (STEM), unit with a high-angle annular dark-field detector (HAADF) operating at 200 kV.

Reference catalysts were prepared by decomposition of ammonium thiomolybdate (ATM). One of them was sulfided ex situ in a tubular reactor with 15% volume H₂S/H₂ flow at 673 K for 4 h (heating rate 4 K/min) before catalytic testing; the other one was left to be sulfided in situ during the reaction. The decomposition of ATM precursor is a well-known reaction that occurs very fast, generating MoS₂, NH₃, and H₂S [10].

The HDS of dibenzothiophene (DBT) has been studied as a model reaction of HDS of petroleum feedstock. For this work the HDS was carried out in a Parr Model 4522 high-pressure batch reactor. The catalysts were placed in the reactor (ex situ catalysts (1.0 g) or in situ catalysts, the appropriate amount of ATM to yield 1 g of MoS₂ along with the reaction mixture (5% weight of DBT in decaline; total volume 150 ml), then pressurized with hydrogen and heated to 623 K at a rate of 10 K/min under a constant agitation of 600 rpm.

When the working temperature was reached, sampling for chromatographic analysis was performed to determine conversion versus time dependence; the reaction was run for 5 h. Reaction products were analyzed with an AutoSystem XL gas chromatograph (Perkin Elmer Instruments) with a 9-ft, 1/8-inch-diameter packed column containing OV-17, on Chromosorb WAW 80/100 as the separating phase.

Results and Discussion

A, X-ray diffraction showed the presence of two crystalline phases, molybdenum dioxide (Tugarinovite, JCPDS 78-1073) and molybdenum disulfide (Molybdenite-2H, JCPDS 65-0160) (Figure 1). The MoO₂ phase shows sharper and better-defined peaks than the MoS₂, suggesting that the sulfide is presents as small crystallites that present an overall short-range order we also perform the quantitative phase analysis by X-ray powder diffraction dates by the internal-standard method and the amounts of the MoO₂ phase and the MoS₂ phase were determined and these are 80 % and 20 % in weight respectively.

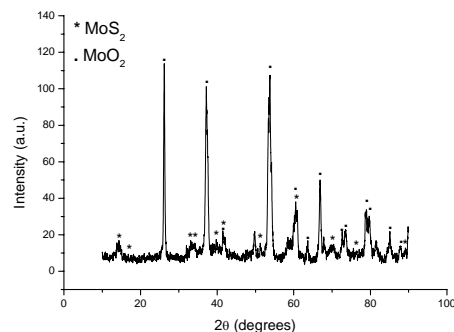


Figure 1. X- ray diffraction pattern of the sample A tested for the catalytic properties.

We studied the catalysts using different TEM methods including High resolution, High angle annular dark field HAADF-STEM and conventional dark field and electron diffraction.

Since in the diffraction patterns the reflections of the MoS₂ and of the MoO₂ are spatially separated. It is possible to use conventional dark-field imaging (DF) of the rod-like particles to distinguish between the MoS₂-like phase growing on the surface and the MoO₂ matrix.

The bright field image of the catalyst is shown in the figure 2. As can be seen there is a core which is MoO₂ and from that MoS₂ crystallites are being formed on the surface. The HAADF-STEM image clearly showed that the crystallites have either a conical shape or an arrow shape and they are extremely thin along the perpendicular direction. A typical image of HAADF-STEM is showed.

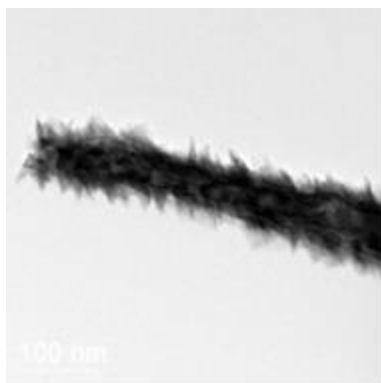


Figure 2. Bright field image of the catalyst A shows a core which is MoO₂ and from that MoS₂ crystallites are being formed on the surface.

The HDS of DBT yields two main products: biphenyl (BP) through the so-called direct desulfurization pathway (DDS) and cyclohexilbenzene (CHB) and tetrahydrodibenzothiophene (TH-DBT) through the hydrogenative pathway (HYD). Since these two pathways are parallel and competitive, the selectivity (HYD/DDS) is determined by [11]:

$$\text{HYD/DDS} = \frac{[\text{CHB}] + [\text{TH-DBT}]}{[\text{BP}]} \quad \dots\dots(1)$$

The experimental constant rate (pseudo-zero-order because the DBT concentration decreased linearly with time) is given in moles of DBT transformed by second in 1 g of catalyst, and it was calculated from the experimental slope of the plots of DBT concentration versus time according to the equation:

$$[\text{Slope (1/Hr)}] \times (\text{Hr}/3600 \text{ s}) \times (1 \text{ mol}/1000\text{mmol}) \times 34 \text{ mmol} \times (1/\text{g}_{\text{cat}}), \quad \dots\dots(2)$$

where 34 mmol is the initial concentration of DBT.

The optimized catalyst A contains MoS₂ nanoplatelets with exfoliated layers and it was prepared as α -MoO₃ nanoribbons, and it has the highest percentage of the element S concentration on its surface.

Interestingly, that the catalyst A showed maximal activity for HDS ($10.5 \times 10^{-7} \text{ mol s}^{-1} \text{ g}^{-1}$) and the maximal selectivity for hydrogenation 2.2.

We have shown the synthesis of a nanostructured self-supported catalyst containing MoS_{2+x} nanoplatelets and that MoS₂ nanoplatelets deviate considerably in geometry and electronic structure from the bulk. Upon sulfidation the nanoplatelets will restructure to a saw tooth shape which is probably more stable. This increases the number of active sites on the catalyst. Adsorption of S dimers at the edges then increases the number of metallic sites.

We can conclude that the adsorbed species are coordinated to the sulfided Mo edges, and that the molecules must be intermediates from a chemical reaction occurring on the active brim sites. The number of adsorption sites are incremented by the presence of kinks at the edges of the nanoplatelets.

Significance

Authors should *briefly* highlight industrial and fundamental significance of this work. as novel catalyst characterization techniques.

References

1. EPA, control of air pollution from new motor vehicles amendment to the tier-2/gasoline sulfur regulations, US Environmental Protection Agency, April 13, 2001, <http://www.epa.gov/fedrgstr/EPA-AIR/2001/April/Day-13/a8927.htm>.
2. C. Song, *Catal. Today* 86, 211 (2003).
3. J. V. Lauritsen, M. Nyberg, R. T. Vang, M. V. Bollinger, B. S. Clausen, H. Topsøe, K. W. Jacobsen, E. Laegsgaard, J. K. Nørskov and F. Besenbacher, *Nanotechnology* 14, 385 (2003).
4. H. Topsøe, B.S. Clausen, R. Candia, C. Wivel and S. Morup. *J. Catal.* 68, 433 (1981).
5. R. Ren, Zongxian Wang, C. Guan and B. Shi. *Fuel Processing Technology* 86,178 (2004).
6. L. Guoran, L. Wei, Z. Minghui, Z. Lianyi, T. Keyi. *Langmuir: The ACS Journal of Surfaces and Colloids*, 22, 5867 (2006).
7. A. Carlsson, M. Brorson and Henrik Topsøe. *Journal of Catalysis* 227 (2004), p. 530.
8. M. Perez De la Rosa, S. Texier, G. Berhault, A. Camacho[§], M. José Yácaman, A. Mehta, S. Fuentes, J. Ascension Montoya, F. Murrieta and R. R. Chianelli. *Journal of Catalysis* 225, 288 (2004).
9. G.A. Camacho-Bragado, M. José Yacamán, *Appl. Phys. A* 82, 19 (2006).
10. T.P. Prasad, E. Diemann and A. Muller, *J. Inorg. Nucl. Chem.* 35, 1895 (1973).
11. D. D. Withehurst, T. Isoda and I. Mochida *Adv. Catal.* 42, 345 (1998).