Structure and Catalytic Characterization of Cobalt-Molybdenum Sulfide Nanoplatelets

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Introduction

The new environmental regulations in most 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 using $CoMo/Al_2O_3$ or a $NiMo/Al_2O_3$ catalyst. Their active phase consists of MoS_2 nanocrystallites well dispersed on a high-surface-specific alumina and promoted by cobalt or nickel atoms [2, 3].

HRTEM is very useful to determine the distribution of the nanoparticles on the surface, and to determine the shape of the MoS_2 catalyst structure. 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.

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[4-6].

Materials and Methods

A self-standing film of cobalt-molybdenum oxide nanobelts was prepared by a hydrothermal process in the presence of a cobalt precursor (Cobalt Acetilacetonate ($Co(C_5H_7O_2)_2$) or Cobalt Carbonate ($CoCO_3$)). The procedure consisted of a dropwise of 4 M solution of HCl to a saturated solution of sodium molybdate mixed with cobalt precursor with atomic ratio $Co/(Co + Mo)$ from .1 to 0.5. The mixture is placed in a Teflon-lined autoclave and left at 423 K for 6 h. Once the reaction time was completed, the product Co-Mo oxide was filtered and dried. Sections of these films were reacted with a stream of H_2S gas mixed with 90 % inert gas N_2 and10% H_2 in a 9/1 volume ratio at 723 K for 1 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 2θ degrees. We used X-ray photoelectron spectroscopy XPS to do surface analysis of the optimized model Co-Mo sulfide catalyst.

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.

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. 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

X-ray diffraction patterns showed the characteristic peaks of the nanostructured cobalt-molybdenum oxide and cobalt-molybdenum sulfide. In Figure 1 it clearly shows the cobalt molibdenum oxide nanobelts from a scanning electron image.
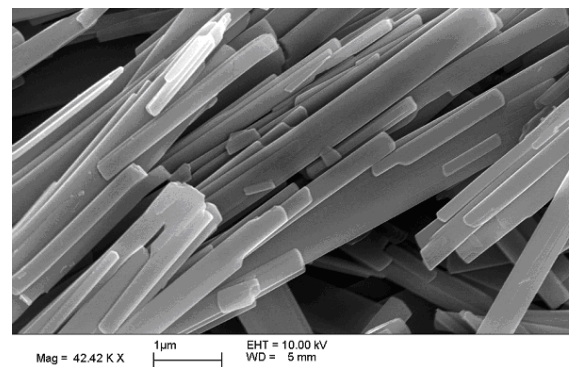
Figure 1. Scanning Electron Micrograph (SEM) of cobalt-molybdenum oxide nanobelts.

The Figure 2 is a scanning electron micrograph that shows a rough surface by the growth of nanorods of cobalt-molybdenum sulfide on the cobalt-molybdenum oxide nanostructured matrix, after 30 min of the reaction in presence of a flux of H_2S/H_2.

The HAAD field image of the catalyst is shown in the figure 3. As can be seen there is a core which is Co-Mo oxide and from that Co-Mo sulfide nanorods 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.

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.
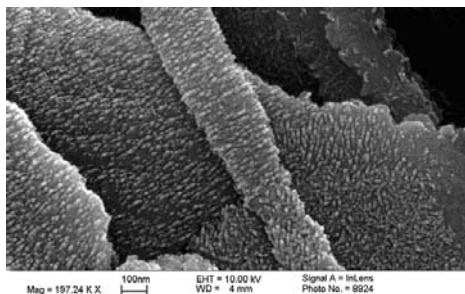

Figure 2. SEM image of the Co-Mo oxide nanobelts after sulfidization, the Co-Mo sulfide phase rod-like nanoparticles growth on them.

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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 [7]:

HYD/DDS = ([CHB] + [TH-DBT])/[BP]   ……..(1)

The optimized catalyst contains Co-Mo sulfide nanoplatelets with exfoliated layers and it was prepared as of Co-Molvbdenum oxide nanobelts, and it has the highest percentage of the element S concentration on its surface.

Interestingly, that this catalyst of Co-Mo sulfide nanoplatelets showed maximal activity for HDS $(15 \times 10^{-7} \text{ mol s}^{-1} \text{ g}^{-1})$ and the maximal selectivity for hydrogenation 2.0 in comparison with the one of MoS_2 nanostructured.

We have shown the synthesis of a nanostructured self-supported catalyst containing $Co\text{-}MoS_{2+x}$ nanoplatelets and that Co-MoSulfide nanoplatelets deviate considerably in geometry and electronic structure from the bulk. The presence of cobalt increases the number of active sites on the catalyst. Adsorption of S dimers at the edges then increases the number of metallic sites.
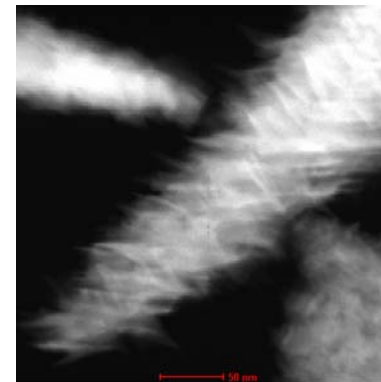

Figure 3. HAADF image of the catalyst shows a core which is Co-Mo oxide nano-structured and from that Co-Mo sulfide nanowires are being formed on the surface.

We can conclude that the adsorbed species are coordinated to the sulfided Co-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 cobalt that acts as promoter at the edges of the nanoplatelets.

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

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