Characterization of low dimensional molybdenum sulfide nanostructures

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ABSTRACT

It is presented a detailed structural characterization of a nanostructured form of molybdenum disulfide. The material consists of a layer of highly textured molybdenum sulfide growing off a molybdenum dioxide core. The structure and chemical composition of the synthesized nanostructured sulfide was compared to two well-known forms of molybdenum disulfide, i.e. a commercial molybdenite sample and a poorly crystalline sulfide. X-ray diffraction, high-resolution electron microscopy and electron diffraction showed that the material reported here presents crystalline nanodomains with a crystal structure corresponding to the 2H polytype of molybdenum disulfide. X-ray photoelectron spectroscopy was used to demonstrate the differences between our sulfide and other materials such as amorphous MoS_3, oxysulfides and poorly crystalline MoS_2, corroborating the molybdenite-2H stacking in this form of sulfide. The material under study showed a high proportion of crystalline planes different from the basal plane.

1. Introduction

Molybdenum disulfide is a layered anisotropic material that presents three polytypes originated from different stacking sequences: the 1T polytype that is the least common, the 2H that has a hexagonal unit cell and the 3R with a rombohedral cell. Besides of these crystalline polytypes, partially crystallized sulfides with stoichiometric (S/Mo) ratios between 2 and 3 have been prepared from thermal decomposition of thiomolybdates [1].

Crystalline and partially crystalline sulfides have been studied for several years because of their potential applications as solid lubricants [2], cathodes in rechargeable batteries [3,4], catalysts [5,6], superconductors [7,8] and so on. More recently, with the continuous miniaturization process and the need for more efficient catalysts, the synthesis and properties of reduced-size particles of this material started to be investigated. Very important examples of these nanosized particles are the inorganic fullerenes and nanotubes [9,10], which present different properties than the bulk material because of their particular size and structure. Another remarkable example of enhanced properties at the nanoscale in the molybdenum sulfide system is the nanoflowers that were reported to have interesting field emission properties [11].

Molybdenum sulfide is also one of the most important hydrotreating catalysts that have been used for decades in the treatment of heavy crude oils to eliminate heteroatoms and break aromatic molecules. However a full understanding of the structure of catalytic sites has not been accomplished. The catalytic properties of molybdenum sulfide have been investigated in relation to its particle size and structure [5,12,13]. More recently, scanning tunneling microscopy studies revealed the occurrence of surface reconstruction in nanosized molybdenum sulfide clusters [14]; thus, the edges of these nanoclusters are not identical to stoichiometric MoS_2. This structural change induced also a distortion of the electronic structure originating one-dimensional metallic

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states. These studies demonstrate the importance of structural characterization of catalytic materials towards a better understanding of the reaction paths and consequently a better design of catalytic sites that allow an increased activity and improved selectivity. Preliminary studies of the catalytic activity of molybdenum sulfide prepared by sulfidation of molybdenum oxide nanoribbons showed an enhanced selectivity as compared with previously reported molybdenum-based catalysts [10]. This material was found to contain molybdenum sulfide nanostructures that do not exactly correspond with the phases that are regularly found in hydrodesulfurization (HDS) catalysts prepared by in-situ or ex-situ decomposition of ammonium molybdates and thiomolybdates deposited on alumina supports; such as highly destacked molybdenum sulfide, poorly crystalline MoS_2 or bent layers of molybdenum sulfide. Thus, a more detailed structural characterization was needed in order to understand the relationship between this particular morphology and the observed catalytic properties. In the present paper we present a complete structural characterization of the model bulk catalyst synthesized by sulfidation of molybdenum oxide nanoribbons [6,15]. There were used a set of characterization techniques that provided complementary information about the synthesized material, the same techniques were applied to two forms of molybdenum sulfide, commercial molybdenite and poorly crystalline sulfide, in order to establish a comparison with our nanostructured molybdenum sulfide.

2. Experimental

The nanostructured molybdenum sulphide samples (Ns) were prepared by sulfidizing molybdite (α-MoO_3) nanoribbons. The precursor oxide was synthesized under hydrothermal conditions in the following way: 7 mL of a 4 M HCl solution were added dropwise to 2 mL of a saturated solution of sodium molybdate. The resulting clear yellow liquid was placed in a Teflon lined autoclave and kept at 423 K for 12 h. Once the reaction time was completed, the product was filtered and dried [15]. The resulting nanoribbons were sulfidized at 723 K for 1 h. The sulfidizing atmosphere was a mixture of H_2S, N_2 and H_2 in 90:9:1 volume ratios. The unreacted excess of H_2S was neutralized with a saturated solution of NaOH. For comparison, a standard sample of commercial MoS_2 (Across, 98.5%) and poorly crystalline molybdenum sulfide (pc) were used. The pc samples were prepared by thermal decomposition of $(NH_4)_2MoS_4$ at 723 K for 3 h under nitrogen atmosphere.

The morphology of all the samples was studied by scanning electron microscopy (SEM) in a Hitachi S-4500 field emission SEM operating at 5 kV. The samples were deposited on carbon tape and Au-coated. Crystal structure identification was carried out by X-ray diffraction (XRD) in a Phillips automated vertical scanning powder diffractometer. The spectra were obtained from 20 to 80 2θ degrees.

Transmission electron microscopy (TEM) samples were prepared by spraying ultra-fine powders on lacey carbon copper grids without the use of solvents in order to minimize carbon contamination. TEM was performed in a JEOL Jem-2010F microscope equipped with a Schottky-type field emission gun, ultra-high-resolution pole piece (Cs = 0.5 mm), and a Scanning-Transmission (STEM) unit with a high angle annular dark field detector (HAADF) operating at 200 kV. An Oxford spectrometer, attached to the Jem-2010F was used for energy dispersive X-ray spectroscopy (EDS).

Electron energy loss spectra (EELS) were recorded with a Gatan Enfina spectrometer. EEL spectra were taken in the STEM mode, with a 0.3 nm probe at a convergence semi-angle of about 12–15 mrad. Low loss spectra were taken with a 1 mm spectrometer aperture (40 mrad collection angle), sulfur core loss spectra were taken with a 3 mm aperture (120 mrad collection angle). The spectra resolution was between 1.2 and 1.4 eV.

The data was processed using the GATAN Digital Micrograph® program. The background in the core loss region was fitted to a power-law model and subtracted from the corresponding spectra. The pre-edge fitting windows (δ) for background subtraction were chosen to contain more than 10 channels but less than 30% E_k, where E_k is the energy of the edge [16]. For the conditions used in the collection of spectra and the sulfur edge, the values of δ were in the 5–50 eV range. The plural scattering was removed by the Fourier-ratio deconvolution method, using Digital Micrograph. Focal-thickness series were generated with the MacTempas® software to compare with the experimental high-resolution electron microscopy (HREM) images.

3. Results and Discussion

As previously mentioned, it has been demonstrated that the activity of molybdenum sulfide-based catalysts strongly depends on the kind of crystalline planes (sites) exposed at the surface due to the different chemical environments present in each crystallographic orientation [5]. Given the importance of determining the surface structure, we have applied a series of complementary techniques to provide a full characterization of the nanostructured molybdenum sulfide (Ns) prepared by sulfidation of molybdite (α-MoO_3) nanoribbons. The structure and chemical composition of the Ns samples are compared to those of two other known forms of molybdenum sulfides; one of them is a commercially available well-crystallized molybdenite sample (std) and the other one being a poorly crystalline molybdenum sulfide prepared by thermal decomposition of ammonium thiomolybdate (pc).

3.1. *Morphology (Oxide Nanoribbons vs. Sulfidized Sample)*

Ns samples were prepared by thermal treatment of molybdenum oxide nanoribbons in a strong sulfo-reducing atmosphere. The oxide nanocrystals were prepared via a hydrothermal method. Previously to sulfidation, the oxide crystallites had smooth surfaces and a well-defined rectangular cross section (Fig. 1A). These particles were about 5 microns long, and 150 nm wide as determined from the SEM images. After the reaction, the resulting material consisted of elongated rod-like particles with very rough surfaces (Fig. 1B); at higher magnifications, it was observed that the roughness was due to spike-shaped particles growing perpendicularly to the long-axis.