

Spherical MoS₂ micro particles and their surface dispersion due to addition of cobalt promoters

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We present here a hydrothermal synthesis on spherical shape molybdenum di-sulfide (MoS₂) micro-particles using thiomolybdate salts and sodium silicate as reducing agent. To understand the role of cobalt promoters on this particular MoS₂ spherical shape a second reaction was carried out using same precursors plus addition of Co following same pressure and temperature conditions. Both products (before and after Co promoter) were characterized using scanning electron and transmission electron microscopic analysis. From SEM measurements a spherical average size diameter of $\sim 2.855 \mu\text{m}$ on pure MoS₂ is observed and disperse surface once cobalt is incorporated into the reaction. From TEM observations an interlayer average distance of $\sim 0.63 \text{ nm}$ is obtained for MoS₂-MoS₂ slabs on samples with Co content. X-ray diffraction indicated principal crystallographic planes to be (002), (100), (101), (102), (103), (006), (105), and (110) for both MoS₂ and MoS₂/Co samples.

Keywords: Molybdenum sulfide; cobalt; X-ray; TEM.

Presentamos aquí una síntesis química de micropartículas esféricas de sulfuro de molibdeno (MoS₂) utilizando sales de tiomolibdato y silicato de sodio como agente reductor. Para comprender el rol de los promotores de cobalto (Co) en estas particulares micro-esferas de MoS₂, una segunda reacción fue realizada utilizando los mismos precursores y la adición de Cobalto bajo las mismas condiciones de presión y temperatura. Ambos productos (antes y después del Co) fueron caracterizados utilizando microscopios de barrido y transmisión electrónicos (SEM y TEM). Los resultados del SEM indican un diámetro promedio de $\sim 2.855 \mu\text{m}$ en esferas de puro MoS₂, así como una dispersión cuando el cobalto es incorporado en la reacción. Observaciones en TEM indican una distancia promedio de $\sim 0.63 \text{ nm}$ en las laminas de MoS₂ para muestras que contienen cobalto. Los resultados de rayos-X indican que los principales planos de difracción son: (002), (100), (101), (102), (103), (006), (105), y (110) para ambas muestras las de MoS₂ and MoS₂/Co.

Descriptores: Sulfuro de molibdeno; cobalto; rayos-X; TEM.

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1. Introduction

Molybdenum di-sulfide has several applications, in which most important found are hydrodesulphurization of dibenzothiophene also known as HDS [1], one can find also published in the literature several research articles indicating its potent properties when used as lubricant in high vacuum conditions [2]. From the literature molybdenum di-sulfide unit cell is found to have a coordinated tetragonal S-Mo-S bonding array usually called slabs, which are stack in an array due to Van der Waals bonding fact that make it relative easy to glide when is used as lubricant [3]. But also it has been discovered that MoS₂ can have a different final array in the structure, depending on the synthesis method [4,5], that structure is due to the array of MoS₂ slabs which could be spherical shape, nano-tubes, flakes and nano-rods [4-6]. Also the structure/function relation tells us that properties in those MoS₂-based nanostructures will depend strongly on final shape formed after synthesis [7]. Based on that an elegant three-dimensional MoS₂ micro-flowers were recently

synthesized by heating a precursor MoO₂ thin film in a vapor sulfur atmosphere and used because it appeared to be excellent field emitters [8], that investigation lead to a conclusion which is the role of sodium silicate on forming of those MoS₂ flower-like structures [9]. Now, when using MoS₂ as a catalyst on a HDS reaction, previous investigations prove that catalytic activity almost doubled when using a promoter such as nickel (Ni), cobalt (Co) or tungsten (W), leading also a new phase first discovered by meaning of Mössbauer spectroscopy [10], and later under x-ray synchrotron [11], and x-ray photoelectron spectroscopy [12], after those investigations a new term was coined called “CoMoS” in the case of Co-promoter and NiMoS in case of Ni-promoter, reason why when MoS₂/Co are in contact its mean to say a CoMoS phase has been formed [10]. One simple technique to understand final structure/function after synthesis is by observing final products under microscopy techniques, which can be scanning electron microscope (SEM) or transmission electron microscopy (TEM), the comparison between techniques is the way electrons are accelerated and also sample thickness

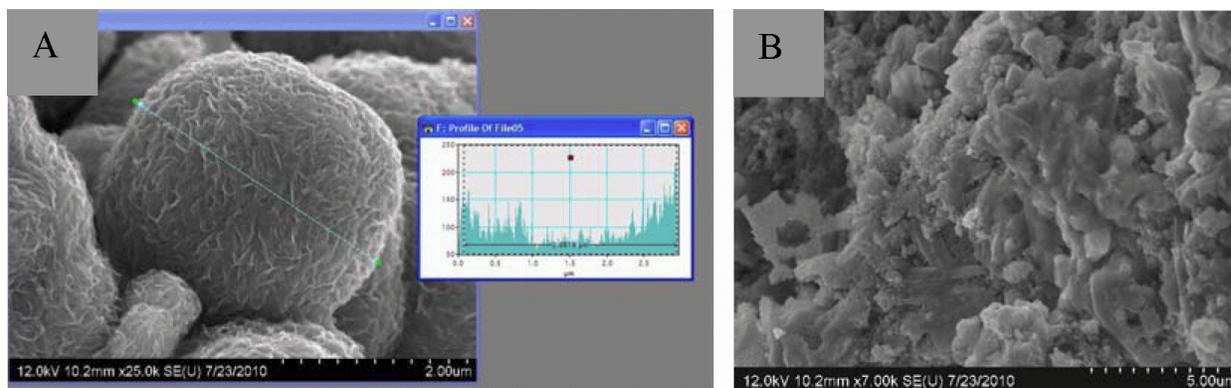


FIGURE 1. A) SEM image of MoS₂ micro-spheres with average size diameter of 2.86 μm. B) Surface dispersion due to Co-promoter addition.

which in most cases thick specimens won't let electrons to penetrate through the sample, provoking almost zero transmission. This research report is divided into three sections which is 1) Synthesis of spherical shape MoS₂ and synthesis of MoS₂ with the addition Co by meaning of Hydrothermal methods; 2) TEM and SEM observations in final products and 3) X-ray powder diffraction for both spherical MoS₂ and MoS₂/Co cases.

2. Hydrothermal synthesis of spherical shape MoS₂ and MoS₂/Co

The experimental procedure is following previous investigations found in the literature [2-4] as follows: 3 mmol of sodium molybdate (Na₂MoO₄·2H₂O) and 9 mmol of thioacetamide (CH₃CSNH₂) were dissolved in 30 mL of deionized

water, and then 0.5 g of sodium silicate (Na₂SiO₃·9H₂O) was added into the solution under violent stirring. The pH value of the solution was adjusted to 6.0 by dropping 12 M hydrochloric acid (HCl) solution while violent stirring. 0.50 g of cobalt chloride (CoCl₂) was added to the solution before the hydrothermal reaction. Once cobalt is added the new solution became magenta color-like. The resulting magenta solution was transferred to a 50 mL Teflon-lined and placed inside the hydrothermal reactor rising temperature value to 220°C for 24 h and allowed to cool down naturally. The black resulting precipitates were collected and washed first with 1M of Sodium Hydroxide (NaOH) solution for several times to remove possible residues specially from silicic acid and later with deionized water and absolute ethanol, finally both products were dried separate at 60°C for 6 h in open flow furnace.

The reaction could be described as follows:

- 1) $6\text{CoCl}_2 \cdot 6\text{H}_2\text{O} + 12\text{Na}_2\text{MoO}_4 + \text{Na}_2\text{SiO}_3 + 26\text{HCl} \longrightarrow \text{H}_4\text{SiCo}_6\text{Mo}_{12}\text{O}_{40} + 26\text{NaCl} + 47\text{H}_2\text{O} + 6\text{Cl}_2$
- 2) $\text{CH}_3\text{CSNH}_2 + 2\text{H}_2\text{O} \longrightarrow \text{CH}_3\text{COOH} + \text{NH}_3 + \text{H}_2\text{S}$
- 3) $\text{H}_4\text{SiCo}_6\text{Mo}_{12}\text{O}_{40} + 27\text{H}_2\text{S} \longrightarrow 12\text{Co}_{0.5}\text{MoS}_2 + \text{H}_2\text{SiO}_3 + 3\text{H}_2\text{SO}_4 + 25\text{H}_2\text{O}$

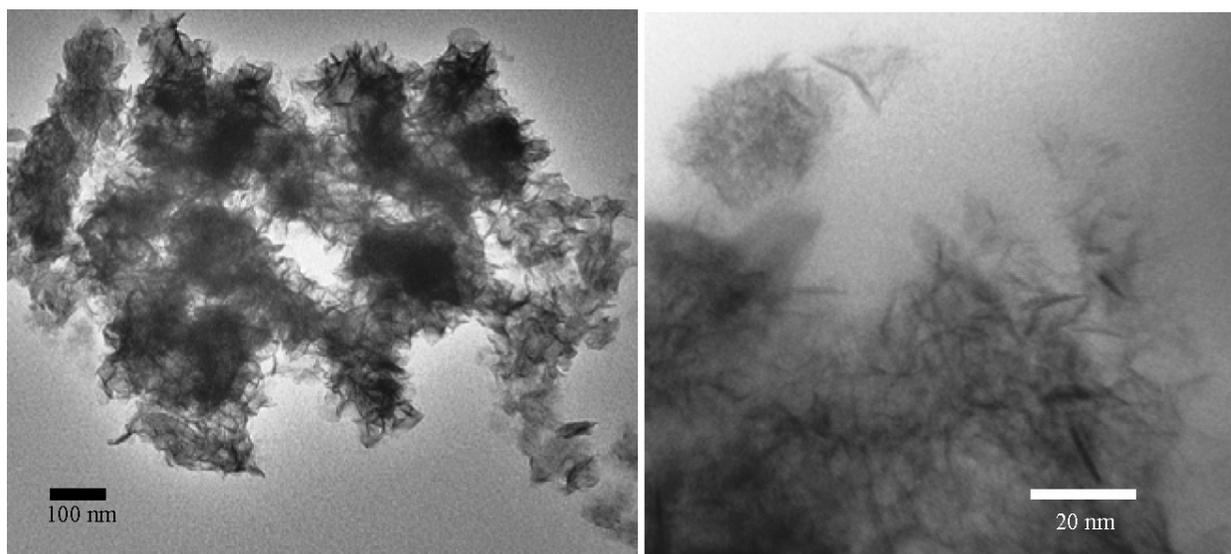


FIGURE 2. Left: TEM image of spherical shape MoS₂. Right: TEM image of spherical shape surface dispersion due to addition of Cobalt.

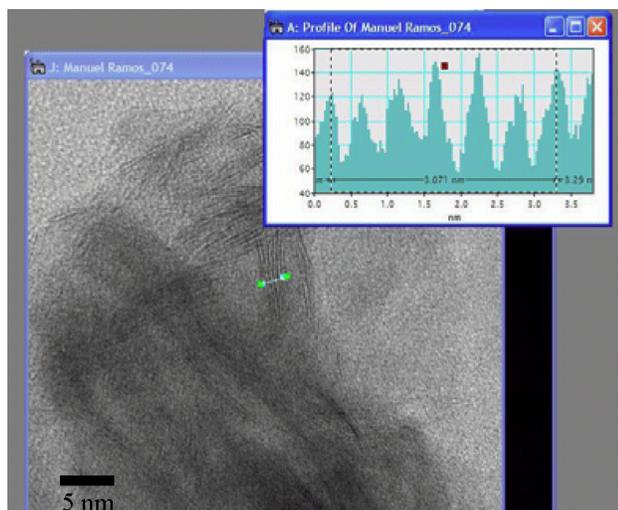


FIGURE 3. High Resolution TEM image of disperse spherical shape MoS_2/Co indicating a interlayer distance of 0.52 nm in MoS_2 structure.

3. Characterization of MoS_2 samples by XRD, SEM and TEM

Each individual MoS_2 and MoS_2/Co product were placed subjected to XRD analysis using a Rigaku XRD diffraction system Miniflex goniometry at room temperature with a step size of 0.05 and $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418$ nm).

SEM was done on a field emission gun model Hitachi S-4800, each individual product were stick directly to a carbon double sided tape and placed on the high vacuum chamber with an accelerating voltage of 12 kV and current value of 8-10 A to avoid electron charge in the surface. Finally TEM were obtained using a Hitachi with an operational voltage of 200 kV, both products were dispersed individually in isopropanol using ultrasonic bath for 15 min, and then one drop of the resulted solution placed onto a Cu/C 200 mesh TEM grid allowing them to dry naturally.

4. Results and discussion

SEM images presented in Fig. 1 show a spherical shape made of MoS_2 slabs stacking naturally, the particle average size diameter is found to be $\sim 2.86 \mu\text{m}$ as measured using Digital Micrograph software. Bending on the layers is also observed on the MoS_2 slabs could be due to high energetic while at hydrothermal reaction. Figure 2 presents a spherical surface dispersion in samples with cobalt content, this could be attributed that Co-promoters have a principal $(10\bar{1}0)$ planar nucleation site as described by theoretical and experimental methods found in the literature [16-18].

Results from Transmission Electron Microscope indicate fringes-like structure which is characteristic of MoS_2 as described by others [15]; one can observed also the presence of MoS_2 and MoS_2/Co phases, as it is presented Fig. 2. Using Digital Micrograph Software (precision of 0.01 +/- nm) images of 2 nm in resolution an interlayer distance value of

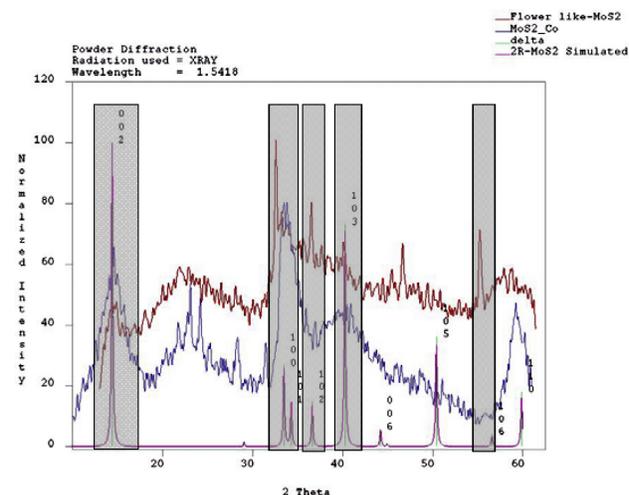


FIGURE 4. XRD data of MoS_2 and MoS_2/Co as compared with MoS_2 simulated for rhombohedra MoS_2 ideal crystallographic structure.

0.52 nm is obtained for MoS_2 ; this value seems to be smaller when comparing to 0.62 nm of an ideal MoS_2 crystal structure [15], this latter can be attributed to engineered nano-scaled stress cause from the interaction of Cobalt and MoS_2 as observed in Fig. 3.

Principal planar directions obtained from XRD were (002), (100), (101), (102), (103), (006), (105), and (110) as compared with simulated XRD on rhombohedra MoS_2 using Cerius² molecular modeling package, Fig. 4 presents obtained results. Broadening is observed from XRD peaks (blue line) corresponding to Co addition onto the MoS_2 could be due to engineered induced nano-scaled stress from dispersing MoS_2 spherical surface, slabs have form nano-crystals as observed in SEM images.

5. Conclusions

We present here a successful synthesis of spherical shape MoS_2 , using a hydrothermal synthesis method. In order to study the effect that cobalt can cause on the structure a second reaction was carried out; addition of Co created a dispersion of spherical MoS_2 surface as confirmed by XRD, SEM and TEM characterization techniques. The dispersion effect can be interpreted due to nucleation affinity between principal $(10\bar{1}0)$ - MoS_2 plane to Co atoms as it is described by others [18]. Since MoS_2 when is promoted with cobalt (addition of cobalt) enhances its catalytic properties authors proposed as future work to measure the catalytic activity on MoS_2/Co samples.

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