

LETTER TO THE EDITOR

Formation of Novel Molybdenum and Tungsten Sulfides by Reduction of MoS₂ and WS₂: A New Route to Chevrel Phases*

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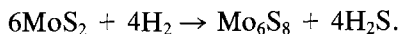
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Pt-catalyzed hydrogen reduction of MoS₂ and WS₂ at 1000–1050°C yields new metal-rich sulfides M₂₁S₈ and M₁₄S₅ (M = Mo or W). The reduction of MoS₂ proceeds via the intermediate Mo₆S₈. Chevrel phases, Cu_xMo₆S₈ (x < 4.0) and Ni₂Mo₆S₈, are readily prepared by hydrogen reduction of MoS₂ in the presence of the ternary metal. © 1987 Academic Press, Inc.

Introduction

A number of binary sulfides have been reported in the Mo–S system of which MoS₂ (hexagonal and rhombohedral), Mo₂S₃, and Mo₆S₈ are well-characterized (1–3). Of these, Mo₆S₈ which constitutes the host material for the Chevrel phases can only be prepared by indirect means (4, 5). WS₂ is the only well-characterized binary sulfide in the W–S system (2, 3). In addition to these crystalline sulfides both molybdenum and tungsten form amorphous trisulfides (6, 7). Chemically speaking, it is possible to envisage the formation of lower-valence molybdenum and tungsten sulfides starting from MoS₂ and WS₂ by a reduction process. For example, Mo₆S₈ may be considered to be formed by



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We explored the possibility of synthesizing lower-valence molybdenum and tungsten sulfides by reduction of MoS₂ and WS₂. Because it is known that MoS₂ and WS₂ do not undergo reduction in hydrogen readily (2, 3),¹ we investigated the reduction reaction in the presence of a platinum catalyst. Platinum is known to act as a catalyst in hydrogen-reduction reactions by a spillover mechanism (8). In this communication, we describe the formation of novel metal-rich sulfides of molybdenum and tungsten including Mo₆S₈ during the platinum-catalyzed hydrogen reduction of MoS₂ and WS₂ at 1000–1050°C. The investigations have enabled us to develop a new method for the synthesis of Chevrel phases.

¹ MoS₂ and WS₂, however, undergo reduction in hydrogen in the presence of alkali metals to give reduced products; see for example M. Sergent and J. Prigent (*C. R. Acad. Sci. Paris* **261**, 5135 (1965)) and R. J. Behlok and W. R. Robinson (*Mater. Res. Bull.* **18**, 1069 (1983)).

Experimental

MoS₂ and WS₂ were prepared by thermal decomposition of ammonium tetrathiomellates at ~900°C in a stream of H₂S (6, 7). Powder X-ray diffraction patterns were similar to the 2H forms of MoS₂ and WS₂ reported in the literature (9). The disulfides (~2 g) dispersed with 1 at% of Pt (in the form of H₂PtCl₆ in ethanol) were reduced at elevated temperatures in a stream of pure and dry hydrogen (flow rate ~3 ml/min).

The reaction was monitored by weight loss and X-ray powder diffractometry. A JEOL JDX-8P X-ray powder diffractometer equipped with CuK α radiation was used to record the patterns.

For the synthesis of Chevrel phases, the ternary metal (Cu/Ni) was mixed with MoS₂ (dispersed with Pt) in the required stoichiometry and the mixture reduced in hydrogen. Chemical compositions of the lower-valence sulfides formed by reduction were determined by quantitative analysis of

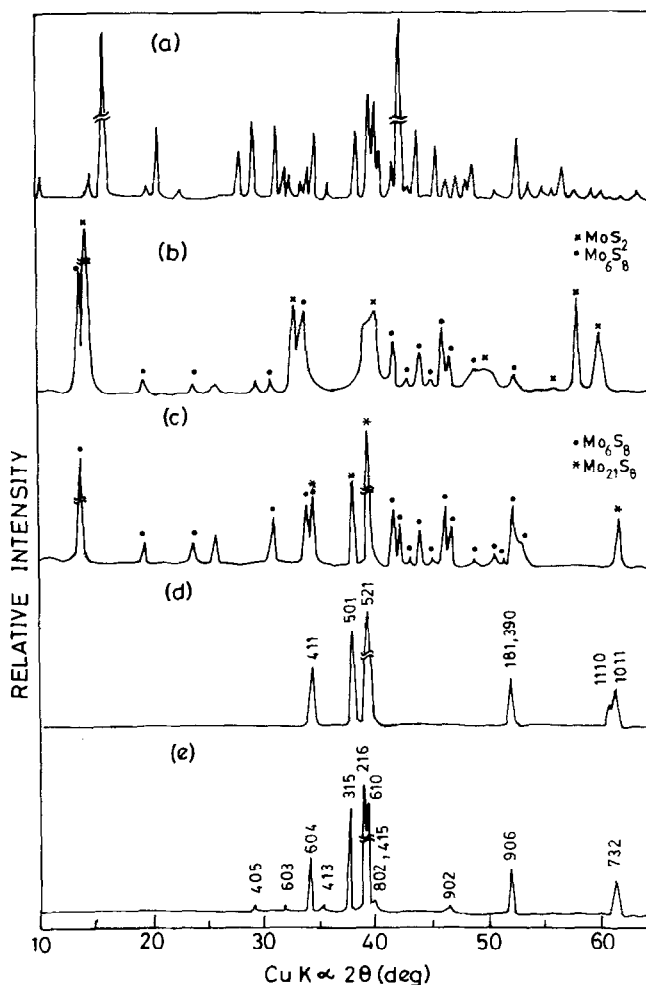


FIG. 1. X-ray powder diffraction patterns of the hydrogen-reduction products of MoS₂ + 1 at% Pt. (a) Mo₂S₃ formed at 850°C, 3 days; (b) Mo₆S₈ + MoS₂ formed at 1000°C, 3 days; (c) Mo₆S₈ + Mo₂₁S₈ formed at 1000°C, 5 days; (d) Mo₂₁S₈ formed at 1000°C, 6 days; (e) Mo₁₄S₇ formed at 1000°C, 8 days.

sulfur and Mo/W. Sulfur was determined as BaSO_4 after oxidizing the samples with Br_2 in CCl_4 followed by a treatment with concentrated HNO_3 . Mo and W were determined by standard methods (10).

Results and Discussion

Preliminary experiments showed that pure MoS_2 and WS_2 did not undergo reduction up to 1000°C . In the presence of a platinum catalyst, reduction of MoS_2 starts around 850°C , yielding Mo_2S_3 (Fig. 1). Continued reduction at this temperature results in the formation of molybdenum metal. More interestingly, when the reduction is carried out at 1000°C , we see the formation of Mo_6S_8 (Fig. 1). We could not, however, prepare pure Mo_6S_8 by this method, since continued reduction at this temperature yields other metal-rich sulfides. We have identified two metal-rich sulfides, one with a S/Mo ratio of 0.385 and the other with a ratio of 0.350 (Table I). The X-ray pattern of the first phase (Fig. 1) is indexable on a tetragonal cell with $a = 16.76$ and $c = 3.35$ Å, indicating that it is probably isostructural with Nb_{21}S_8 (11). The diffraction pat-

TABLE I
REDUCTION OF MoS_2 AND WS_2 IN PRESENCE OF PLATINUM (1 ATOM %) BY HYDROGEN

Product	Reaction conditions ($^\circ\text{C}/\text{days}$)	Weight loss (%)	S/M ratio	Lattice parameters (Å)
Mo_2S_3	850/3	10.2	1.504	Monoclinic: $a = 6.09$, $b = 3.21$, $c = 8.63$, $\beta = 102.4^\circ$
$\text{Mo}_6\text{S}_8 + \text{MoS}_2$	1000/3	—	—	—
$\text{Mo}_6\text{S}_8 + \text{Mo}_2\text{S}_3$	1000/5	—	—	—
Mo_{21}S_8	1000/6	32.0	0.385	Tetragonal: $a = 16.76$, $c = 3.35$
Mo_{14}S_5	1000/8	32.8	0.350	Orthorhombic: $a = 18.48$, $b = 3.37$, $c = 19.79$
W_{21}S_8	1050/8	21.0	0.384	Tetragonal: $a = 16.77$, $b = 3.35$
W_{14}S_5	1050/10	21.4	0.351	Orthorhombic: $a = 18.48$, $b = 3.37$, $c = 19.80$

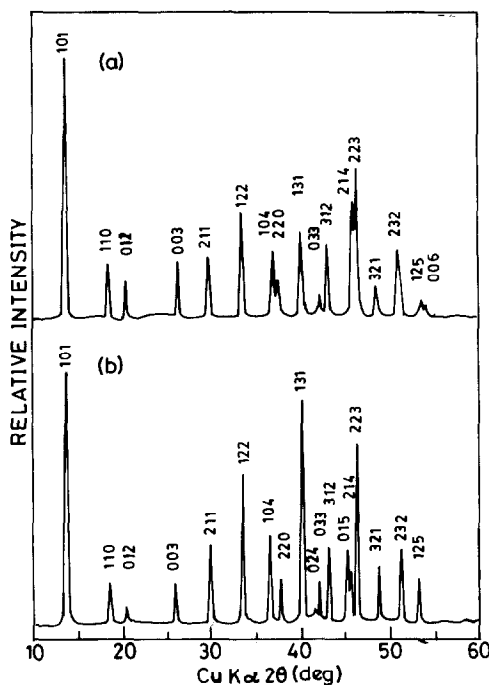


FIG. 2. X-ray powder diffraction patterns of (a) $\text{Cu}_{3.6}\text{Mo}_6\text{S}_8$ and (b) $\text{Ni}_2\text{Mo}_6\text{S}_8$.

tern of the second phase is indexable on an orthorhombic cell with $a = 18.48$, $b = 3.37$, and $c = 19.79$ Å, revealing that it may be similar to Nb_{14}S_5 (12). Reduction of WS_2 in presence of platinum at 1050°C proceeds directly to give metal-rich W_{21}S_8 and W_{14}S_5 (Table I). We see no evidence for the formation of W_2S_3 or W_6S_8 .

The structures of both Nb_{21}S_8 and Nb_{14}S_5 are derived by condensation of the octahedral Nb_6S_8 units (13). Since the reduction of MoS_2 and WS_2 in the presence of platinum catalyst yields products that are isostructural with Nb_{21}S_8 and Nb_{14}S_5 , it is most likely that the reduction proceeds via the formation of intermediate M_6S_8 clusters which condense further to give metal-rich sulfides on removal of sulfur. The formation of Mo_6S_8 during the reduction of MoS_2 is of special significance because direct synthesis of this sulfide from the elements is not possible. Moreover, it has been claimed

(14) that Mo_6S_8 prepared by indirect methods is unstable above 450°C .

The formation of Mo_6S_8 during the reduction of MoS_2 suggested that it may be possible to synthesize $M_x\text{Mo}_6\text{S}_8$ Chevrel phases by the hydrogen-reduction route. Accordingly, we could prepare $\text{Cu}_{3.6}\text{Mo}_6\text{S}_8$, $\text{Cu}_2\text{Mo}_6\text{S}_8$, and $\text{Ni}_2\text{Mo}_6\text{S}_8$ by reacting appropriate mixtures of Cu/Ni and MoS_2 (dispersed with 1 at% Pt) in hydrogen at 1000°C for 2 days. The powder diffraction patterns of the products (Fig. 2) are identical to those of the corresponding Chevrel phases reported in the literature (5, 15, 16). The method is potentially useful for the synthesis of a wide variety of Chevrel phases.

Acknowledgments

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