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Surfactant-Assisted Synthesis of Highly Dispersed Molybdenum Sulfide

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A simple preparation method of high surface area MoS_2 using reactions in aqueous solution in the presence of an organic surfactant has been reported. Molybdenum sulfide was obtained from the reactions of aqueous $(NH_4)_2MoS_4$ with N_2H_4 or $NH_2OH{\cdot}H_2SO_4$, followed by thermal treatment under nitrogen flow. The solids were characterized by X-ray diffraction, chemical analysis, surface and porosity measurements, photoelectron spectroscopy (XPS), and high-resolution transmission electron microscopy (HREM). Addition of the cetyltrimetylammonium chloride surfactant to the reaction mixtures led to the increase of specific surface area up to 210 m^2/g and disappearance of MoS_2 layers stacking. Single layer, short fringes of MoS_2 were observed by HREM. The solids contained 4−8 wt % of carbon impurity, which probably acts as a textural stabilizer.

Molybdenum sulfide (MoS_2) presents considerable interest in several fields such as catalysis and photochemistry or as an additive for lubricating oils. Various applications of MoS_2 arise from the highly anisotropic nature of this layered compound. Within one layer its structure can be viewed as a two-dimensional macromolecule with each Mo ion surrounded by six sulfur anions in a trigonal prismatic arrangement. In this configuration, each sulfur ion is bound to three Mo which results in a weak interaction with the next layer. The van der Waals gap is an important feature of interest with regard to intercalation and lubricant properties. From a catalytic point of view, MoS_2 possesses outstanding properties toward hydrogenolysis and hydrodesulfurization reactions, and it has been demonstrated that the activity depends on the relative amount of edge Mo atoms where sulfur vacancies can be easily formed. However, the activity of MoS_2 depends not only on the particle size but also on the number of layers, demonstrating that the morphology is also an important parameter for such an application. The synthesis of dispersed MoS_2 generally involves thermal decomposition of $(NH_4)_2MoS_4$ (ATTM),[1] sulfidation of molybdenum oxide, or sonochemical[2] or metathesis reactions.[3] All these methods lead to microporous solids having particle lengths ranging from 5 to 30 nm and the average stacking number is always higher than 4 and generally ranging between 4 and 15.

Inorganic syntheses using organic surfactants such as tetraalkylammonium templates are successfully applied for the preparation of various mesoporous materials. If the preparation of lamellar or cubic templated phases is relatively easy, the subsequent template elimination without destruction of the mesoporous texture remains a difficult step. Template removal involves an oxidation step carried out either by air calcination or by reactions with some strongly oxidizing species. Since inorganic sulfides are highly oxidizable materials, alkylammonium templates cannot be burned off or eliminated by other oxidation procedures from the mesoporous sulfides. On the other hand, when these solids are calcined under an inert atmosphere, dense carbonaceous residuals are formed. These coke-like impurities are undesirable for oxides, particularly when they are further applied as catalytic supports and/or soft acid catalysts. On the other hand, the presence of C species was found to have a stabilizing effect on the textural properties of MoS_2 or WS_2 when these sulfides are prepared in the presence of hydrocarbons[4] or by sulfidation of Mo(VI) naphthenates.[5]

This work reports a simple preparation method of high surface area MoS_2 using reactions in aqueous solution in the presence of an organic template. As for many metals, aqueous precipitation of the corresponding sulfides can be easily achieved using H_2S or an alkali metal sulfide,[6] there are no examples of aqueous preparations of MoS_2. By contrast, amorphous MoS_3 may be prepared by acidification of ATTM solutions according to the following equation:[7]

$$MoS_4^{\,2-} + 2H^+ \Rightarrow MoS_3 + H_2S \qquad (1)$$

Heating the resulting MoS_3 at ~623−673K provokes its

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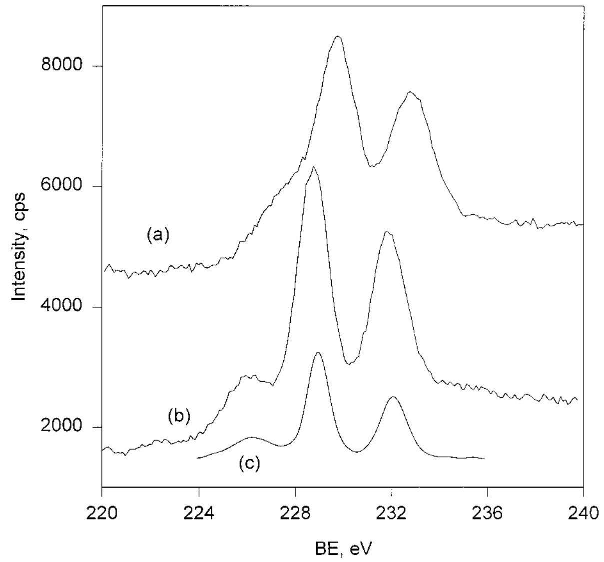

Figure 1. Mo3d XPS signals of the noncalcined solids ATTM-NH_2OH (a), ATTM-N_2H_4 (b), and monocrystal MoS_2 reference (c).

Table 1. Chemical Composition and Textural Properties (Specific Surface Area, *S*, and Pore Volume, V_p) of the Solids Obtained in This Work

sample name, treatment conditions	composition, MoS_yC_z	*S*, m^2/g	V_p, cm^3/g
ATTM-NH_2OH, noncalc.	$MoS_{3.05}$		
ATTM-NH_2OH, calc. 773 K	$MoS_{2.14}$	88	0.08
ATTM-NH_2OH-NR_4Cl, noncalc	$MoS_{3.2}C_{4.1}$		
ATTM-NH_2OH-NR_4Cl, calc. 773 K	$MoS_{2.19}C_{1.62}$	166	0.09
ATTM-N_2H_4, noncalc.	$MoS_{2.4}$	5.1	
ATTM- $N_2H_4-NR_4Cl$, calc. 773 K	$MoS_{2.1}C_{1.58}$	211	0.15
ATTM- $N_2H_4-NR_4Cl$, reduced H_2 723K	$MoS_{1.96}C_{0.48}$	156	0.14
ATTM, thermal decomposition 773 K	$MoS_{2.09}$	31	0.04

autoreduction,[8] leading to MoS_2 according to

$$MoS_3 \Rightarrow MoS_2 + (1/x)S_x \qquad (2)$$

Starting from aqueous solutions of ATTM, the addition of some reducing reagents is thus required to produce MoS_2 in aqueous solution. In this work, we have studied the effect of the surfactant on the morphology and stability of molybdenum sulfide prepared by reactions of aqueous solutions of ATTM with reducing reagents, such as hydroxylamine and hydrazine, which are known to reduce oxidic Mo(VI) species to Mo(IV).[9]

The procedure utilized was as follows: 2.8 g of homemade $(NH_4)_2MoS_4$ were dissolved in 100 mL of distilled water, and then 8 g of hydroxylamine sulfate or 2 mL of aqueous hydrazine in 100 mL of water, containing or not 0.1 M cetyltrimethylammonium chloride (thereafter designed by NR_4) used as surfactant, was added. The reaction mixture was heated and kept at reflux for 6 h in a reaction vessel equipped with a cooler. The precipitate was filtered, thoroughly washed with distilled water, and then oven-dried at 373 K. Then, the solids were calcined for 2 h under a nitrogen flow at a temperature ranging from 573 to 873 K.

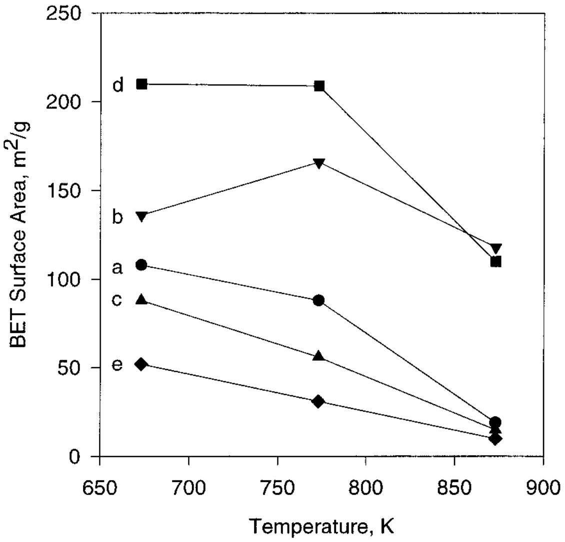

Figure 2. Specific surface area vs temperature of calcination under nitrogen flow for the solids ATTM-NH_2OH (a), ATTM-NH_2OH-NR_4 (b), ATTM-N_2H_4 (c), ATTM-N_2H_4-NR_4 (d), and ATTM thermal decomposition product (e).

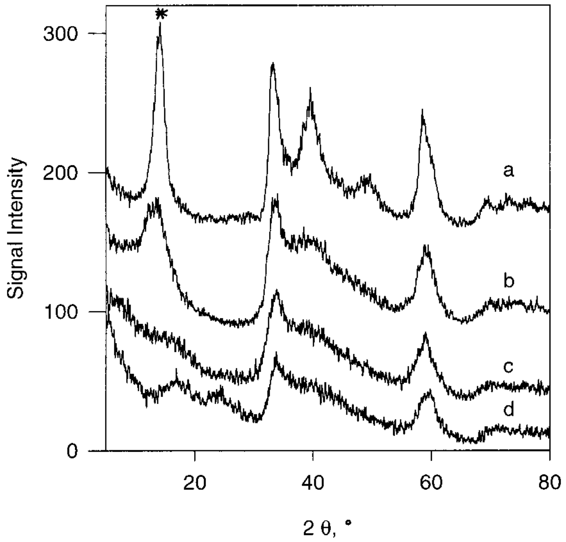

Figure 3. XRD patterns of the ATTM-NH_2OH (a), ATTM-N_2H_4 (b), ATTM-NH_2OH-NR_4 (c), and ATTM-N_2H_4-NR_4 (d) samples, calcined under nitrogen at 773 K. Marked peak (*) indicates the (002) line, corresponding to the layer stacking.

The solids were characterized by X-ray diffraction (XRD), chemical analysis, and high-resolution transmission electron microscopy (HREM). Their surface areas and pore volumes were determined by low-temperature nitrogen adsorption using respectively the BET and the BJH equations. The Mo oxidation state was determined by photoelectron spectroscopy (XPS) using the C1s binding energy (BE) at 284.5 eV as reference.

The composition and textural properties of the obtained solids are listed in Table 1. Chemical analysis shows that the sulfur content corresponds rather to MoS_3 when hydroxylamine is used as reducer, while a composition closer to MoS_2 is obtained in the presence of hydrazine. The Mo 3d $^5/_2$ and $^3/_2$ BE were found

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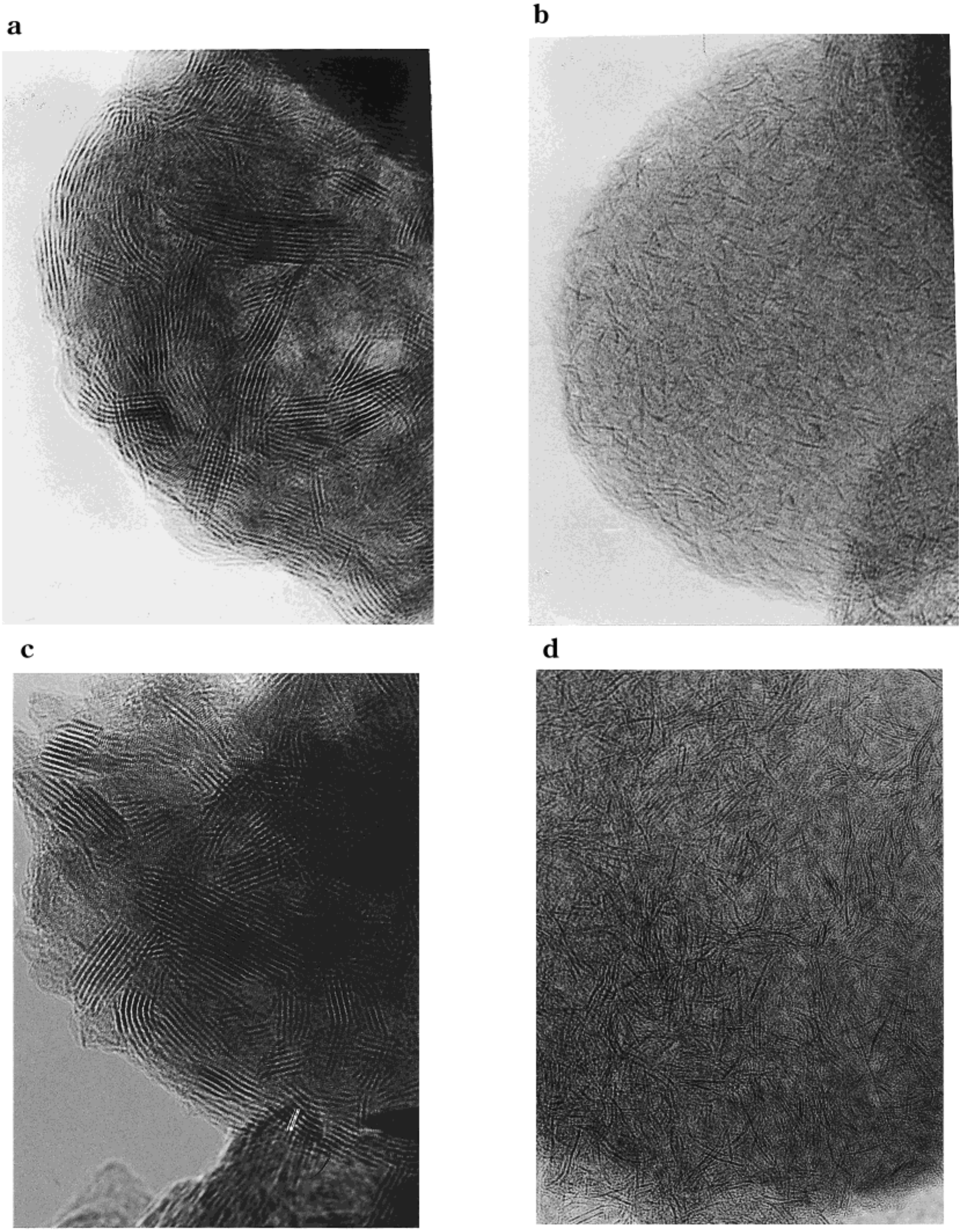

Figure 4. HREM images of the samples ATTM-NH_2OH (a), ATTM-NH_2OH-NR_4 (b), ATTM-N_2H_4 (c), and ATTM-N_2H_4-NR_4 (d), calcined under nitrogen at 773 K.

respectively at 229.7 and 232.9 eV (Figure 1a) for the hydroxylamine-derived sample, while a shift toward lower BE of ~1 eV was observed when using hydrazine as reducing reagent, leading to a similar spectrum as that of MoS_2 monocrystal reference (Figure 1c). This indicates that molybdenum reduction occurs in the hydrazine-derived sample, in agreement with chemical analysis. Indeed, according to the literature, the signal with Mo3$d_{5/2}$ BE of ~229 eV and lower can be attributed to Mo(IV) sulfide,[10] whereas Mo(V) should have ~1 eV higher BE value.

We suppose that the reducing power of hydroxylamine is thus insufficient to reduce thiomolybdate ions, and the precipitation of MoS_3 takes place according to eq 1 due to the acidic character of the aqueous solution of hydroxylamine sulfate. By contrast, the stronger reducing character of hydrazine allows the reduction of the initial Mo(VI) species into Mo(IV) probably according to the overall reaction:

$$(NH_4)_2MoS_4 + {}^1/_2N_2H_4 \Rightarrow MoS_2 + {}^1/_2N_2 + (NH_4)_2S + H_2S \quad (3)$$

The presence of a template in the reaction mixture does not affect strongly the S/Mo ratios in the noncal-

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cined solids and the high C content indicates that large amounts of NR_4 are included in the precipitates (Table 1). After calcination at 773 K under a nitrogen flow, the C amount was reduced down to ~8−10 wt %, which still represents a high atomic proportion because of its small atomic weight relative to Mo. Further decrease in C content could be achieved by reduction in hydrogen at 723 K, and this treatment did not diminish substantially the S/Mo ratio.

MoS_2 derived from these aqueous preparations present advantageous textural properties with respect to the solids prepared by thermal decomposition of ATTM or other thiomolybdate precursors.[1,11] Moreover, the use of NR_4 drastically increases the specific surface area of the solids. The highest surface areas and pore volume were provided by alkylammonium-doped solids obtained from hydrazine reactions. The effect of template not only enlarges the BET surface area, but also improves the thermal stability of the solids (Figure 2).

XRD patterns show that all the noncalcined solids were virtually amorphous regardless of the preparation method used. During heating under nitrogen, crystallization began at ~573 K, and at 673 K the diffracting lines of the MoS_2 phase were clearly observed. However, for the NR_4-doped solids, the (002) reflections are remarkably missing, suggesting the absence of stacking. The same effect was observed independent of the nature of the reducing reagent. Somewhat poorer quality of patterns of the N_2H_4-derived samples (Figure 3c,d) compared to those from hydroxylamine reactions (Figure 3a,b) is probably related to the smaller domain size, consistently with their higher surface areas.

The striking change of sulfide morphology induced by the surfactant is obviously confirmed by the HREM images (Figure 4). In agreement with XRD data, the solids prepared without surfactant consisted of stacks of 5−10 fringes, whereas only single sheets of MoS_2 could be found in the NR_4-derived samples.

Sulfidation of small MoO_3 particles or supported polymolybdate species leads usually to bulk MoS_2 or to the clusters stacked MoS_2 layers.[10] The single layers of MoS_2 were earlier obtained only in water suspensions by exfoliation of bulk nanosized $LiMoS_2$ particles. However, such monolayers are unstable and were easily restacked on further filtration, evaporation, or slight heating.[12] Here, probably due to the presence of C impurities, monolayer morphology is stable up to 873 K.

The contribution of carbonaceous matter to the overall surface area remains unknown. However, mostly single layer and short fringes of MoS_2 are observed in HREM. Therefore, we conclude that MoS_2 accounts for the major part of measured surface areas.

We observed that addition of tetraalkylammonium salts to the ammonium thiomolybdate solutions produced precipitation of the corresponding tetraalkylammonium thiomolybdates. Using cetyltrimethylammonium chloride, an orange precipitate of the corresponding NR4 thiomolybdate was obtained. Further refluxing with the reducing agents used in this work led to its decomposition with formation of the dark brown or black molybdenum sulfide powders. This might give an idea about how the decomposition of thiomolybdate together with a structure-directing agent works. Probably, in our case no formation of ordered mesostructure occurred, but decomposition of amorphous organic thiomolybdate took place.

The decrease of MoS_2 layer stacking and textural stabilization due to the presence of organic matter seems to be a general phenomenon. The carbonaceous matter of any origin prevents the crystallization of the sulfide. The role of the organic molecule is rather that of scaffolding and preventing the agglomeration of layered sulfide fringes. This work describes a simple preparation method leading to pure or carbon-doped molybdenum sulfides, having peculiar textural properties and morphologies.

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