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# Aqueous Preparation of Highly Dispersed Molybdenum Sulfide

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Molybdenum sulfide ($MoS_2$) presents considerable interest in several fields such as catalysis, photochemistry, and production of lubricating oils. Layered $MoS_2$ structure can be viewed as a two-dimensional macromolecule with each Mo ion surrounded by six sulfur anions in a trigonal prismatic arrangement. The active centers of $MoS_2$-based catalysts are located on the edges of the layers, where sulfur vacancies are formed. Therefore, catalytic activity of bulk or supported $MoS_2$ depends strongly on its dispersion. The syntheses of dispersed $MoS_2$ involve thermal decomposition of $(NH_4)_2MoS_4$ (ATM) salt,[1] sulfidation of molybdenum oxide, metathesis reactions,[2] or gas-phase decomposition of $Mo(CO)_6$ in the presence of $H_2S$.[3] To increase the dispersion of molybdenum sulfide particles, sonochemical[4] and even $\gamma$-irradiation[5] methods were applied.

For many metals precipitation of the corresponding sulfides can be easily achieved using $H_2S$ or alkali metal sulfides,[6] but there is actually no aqueous preparation of $MoS_2$ described in the literature.

In the previous work[7] we used reactions of ATM with hydroxylamine and hydrazine solutions to obtain molybdenum sulfide materials. However, mostly organic-template-containing products after calcination at 673−773 K were characterized. Here, we focus our attention on the aqueous reaction between $N_2H_4$ and $(NH_4)_2MoS_4$ and properties of the as-prepared solids.

The procedure utilized was as follows. A total of 1.3 g (0.005 mol) of homemade $(NH_4)_2MoS_4$ (ATM) was dissolved in 50 mL of distilled water. Then 100 mL of aqueous solution containing the desired amount of $N_2H_4{\cdot}H_2O$ with ammonia solution or HCl solution (for adjusting pH) was added with stirring. The reaction mixture was put in a thermostat and kept under an Ar flow at 90 °C for a time necessary for reaction to be completed. The black precipitate was filtered and thoroughly washed with $CS_2$ and acetone. Then it was dried in the argon flow at 373 K.

The solids were characterized by X-ray diffraction (XRD), chemical analysis, and high-resolution transmission electron microscopy (HREM). The surface areas were determined by low-temperature nitrogen adsorption. The molybdenum oxidation state was controlled by X- ray photoelectron spectroscopy (XPS) using the C 1S binding energy (BE) at 284.5 eV as a reference.

Gaseous products of the aqueous reaction were studied using a mass spectrometer (FISONS Instruments).

**Table 1.** Chemical Composition and Specific Surface Areas of the Solids Obtained in This Work

| no. | starting pH | $N_2H_4$ concn, mol/L | *S*,[a] $m^2/g$ | S/Mo[b] |
|---|---|---|---|---|
| 1 | 10.3 | 0.13 | 40 | 2.2 |
| 2 | 9.8 | 0.52 | 10 | 2.2 |
| 3 | 8.4 | 0.13 | 110 | 2.2 |
| 4 | 8.0 | 0.065 | 169 | 2.5 |
| 5 | 7.5 | 0.13 | 108 | 2.3 |
| 6 | decomposition of ATM at 673 K | | 48 | 2.2 |

[a] Surface area measured after evacuation at 573 K for 2 h. [b] Determined by chemical analysis.

The reaction conditions and properties of the selected solids are listed in Table 1. The results of chemical analysis indicate that composition of the materials prepared is very close to $MoS_2$. Some overstoichiometric sulfur are present in the samples, as is usually the case for $MoS_2$ dispersions obtained at low temperature.[8] The nitrogen amount was low, not exceeding 2 wt %, and was present probably in the form of adsorbed ammonia cations, since the FT-IR spectra of solids cattied out in KBr pellets showed weak absorption bands at 1410 and 3200 $cm^{-1}$, characteristic of inorganic ammonium salts.[9]

According to the XPS analysis, 80% of the Mo 3d signal is due to Mo(IV) species in $MoS_2$ (Mo $3d_{5/2}$, BE = 228.4 eV). At the same time more than 85% of sulfur was present as $S^{2-}$ species (S $2p_{3/2}$, BE = 161.8 eV). The last value is typical of the $MoS_2$ sulfide, clearly distinguishing it from that for the amorphous $MoS_3$ phase (162.9 eV).[10]

The XRD patterns (Figure 1a) contain characteristic $MoS_2$ peaks at $2\theta > 30°$, whereas the (002) reflection is absent. These features are indicative of low stacking and highly disordered packing of $MoS_2$ layers.[11] The HREM study led to the same conclusion. On the images of freshly prepared samples (Figure 2), single layers or weakly stacked short fringes of $MoS_2$ were observed. The stacking number varies from 1 to 3, and the interlayer distance is close to 0.6 nm, which is characteristic of the interlayer distance in $MoS_2$. After calcination at 673 K under Ar flow, the crystallinity of $MoS_2$ increased but no phases other than molybdenum sulfide appeared (Figure 1b).

It follows from the data of Table 1 that some $MoS_2$ samples from these aqueous preparations present exceptionally high surface areas. Indeed the conventional chemical routes typically give solids having $S_{BET}$ of about 50 $m^2/g$. In some cases high surface areas were provided by carbon residue originating from organic molecules present in the precursors.[7,12]

To have an idea about the reaction mechanism, gaseous products were analyzed using mass spectrometry (Figure 3). During the induction period, some gases were evolved but no precipitate was formed. If the ATM solution were preliminarily heated at

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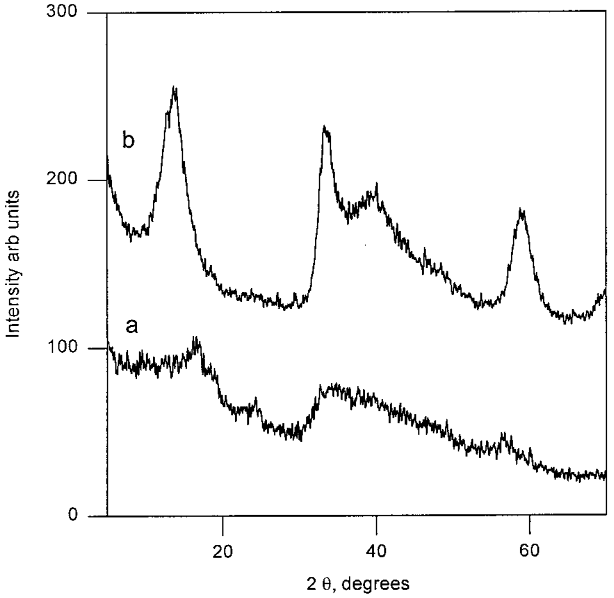

**Figure 1.** XRD patterns of the Ar-dried ATM$-$$N_2H_4$ (sample 1 in Table 1) (a) and the same solid calcined under Ar flow at 673 K (b).

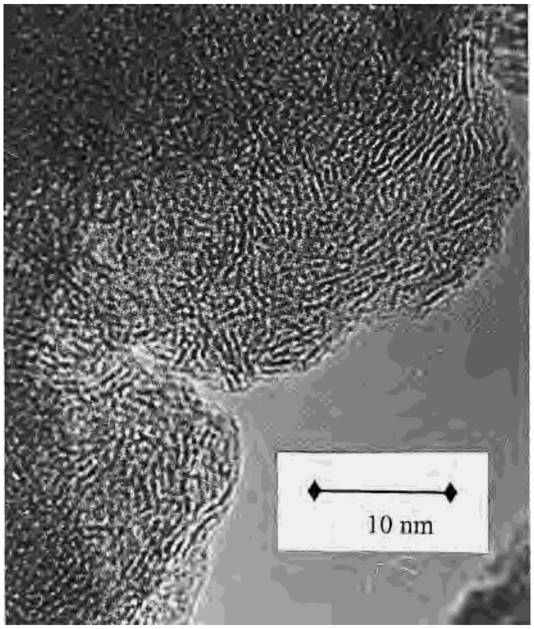


**Figure 2.** HREM images of the freshly prepared sample ATM$-$$N_2H_4$ (sample 1 in Table 1).

the same time as the induction period was, then addition of hydrazine would lead to the immediate formation of a precipitate.

The signal of hydrogen sulfide in the mass spectra appears prior to formation of $MoS_2$. The UV$-$visible spectra of the reaction mixture just before the moment of nitrogen formation showed that in addition to absorption lines of initial ATM (242, 317, and 467 nm) new lines appeared at 227 and 394 nm, suggesting formation of $MoS_3O^{2-}$ anions.[13] This permits us to suppose that during the induction period partial hydrolysis of tetrathiomolybdate anions occurs:

$$MoS_4^{\,2-} + H_2O \Leftrightarrow MoOS_3^{\,2-} + H_2S \tag{1}$$

$$nMoS_4^{\,2-} \Leftrightarrow Mo_nS_{4n-x}^{\,2(n-x)-} + xS^{2-} \tag{2}$$

Besides hydrolysis, condensation of thiomolybdate anions might proceed, which has been observed upon heating of ATM solutions.[14] The processes during the induction period are at equilibrium; the reaction does not occur at all after addition of a 10-fold excess of ammonium sulfide to the reaction mixture, which hinders both hydrolysis and condensation reactions.

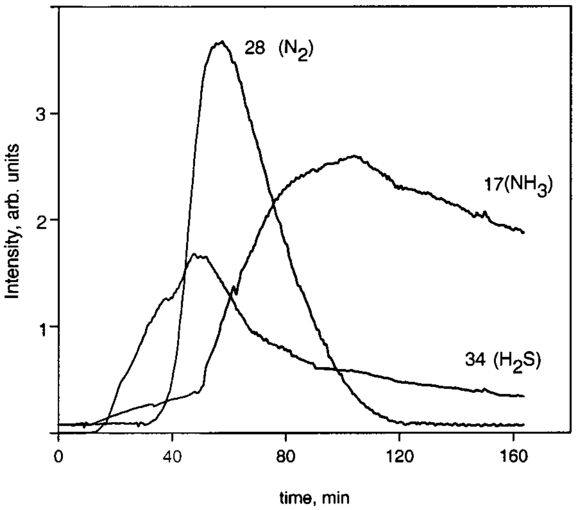

**Figure 3.** Mass spectra of gases evolved from the reaction mixture (0.03 M ATM, 0.13 M $N_2H_4$, pH = 9). The *m/z* values and the corresponding species are indicated over the curves.

It was found that the beginning of precipitate formation coincides with production of $N_2$, which is seen in the mass spectra. Gaseous ammoniac was seen in all cases, even in the reaction mixtures where no aqueous ammonia was added to adjust pH. The ammoniac signal was not in step with that of nitrogen. The large solubility of ammoniac in water does not allow us to conclude whether it was formed at once with nitrogen (due to one-electron oxidation of $N_2H_4$[15]) or whether it was produced because of the heterogeneous catalytic decomposition of hydrazine on the molybdenum sulfide particles.

Formation of $MoS_2$ was possible in the pH range 7$-$10. Too low a pH leads to precipitation of amorphous $MoS_3$ according to the reaction

$$MoS_4^{\,2-} + 2H^+ \Rightarrow MoS_3 + H_2S \tag{3}$$

On the other hand, the samples prepared at too high a pH contain some impurities of $MoO_2$ (seen in the XRD pattern of the samples heated in nitrogen to 773 K). This fact can be explained by progressive hydrolysis of ATM to oxomolybdate, which reacts further with hydrazine, giving $MoO_2$.

The synthesis described here is somewhat analogous to the aqueous preparations of transition metal oxides $AMO_x$ and $MO_y$ (M = V, Cr, Mn, Mo, and W; A = Na, K) by the reduction of oxoanions with soluble borohydride salts, as described by Manthiram et al.[16,17]

In conclusion, the soft aqueous route is found for the preparation of highly dispersed $MoS_2$ possessing a surface area that is the highest ever obtained for pure molybdenum sulfide. Hydrazine, employed as a reducing agent, is volatile and easily decomposable, allowing it to be prepared as pure molybdenum sulfide.

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