CHARACTERIZATION OF HIGHLY DISPERSED MOLYBDENUM SULFIDE PREPARED BY W/O EMULSION-MEDIATED SYNTHESIS

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Recibido: Enero 2012. Aprobado: Junio 2012.
Publicado: Julio 2012.

ABSTRACT

In this work the TEM characterization of ultradisperse MoS_2-type solids, synthesized through the thermal decomposition of water-in-oil emulsions, was carried out in order to assess feasible active phases in novel ultradispersed catalytic systems currently employed for the conversion of heavy hydrocarbons. Ammonium heptamolybdate tetra-hydrated ($(NH_4)_6Mo_7O_{24}.4H_2O$) and ammonium sulfide ($(NH_4)_2S$) were selected as precursor salt and sulfurizing agent, respectively, and dissolved simultaneously in the aqueous phase of the emulsion. A slight decrease in the average emulsion droplet size was observed when the concentration of ammonium sulfide present in the aqueous phase was low. TEM images showed the formation of typical layered MoS_2 structures with different lengths. Additionally, average stacking degree values between 4 and 6 were determined for the structures. Finally, our results suggest that a low concentration of surfactant promotes the formation of stoichiometric MoS_2 phases (atomic S/Mo ratio ~ 2) as well as less stacking of the structures.

Keywords: Molibdenum sulfide, disperse catalysts, w/o emulsions.

SINTESIS MEDIANTE EMULSIONES W/O DE SULFUROS DE MOLIBDENO ALTAMENTE DISPERSOS

RESUMEN

En el presente trabajo se realizó la caracterización por microscopía electrónica de transmisión de sólidos sulfurados ultradispersos tipo MoS_2, sintetizados mediante la descomposición térmica de emulsiones agua/aceite (W/O), con el fin de estudiar fases posiblemente activas que pudieran generarse en novedosos catalizadores ultradispersos para la conversión de hidrocarburos pesados. Se utilizaron conjuntamente en la fase acuosa de la emulsión heptamolibdato de amonio tetrahidratado ($(NH_4)_6Mo_7O_{24}.4H_2O$) y sulfuro de amonio ($(NH_4)_2S$) como sal precursora y agente sulfurante, respectivamente. Se encontró una disminución en el tamaño de gota de la emulsión al disminuir la concentración de sulfuro de amonio en la fase acuosa. Las imágenes de TEM mostraron la formación de estructuras apiladas típicas de MoS_2 con diferentes elongaciones. Adicionalmente, se determinó que el número promedio de apilamiento de las estructuras está entre 4 y 6. Finalmente, los resultados sugieren que una disminución en la concentración de surfactante favorece a la formación de la fase estequiométrica MoS_2 (relación atómica S/Mo ~2), así como la disminución del grado de apilamiento en las estructuras.

Palabras claves: Sulfuro de molibdeno, catalizadores dispersos, emulsiones w/o.

INTRODUCTION

The use of unsupported dispersed catalysts is currently an attractive option to the generation of active phases to target the conversion of heavy hydrocarbon feedstocks, avoiding drawbacks commonly associated with the use of conventional supported catalysts [1]. In this way, the introduction in a controlled way of relatively large amounts of active elements may be possible, achieving potentially a high degree of dispersion when the particles are generated in-situ at process conditions, maximizing the catalytically exposed active phase per total volume, being this approach used especially for refractory heavy hydrocarbon feedstocks. Unsupported molybdenum sulfide particles largely employed for this purpose in hydrotreatment processes can be prepared in homogeneous phase by various methods, including the direct precipitation of sulfides [2] and thiosalts decomposition [3], the latter being one of the most is widely used for to preparation of catalysts for hydrotreating processes.

Recently, a novel catalytic system based on the use of water-in-oil (w/o) emulsions has been proposed as a vehicle to synthesize highly dispersed metal sulfide catalysts and to promote the ultradispersion of metal sulfide catalysts [4-6]. W/O emulsions are produced when water is dispersed commonly in a continuous hydrocarbon phase, and these systems are normally stabilized by the addition of a surfactant agent. Normally, this formulation leads to spherical aggregates known as reverse micelles. Water soluble reagents confined inside the discontinuous drops may react upon mixing or after appropriate thermal treatments. In this way, micelles are considered as ‘‘nanoreactors’’, providing a suitable environment for controlled nucleation and growth, which is of paramount importance to nanoparticle synthesis [6].

In the present work, unsupported highly disperse molybdenum sulfides were first prepared by thermal decomposition of w/o emulsions [4,7], and then characterized to get further insight into the structure of this interesting phases.

MATERIALS AND METHODS

For the preparation of the emulsions, 1-metyl naphthalene was selected as the organic phase ($C_{11}H_{10}$, >96%), as an appropriate hydrocarbon to model heavy feedstocks. The aqueous phase was composed of a solution of 13.9 wt% ammonium heptamolybdate ((NH4)6Mo7O24.4H2O, 99%), together with 6 and 10 wt% ammonium sulfide ((NH4)2S + aq. 23.7%) to test the effect of the concentration of sulfidizing agent. Additionally, different amounts of surfactant were used (0.5, 1.5 and 3 wt%). Table 1 shows the emulsion identification and composition and their average droplet size.

The emulsions were characterized using a light transmission microscope Olympus BX51 and the droplet size was measured using the software Image-Pro Plus 5.0.

Thermal decomposition of the emulsions was carried out in a 300 ml Parr reactor, kept at 350 °C and 68 atm of H_2 pressure during 8 min. Solid products of the reaction were collected by centrifugation, washed with toluene and dried in vacuum for two hours at 120°C.

Table I. Composition of the emulsions.

Emulsion	%wt $(NH_4)_2S$ in aqueous phase	%wt Surfactant in the emulsion	Droplet size (µm)
A(0.5)S-10	10	0.5	12
A(1.5)S-10	10	1.5	13
A(3)S-10	10	3.0	13
A(3)S-6	6	3.0	11
A(1.5)S-3.5	3.5	1.5	6

Solids Characterization

Chemical elemental analysis of the clean solids was determinate by ICP. WDS analysis was carried out in a EPMA JEOL JX-8900 operated at 20 kV accelerating voltage. The samples were prepared in pellet shape to obtain a flat sample surface. Then, the samples were fixed to the sample holder using graphite tape.

Morphologic evaluation of sulfide residues by transmission electron microscopy (TEM) was carried out in a FEI Titan 80-300 instrument, operated at 200 kV accelerating voltage. Specimens were prepared by ultrasonic dispersion of the slightly grounded samples in a 40% ethanol–water solution, and then a drop of the suspension was placed on collodion graphite coated copper grids.

RESULTS AND DISCUSSIONS

All the emulsions presented a characteristic yellow-orange color after the preparation. We found that the average diameter of the droplets of aqueous phase in all the different emulsions was between 6 and 13 µm, without any clear trend between drop size and surfactant concentrations. However, we found a slight decrease in droplet size when the concentration of ammonium sulfide in the aqueous phase decreases. Figure 1 shows typical light microscopy images of the emulsions A(0.5)S-10 (Fig. 1a) and A(1.5)S-10 (Fig. 1b).

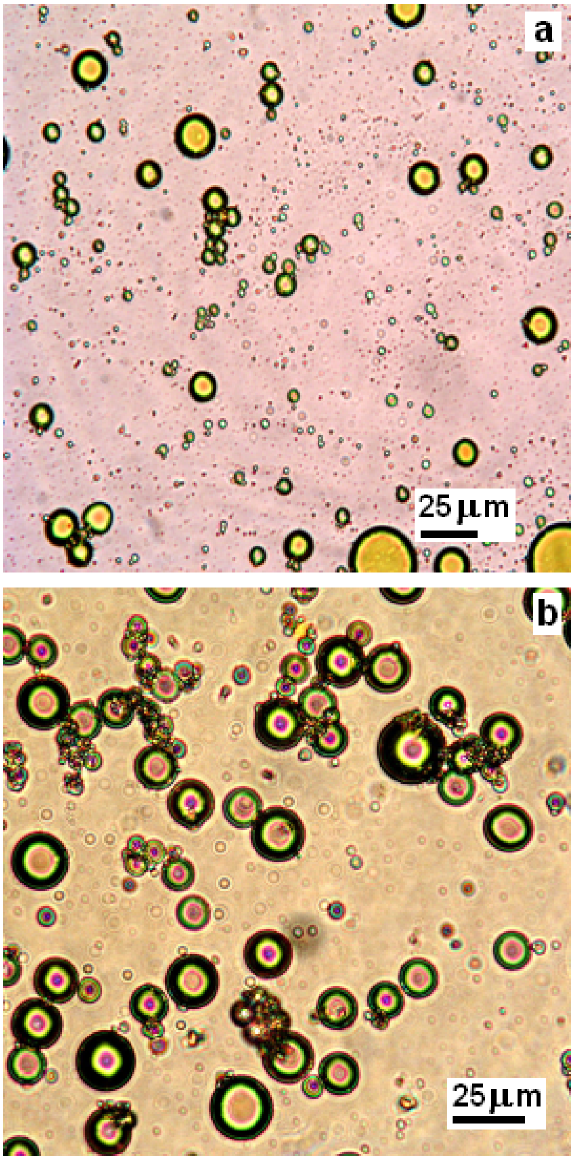

Fig. 1. Optical microscopy images of the Emulsions a) A(0.5)S-10 and b) A(1.5)S-10.

In Table II are showed the ICP and WDS Mo/S atomic ratios for the solids prepared after the thermal decomposition process.

In principle, values of S/Mo atomic ratio close to 2 would be in theory the most appropriate for the preparation of stoichiometric MoS_2 phases, and the efforts in the formulation and preparation of this kind of emulsions should contribute to the synthesis of potentially catalytic solids.

The results show a reasonably trend, since a higher S/Mo ratio was found in the solids when the concentration of ammonium sulfide present initially in the aqueous phase of the emulsion was increased, presumably with the formation of intermediate oxosulfide compounds, such MoO_xS_{4-x}.

In contrast, the results show that the S/Mo atomic ratio decreases when large surfactant concentrations are employed during the preparation of the emulsion. It is possible that larger amounts of surfactant delay the thermal decomposition of the precursor as well as the necessary reduction and sulfidation of molybdenum. In the other hand, the S/Mo ratios determinated by WDS are slightly larger than those obtained by ICP. In spite that the deep sensitivity of the WDS technique is of about 1 µm and therefore this mean that it is not properly recognized as a surface analysis, this possibly suggest that the sulfur present in the samples has preference toward the solid surface, which is in accordance with work previously reported in the literature.[4]

Tabla II. Sulfide solids S/Mo atomic rations.

Solid	S/Mo Atomic ratio	
	ICP	WDS
A(0.5)S-10	2.79	2.12
A(1.5)S-10	1.90	2.07
A(3)S-10	1.71	2.10
A(3)S-6	1.32	1.34
A(1.5)S-3.5	0.60	0.76

TEM images of the A(3)S-10 sample show a high density of structures typical of layered MoS_2 phase (Figure 2), with some particular areas presenting elongated and well-stacked structures (Fig. 2a), and other areas with more disordered structures, with folds and curves and a clearly lower stacking degree (Fig. 2b).

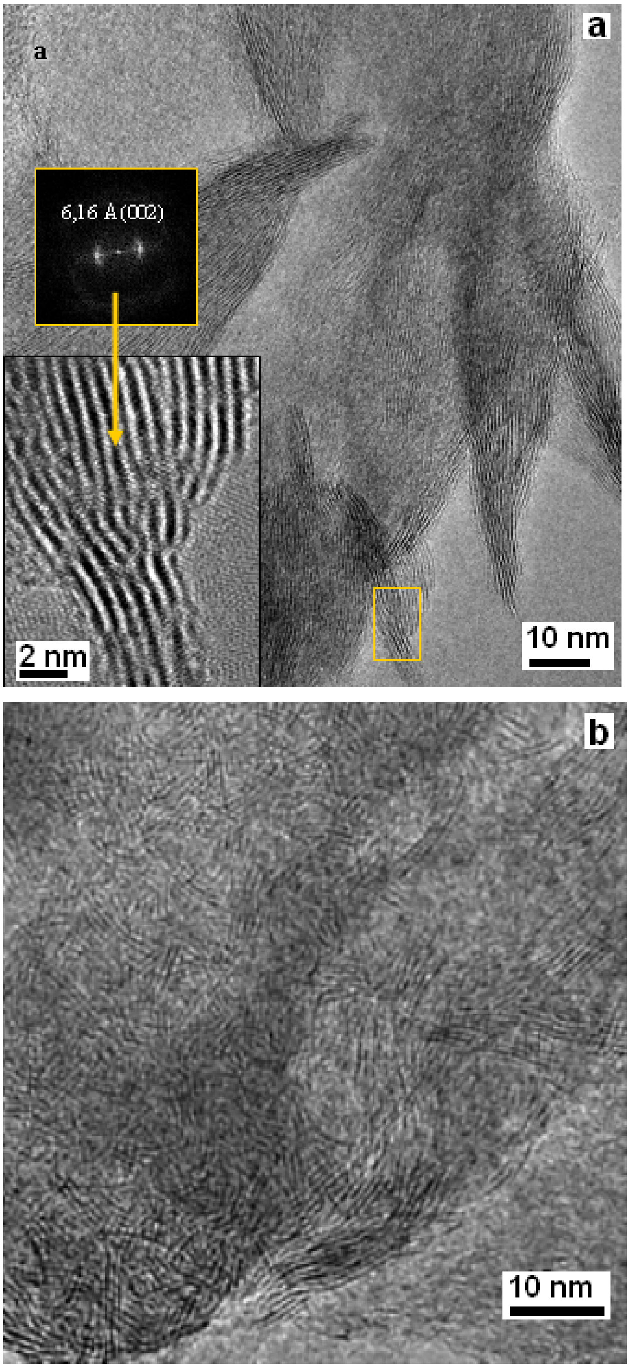

Fig. 2. Solid A(3)S-10: Well-stacked structures (2a), folds and curves and structures (2b).

The lattice fringes observed have a spacing of about 6.17 Å, which are comparable to the 6.15 Å separation reported for the basal planes (002) of pure MoS_2 [8]. The Fourier transformed analysis taken in selected areas of the image (inserted in the micrographs), showed reflections corresponding to a basal plane orientation (002) of a phase hexagonal molybdenite crystal.

On the other hand, for the sample A(3)S-6 prepared with a low concentration of ammonium sulfide, structures with a remarkable degree of stacking were observed, but in smaller quantities and with a large dispersion (figure 3). This system shows a different morphology with a much more extended configuration and less folds and curves. For this case, Fourier transform analysis showed reflections with interplanar spacing of 6.181 and 2.732 Å corresponding to the planes (002) (6.155 Å) and (100) (2.738 Å) respectively, also typical of a hexagonal molybdenite crystal phase (PDF 37-1492). However, it is also possible to find in the micrographs some areas where the stacked structures are not clearly observed due to the fact that the (101) plane orientation is perpendicular to the direction of the incident electron beam. For instance, results collected for the sample A(1.5)S-10 (figure 4) show an area with interplanar spacing of 2.66 Å matching with (101) plane of MoS_2 (shown in the insert of figure 4). It is well known for MoS_2 morphology characterization that the (002) crystallographic orientation corresponding to the basal plane is related to the crystal height in epitaxial direction, while the (110) and the (100) planes are related to the corners and edges, respectively.

The unsupported MoS_2 systems synthesized in the present work manifest structural properties analogous with those previously reported for supported MoS_2-based catalysts [9,10], where the corresponding arrangement appear comparatively less crystalline with significantly more folded layers, as confirmed by electron tomography [10]. In our case, the evidence is suggestive of a rather larger stacking in the unsupported MoS_2 structures prepared by the emulsion mediated synthesis discussed here. Contrarily, formation of less stacking and more bolds yield to more corner and defects in the structures, which favors the presence of more catalytic sites.

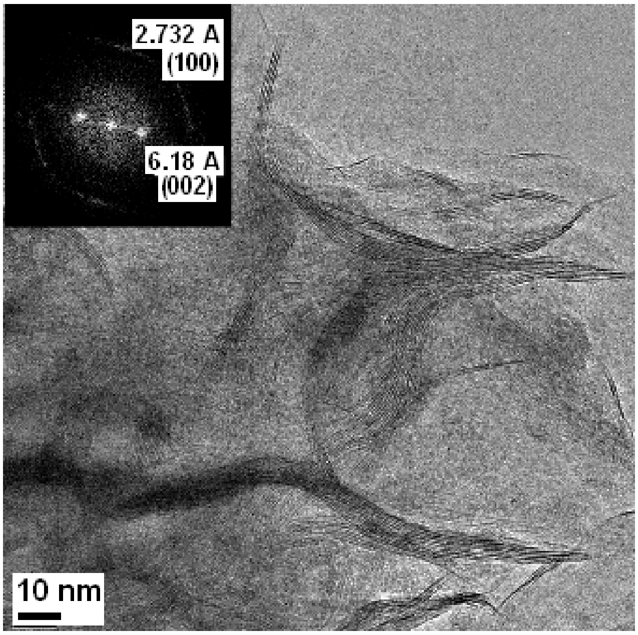

Fig. 3. Morphology of the solid A(3)S-6. Straight slabs and thick stacking are noticeable in the configuration of MoS_2.

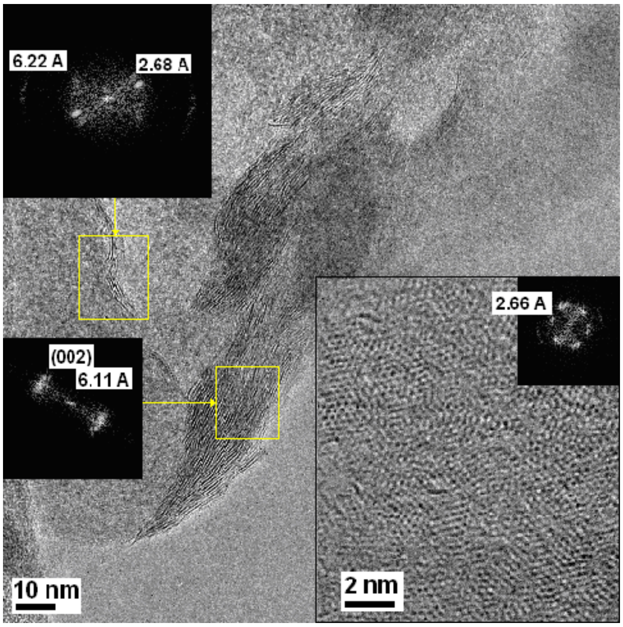

Fig. 4. Staking morphology in the solid A(1,5)S-10. The insert shows the crystallographic orientation of the plane (101) for the same solid.

Noguira et al. [11] synthesized unsupported and Al_2O_3-supported MoS_2, reporting curved and straight slabs as well as regions with strongly localized distorted zones, suggesting the creation of very active defect sites on basal planes. They reported that the nature of the sulfur-containing precursor used for the preparation of the catalysts is of key significance to the morphology of the resulting MoS_2 structures.

Recently, it was reported that amorphous MoS_2 with folded multi-layered structure presented a significantly greater activity toward hydrodeoxygenation reaction than well crystalline and ordered multi-layered MoS_2 [12].

Other important aspect in the morphological characterization of MoS_2 is the consideration of the stacking degree of its structure. In the present work the layer stacking number distribution was calculated for the solids prepared here. The two solids synthesized here using 3% of surfactant, A(3)S-10 and A(3)S-6), showed an average stacking number around 6, which suggests that this parameter is not influenced by the concentration of ammonium sulfide used in the parent emulsion. However, the comparison of solids A(3)S-10 and A(1.5)S-10 indicated a slight decrease in the degree of stacking (6 to 4) when the lower amount of surfactant was used (1.5%), leading also to a narrower distribution of the stacking frequency (Figure 5).

These parameters are important due to the structure sensitivity of hydrotreatment processes where MoS_2 is involved. Thus, the control of the crystal height and length of the sheets during the process of synthesis may favor the activity of the catalyst [8-9]. Daag and Chianelli [8] proposed a "rim-edges" model correlating stacking parameters with selectivity in the hydrodesulfurization of dibenzothiophene. The two sites were distinguished by their relative location on the structure of the MoS_2 crystal. Rim sites are reported active to perform both C–S bond rupture and hydrogenation reactions and will be located on external faces, while edge sites located on internal slabs are more prone to conduct only C–S bond rupture. Stacking height of the MoS_2 crystals will therefore control HDS selectivity.

In the current work, TEM characterization of MoS_2 dispersed structures synthesized in a hydrocarbon media by an alternative emulsion methodology was used as a tool to help in the structural characterization of this system as a potential catalyst for the transformation of heavy hydrocarbons**.** The usefulness of this microscopic characterization to understand catalytic activity of these solids will be established in future tests.

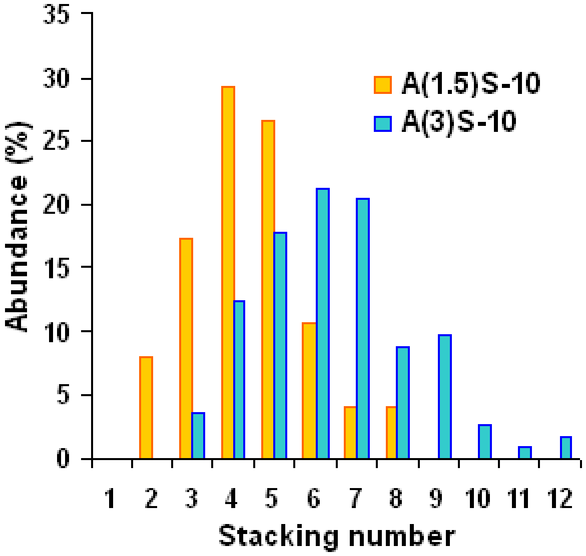

Fig. 5. Distribution of stacking number for the solids A(3)S-10 and A(1.5)S-10.

CONCLUSIONS

The thermal decomposition of water-in-oil emulsions containing a molybdenum precursor salt in conjunction with a sulfiding agent is an efficient method to generate dispersed molybdenum sulphide. The amount of sulfur available in the formulation of emulsions using a water-soluble sulfur agent is crucial to control the stoichiometry of the molybdenum sulfides synthesized by this methodology.

TEM studies suggested that all solids synthesized in this work by the emulsion-mediated synthesis are mainly of a MoS_2 phase-type, well dispersed and with a remarkable degree of stacking. A low concentration of surfactant promoted the formation of stoichiometric MoS_2 phases (S/Mo ~ 2) as well as less stacked particles.

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