“Non-hydrolytic” sol-gel synthesis of molybdenum sulfides

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Abstract

Non-hydrolytic sol-gel reactions provide a low temperature solution based synthetic approach to solid-state materials. In this paper, reactions between molybdenum chloride and hexamethyldisilthiane in chloroform were explored, which gave access to both MoS_2 and Mo_2S_3 after heat treatment of as-recovered amorphous samples to 600 to 1000 °C. Interesting morphologies were obtained for MoS_2 , ranging from fused spherical particles to well-defined nanoplatelets and nanoflakes. Both 2H- and 3R- MoS_2 were observed, which formed thin hexagonal and triangular platelets, respectively. The platelets exhibited thicknesses of 10 to 30 nm, which corresponds to 15 to 50 MoS_2 layers. No attempts to prevent agglomeration were made, however, well separated platelets were observed for many samples. Heating at 1000 °C led to formation of Mo_2S_3 for samples that showed well-defined MoS_2 at lower temperatures, while less crystalline samples had a tendency to retain the MoS_2 structure.

Keywords

Molybdenum sulfide; non-hydrolytic sol-gel; polymorphism; nanoplatelets

1. Introduction

Metal sulfides have increasingly attracted the interest of researchers, as they can possess catalytic, electronic and optical properties that are difficult or impossible to achieve with oxides [1]. They are used as catalysts for hydrodesulfurization in the petroleum industry [2, 3], as high temperature lubricants [4, 5], in solar cells [6-8], and as electrodes in lithium batteries [5, 9-12]. While some metal sulfides can be air-sensitive, the improvement in performance offsets the difficulties in handling and protecting these materials, and some compositions remain stable in air for extended periods of time.

Molybdenum sulfides have found applications as dry lubricants and catalysts in hydrodesulfurization, and are also explored for their magnetic, electrical and optical properties. The molybdenum sulfide phase diagram contains two thermodynamically stable phases, MoS_2 and Mo_2S_3 [13]. Both compositions show a narrow phase width and melt around 1750 °C. Mo_2S_3 has a lower limit of stability of 664 ± 50 °C, while MoS_2 is thermodynamically stable at all temperatures. Metastable compositions like Mo_3S_4 have also been reported [14]. Of these, MoS_2 has received the most interest, and is industrially produced as a high temperature lubricant and hydrodesulfurization catalyst. More recently, it has been explored as a graphene analog due to its layered structure. The stacking of MoS_2 sandwich layers results in several polymorphs, trigonal 1T- MoS_2 [15] hexagonal 2H- MoS_2 and rhombohedral 3R- MoS_2 [16]. Of these, 2H- MoS_2 is thermodynamically stable, although 3R- MoS_2 is often found in minerals as well. The intercalation and exfoliation chemistry of layered MoS_2 has been known since the 1980's [17], and the growing interest in single or few layer 2D compounds has made it the subject of many recent investigations. Nanosheets have been prepared by the scotch tape method [18], lithium intercalation and immersion in water [19-22], electro-chemical reduction [23] and solvent

exfoliation with ultrasonication [24-27]. Nanosheets showed superior properties, and applications in batteries [28], catalysis [29, 30], and electronics [31-34] have been proposed. A topic of particular interest is the superior performance of nanoparticles in hydrogen evolution reactions compared to bulk MoS_2 [30, 35-38]. Such particles hold promise for fuel cell or solar hydrogen splitting.

While molybdenum sulfides can be prepared by ceramic methods, the formation of nanostructures benefits from low temperature solution-based methods. In this paper, we are exploring the synthesis of molybdenum sulfides by a route equivalent to the non-hydrolytic sol-gel (NHSG) process used to prepare metal oxides from metal halides and ethers [39-42]. Similar methods for the preparation of metal sulfides were first explored by Schleich *et al.* in the late 1980's [43-47], but have received limited attention since that time. Carmalt *et al.* revisited the reaction of metal halides with hexamethyldisilthiane (HMDST) in 2003 [48], and demonstrated that MoCl_5 reacts with HMDST in diethyl ether at room temperature and toluene under reflux. However, no thorough exploration of reaction variable space was carried out, and the room temperature and reflux samples were heated under completely different conditions (800 °C under flowing H_2S and 550 °C under static and dynamic vacuum, respectively). Formation of MoS_2 was observed under H_2S and static vacuum, while unexplained oxidation occurred under dynamic vacuum. We have recently demonstrated that careful tuning of variables during NHSG reactions can provide facile control over polymorph formation and give targeted access to specific particle morphologies in the iron, copper and tantalum sulfide systems [49-51]. Here we report the formation of amorphous and crystalline MoS_2 nanoparticles with spherical and platelet morphologies, respectively. Formation of 2H- and 3R- MoS_2 was observed at lower temperatures, while Mo_2S_3 could be obtained at 1000 °C. The MoS_2 phases remained nanocrystalline even at

higher temperatures.

2. Materials and methods

2.1. Sample preparation

All samples were prepared by NHSG reactions in CHCl_3 (Fisher Scientific, ACS Grade), using anhydrous MoCl_5 (Strem, 99.6%) and hexamethyldisilthiane (TCI, >95%) as starting materials. CHCl_3 was redistilled from P_2O_5 , while all other materials were used as purchased. Reactions were set up using standard Schlenk and glovebox techniques. In a typical reaction 0.820 g (3 mmol) of MoCl_5 were dissolved in 10 mL of CHCl_3 in a glass ampoule inside the glovebox. The dark brown solution was stirred for 10 min, and 0.85 mL (4 mmol) of hexamethyldisilthiane (HMDST) were added, resulting in darkening of the solution and formation of a black precipitate. The formation of the precipitate was so fast that it interfered with stirring in some cases. After stirring for another 15 min, the ampoule was capped with a septum, transferred to a Schlenk line outside the glovebox, cooled in liquid N_2 , and sealed under vacuum. The sealed ampoule was heated at 70 °C for a period of 7 d. It was pumped back into the glovebox, and the dark powder was recovered by vacuum filtration and washed with a small amount of CHCl_3 . The sample was dried under vacuum. Different parameters like reaction time (5-30 d), reaction temperature (RT-100 °C), starting sulfur to molybdenum ratio (1.5:1 to 3.7:1) and amount of solvent (5-15 mL, resulting in molybdenum concentrations of 0.1 to 0.6 M) were explored to determine suitable reaction conditions. . In contrast to Schleich's original work, Soxhlet extraction was not used to purify the raw powders, as residual starting halides were expected to evaporate during subsequent heat treatments ($T_{\text{bp}}(\text{MoCl}_5) = 268\text{ °C}$).

2.2 Heat treatments

Most as-recovered powders were amorphous and required heat treatment to induce

crystallization. Raw samples were heated at 300 to 1000 °C under argon flow or in sealed ampoules. Heat treatments in the tube furnace ranged from 4 to 24 h, while samples in sealed ampoules were annealed for 4 to 156 h. Heating under argon flow allows for removal of unreacted starting halides and residual organics. Powders were packed into a molybdenum boat inside the glovebox, which was placed inside a quartz tube with inlet and outlet valves. Titanium wire balls were used as upstream oxygen scavengers. The closed quartz tube was taken out of the glovebox and placed into a tube furnace for heat treatments under argon flow. The outlet valve was connected to a bleach bubbler, which was used to destroy volatile sulfur-containing compounds. All parts of the assembly were pre-heated and kept either under vacuum or inside the glove box to prevent oxygen or moisture contamination. Extended heat treatments at 1000 °C (24+ h) were carried out in sealed quartz tubes in a box furnace.

2.2. Characterization methods

Powder X-ray diffraction (PXRD) data were collected on a PANalytical X'Pert Pro diffractometer with an X'Celerator detector or a Scintag XDS-2000 diffractometer equipped with a Moxtek MXP-D1 solid-state detector. Both instruments use Cu K α radiation and Bragg Brentano geometry. Powders were packed into an air-sensitive sample holder inside the glovebox to avoid any potential for surface oxidation that could interfere with additional heat treatments. Phase identification was carried out using JADE 8 [52] and the ICDD PDF-2 database [53]. For elemental analysis, a combination of CHN, thermogravimetric analysis (TGA) and energy dispersive X-ray spectroscopy (EDS) was utilized. Residual organics were quantified using a Perkin-Elmer PE-2400 II CHN analyzer, while the metal content was determined by TGA in air using a TA Instruments SDT 2960 or Q600 DTA-TGA. Chloride contents were estimated by EDS on a Jeol JSM-7500F scanning electron microscope (SEM) with a BRUKER

XFlash 5010 series energy dispersive X-ray spectroscopy (EDS) detector. Voltages of 1 kV and 15 kV were used for imaging and EDS, respectively. Molybdenum to sulfur ratios of the metal sulfide phases were calculated for chloride-free heat treated samples from TGA experiments in air.

3. Results and discussion

Black or dark brown powders were recovered from all reactions. Based on the theoretical yield predicted for formation of MoS_2 , samples clearly contained impurities or excess sulfur. Residual carbon contents determined by CHN analysis ranged from 3 to 6 weight%, indicating reasonable reaction completeness with respect to decomposition of organic residues. Carbon contents were reduced during heat treatments under flowing argon and often became negligible. Chloride contamination in raw samples varied between 5 and 70 atom% (based on analysis of Mo, S and Cl by EDS), with most samples containing 15 to 35 atom% Cl. It is worth noting that a chloride content of 14 atom% corresponds to a 1:10 ratio of unreacted MoCl_5 : MoS_2 . Most as-recovered powders were amorphous, but MoCl_4 and MoCl_5 were observed in the PXRD patterns of several samples. The observation of crystalline molybdenum chlorides was most significant for samples prepared with the highest MoCl_5 concentration (0.6 M). In other samples, it is possible that molybdenum chloride was trapped inside the precipitate if addition of HMDST caused rapid enough precipitation. Heat treatments under argon flow reduced the chloride contents significantly, and halide levels became negligible after heating at temperatures between 700 and 950 °C for all samples. This is not surprising, as MoCl_5 has a boiling point of 268 °C, and the more reduced molybdenum chloride species are prone to disproportionation [54].

TG/DTA experiments conducted on raw samples under nitrogen flow showed that the dark powders contained significant amounts of volatiles (25-45% for most samples). This

includes a combination of residual organic groups, molybdenum halides and potentially excess sulfur. For many samples, a steeper weight loss was observed at 400 to 500 °C, which coincides with the boiling point of sulfur (445 °C). The TGA curves leveled off at 500 to 600 °C, indicating that samples should be heated to 600 °C or higher to remove all volatile constituents. In most samples, an exothermic peak was observed between 400 and 500 °C in the DTA curve, which suggested formation of a crystalline phase (Fig. 1). Some samples showed more complex TG/DTA curves with multiple weight loss regions and a number of overlapping endo- and exothermic events. Molybdenum contents of all samples were determined by TGA analysis in air, as the overlap of the Mo L and S K lines at 2.292 and 2.309 keV reduces the reliability of the molybdenum and sulfur contents determined by EDS. For samples heated to 600 to 800 °C, Mo:S ratios of 1:1.7 to 1:2.4 were calculated. Ratios decreased slightly as the temperature of the sample pre-heat treatment increased. Samples analyzed after annealing at 1000 °C showed a wider range of ratios ranging from 1:1.3 to 1:2.1. Within error, these ratios agree with the phase width of Mo₂S₃ or MoS₂ compositions or mixtures of these phases.

Figure 1: TGA (solid line) and DTA (dotted line) curves of molybdenum sulfide sample prepared with a 2:3 Mo:S ratio in 10 mL of CHCl₃ at 100 °C.

The amorphous molybdenum sulfide samples displayed no tendency to crystallize when heated to 300 or 400 °C. PXRD patterns collected after heating samples to 600-700 °C showed that nanocrystalline MoS₂ started to form in this temperature range (Fig. 2). This phase formed regardless of starting Mo:S ratio in the samples, which agrees with lower stability limit reported

Figure 2: Formation of nano-2H-MoS₂ from a sample prepared with a 1:2 ratio of Mo:S in 10 mL of CHCl₃ ([Mo] = 0.3 M) at 100 °C for 7 d after heating to a) 600 °C, b) 950 °C and c) 1000 °C. The asterisk indicates peak positions for Mo₂C. The PDF view card for 2H-MoS₂ (65-0160) is displayed as well.

for Mo₂S₃ in the Mo-S phase diagram [13]. Crystallinity after the initial heat treatment varied between samples, ranging from samples that gave well defined MoS₂ peaks to samples that showed only very minor signs of crystallization. Generally, samples that contained crystalline halides in the raw powders resulted in more crystalline MoS₂ phases. This is not surprising, as halogens are known to be suitable vapor transport agents for the growth of MoS₂ single crystals. Samples prepared with S:Mo ratios lower than 2 did not crystallize well at low temperatures

unless the ampoules were heated at high temperatures (100 °C) or for extended periods of time. These samples do not contain enough sulfur to allow complete crystallization as MoS₂. Peaks remained broad even after heating at 950 °C to 1000 °C for several hours, indicating that the MoS₂ phase retained its nanosize.

The anisotropic peak broadening observed in the PXRD patterns suggests contributions from both anisotropic particle shape and stacking faults, which makes distinction of the hexagonal and trigonal MoS₂ polymorphs difficult. The majority of samples can be assigned as containing mainly 2H-MoS₂ from the observation of the distinct 103 peak at 39.5° (Fig. 2). However, the possibility of the presence of small amounts of nanocrystalline 3R-MoS₂ cannot be completely excluded from the appearance of the X-ray patterns. On the other hand, several samples showed significant intensity for the 104 and 015 peaks of 3R-MoS₂ (38.2 and 41.1°, Fig. 3), indicating that mixtures containing significant amounts of 3R-MoS₂ were formed. All samples still contained detectable and often considerable quantities of 2H-MoS₂. No single experimental parameter connected the samples that showed significant formation of 3R-MoS₂, and sometimes samples prepared with similar synthetic variables gave different results. This suggests that crystallization kinetics may contribute to the formation of the two phases. Mixtures of these two polymorphs are frequently observed in mineral deposits. The 2H-polymorph is usually more abundant, as it is the thermodynamically stable phase [55]. The formation of 2H-MoS₂ was favored at higher temperatures for 2H/3R-mixed phase samples (Fig. 3).

Figure 3: Formation of mixed phase nano-2H and 3R-MoS₂ from a sample prepared with a 1:2 ratio of Mo:S in 10 mL of CHCl₃ ([Mo] = 0.2 M) at 100 °C for 18 d after heating to a) 700 °C, b) 950 °C and c) 1000 °C. The asterisk indicates peak positions for Mo₂C, the hash mark peak positions for 2H-MoS₂. The PDF view card for 3R-MoS₂ (89-5112) is displayed as well.

Extended heating at 1000 °C resulted in formation of well-crystallized Mo₂S₃ due to sulfur loss for most samples. The sharp peaks indicated formation of microcrystalline particles. Interestingly, some samples showed starting crystallization of Mo₂S₃ within 4 to 8 h at 1000 °C, while other samples retained the 2H-MoS₂ phase even after 96 h at this temperature (Fig. 4). There was a strong correlation between the initial crystallinity of the MoS₂ phase at 600-700 °C and the tendency to form Mo₂S₃ at 1000 °C, suggesting that well-ordered MoS₂ facilitates the transformation into Mo₂S₃, while defects or very small particle size stabilize the MoS₂ polymorph.

Figure 4: a) Poorly crystalline sample prepared by heating at 600 °C for 8 h retaining the MoS₂ structure after b) heating at 1000 °C for 76 h, and c) crystalline sample obtained by heating at 600 °C for 8 h converting to Mo₂S₃ after d) 8 h and e) 24 h at 1000 °C.

The presence of small quantities of Mo₂C was detected for many samples heated at 1000 °C in sealed quartz ampoules. Due to the low molecular weight of carbon, even very small amounts of residual carbon can result in detectable quantities of Mo₂C (e.g., 0.3 wt% C corresponds to 5 wt% Mo₂C and 95 wt% MoS₂). The largest amounts of Mo₂C were formed in samples that were heated directly at 1000 °C without previous treatment under flowing argon at lower temperatures, which demonstrates that the carbon is sequestered from incompletely decomposed organic groups. Interestingly, Mo₂C formation was only observed in samples that still contained MoS₂, while phase pure Mo₂S₃ samples did not show any evidence of carbides, even when this phase was formed during longer heat treatments of MoS₂/Mo₂C mixtures. This suggests that the formation of carbide may result from sulfur deficiency of the MoS₂ phase, and that further sulfur loss during extended heating favors formation of crystalline Mo₂S₃ and amorphous carbon species.

SEM images correlated well with the PXRD results. Raw powders displayed spherical or distorted spherical nanoparticles ranging in size from 50 to 200 nm (Fig. 5a). Retention of the distorted spherical particle shape was observed in samples that showed very broad peaks in the

PXRD patterns (Fig. 5b). These particles gradually flatten and transform into platelets during heating (Fig. 5c+d). It is likely that the initial particle size distribution and the presence of defects within the spheres affects the kinetics of MoS₂ crystallization.

Figure 5: SEM images of a) raw sample, b) poorly crystalline MoS₂ after heating at 950 °C for 4 h, and c) and d) transformation of spheres into platelets after heating at 1000 °C for 96 h.

Heat treated samples that showed well defined MoS₂ peaks in the X-ray patterns displayed distinct platelets. Hexagonal platelets dominated in samples that displayed single phase 2H-MoS₂ (Fig. 6a), while triangular platelets were observed for samples that contained significant amounts of 3R-MoS₂ (Fig. 6b). Mixture of hexagonal and triangular platelets were often found in mixed phase samples, and the transformation of the 3R-polymorph to the 2H-phase at higher temperatures was evident from the loss of sharp corners of the triangular platelets (Fig. 6c+d). Platelet dimensions ranged from a few hundred nanometers to micron size with thicknesses of 10-30 nm. The platelets showed little tendency to form stacks. In some

samples, ultrathin platelets were observed (Fig. 6e+f), some of which appeared semi-transparent.

Figure 6: SEM images of a) 2H-MoS₂, b) 3R-MoS₂, c) and d) phase mixtures of 2H/3R-MoS₂ changing into the 2H-polymorph, e) and f) ultrathin platelets of 2H- and 3R-MoS₂.

In several samples that showed formation of significant amounts of Mo₂C during heating at 1000 °C, formation of large, irregular MoS₂ flakes was seen in the SEM images (Fig. 7a). Formation of Mo₂S₃ at 1000 °C was accompanied by a change to needle or rodlike morphology (Fig. 7b). In some samples that formed large needles, this change could also be detected visually through the appearance of shiny, silvery needles. Mixtures of platelets and rodlike particles were

found in samples that contained both MoS_2 and Mo_2S_3 .

Figure 7: SEM images of a) a sample containing MoS_2 and Mo_2C , b) phase pure Mo_2S_3 and c) a mixture of MoS_2 and Mo_2S_3 .

Conclusions

Non-hydrolytic sol-gel reactions of MoCl_5 and HMDST in CHCl_3 can be used to prepare amorphous molybdenum sulfide samples that contain varying amounts of chloride and carbon. Heat treatments at 700 °C give impurity-free MoS_2 samples in most cases. The formation of 2H- and 3R- MoS_2 appears to be influenced by crystallization kinetics rather than synthetic conditions. In all cases, higher temperatures favored transformation into the thermodynamically stable 2H-polymorph. Extended heating at 1000 °C favors sulfur loss, which results in crystallization of Mo_2C if any residual carbon is present in the samples, and eventually in formation of Mo_2S_3 . Samples that formed well defined MoS_2 at 600-700 °C showed facile conversion into Mo_2S_3 , while less crystalline samples had a tendency to retain the MoS_2 structure. Poorly crystalline MoS_2 phases were composed of nanoparticles that retained the spherical morphology of the initial amorphous powders, while distinct hexagonal and triangular platelets were observed for well crystallized 2H- and 3R- MoS_2 . The very thin platelets showed limited tendency to agglomerate in stacks, suggesting that the powders possess high accessible surface areas that could be beneficial for catalytic applications.

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Overlay of variable pressure X-ray diffraction data of $\text{Al}_2\text{Mo}_3\text{O}_{12}$ collected in a diamond anvil cell. Both subtle and discontinuous phase transitions are clearly observed.