JOURNAL OF SOLID STATE CHEMISTRY **68**, 188–191 (1987)

LETTER TO THE EDITOR

Formation of Novel Molybdenum and Tungsten Sulfides by Reduction of MoS_2 and WS_2: A New Route to Chevrel Phases*

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Communicated by C. N. R. Rao, December 5, 1986

Pt-catalyzed hydrogen reduction of MoS_2 and WS_2 at 1000–1050°C yields new metal-rich sulfides $M_{21}S_8$ and $M_{14}S_5$ (M = Mo or W). The reduction of MoS_2 proceeds via the intermediate Mo_6S_8. Chevrel phases, $Cu_xMo_6S_8$ ($x < 4.0$) and $Ni_2Mo_6S_8$, are readily prepared by hydrogen reduction of MoS_2 in the presence of the ternary metal.

Introduction

A number of binary sulfides have been reported in the Mo–S system of which MoS_2 (hexagonal and rhombohedral), Mo_2S_3, and Mo_6S_8 are well-characterized (*1–3*). Of these, Mo_6S_8 which constitutes the host material for the Chevrel phases can only be prepared by indirect means (*4, 5*). WS_2 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 MoS_2 and WS_2 by a reduction process. For example, Mo_6S_8 may be considered to be formed by

$$6MoS_2 + 4H_2 \rightarrow Mo_6S_8 + 4H_2S.$$

We explored the possibility of synthesizing lower-valence molybdenum and tungsten sulfides by reduction of MoS_2 and WS_2. Because it is known that MoS_2 and WS_2 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 Mo_6S_8 during the platinum-catalyzed hydrogen reduction of MoS_2 and WS_2 at 1000–1050°C. The investigations have enabled us to develop a new method for the synthesis of Chevrel phases.

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* Contribution No. 393 from the Solid State and Structural Chemistry Unit.

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[1] MoS_2 and WS_2, 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)).

0022-4596/87 $3.00

Experimental

MoS_2 and WS_2 were prepared by thermal decomposition of ammonium tetrathiometallates at ~900°C in a stream of H_2S (*6, 7*). Powder X-ray diffraction patterns were similar to the 2H forms of MoS_2 and WS_2 reported in the literature (*9*). The disulfides (~2 g) dispersed with 1 at% of Pt (in the form of H_2PtCl_6 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 Cu*Kα* radiation was used to record the patterns.

For the synthesis of Chevrel phases, the ternary metal (Cu/Ni) was mixed with MoS_2 (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

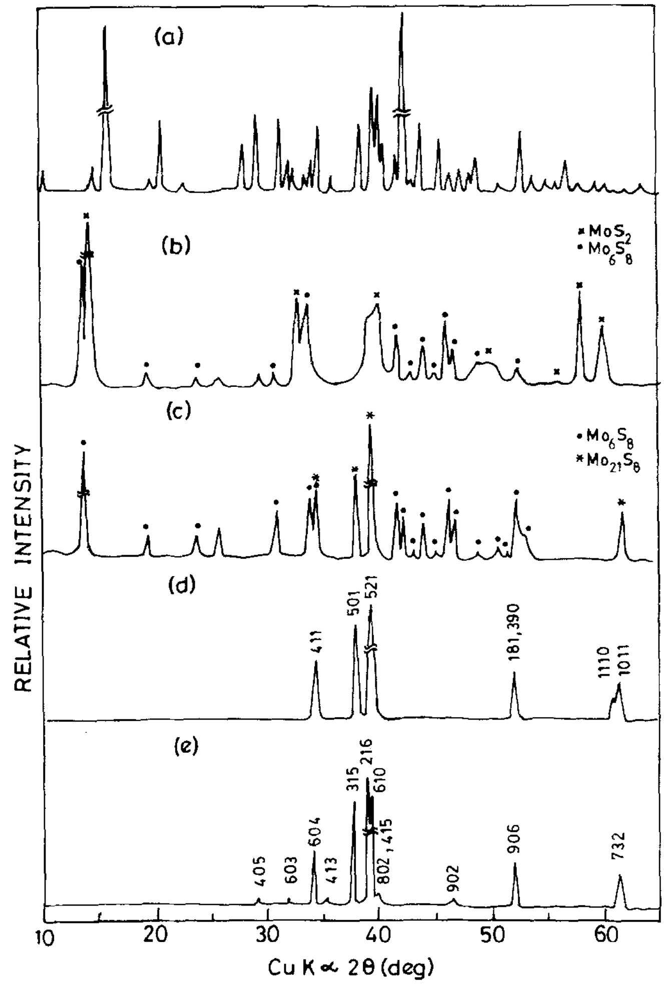

FIG. 1. X-ray powder diffraction patterns of the hydrogen-reduction products of MoS_2 + 1 at% Pt. (a) Mo_2S_3 formed at 850°C, 3 days; (b) Mo_6S_8 + MoS_2 formed at 1000°C, 3 days; (c) Mo_6S_8 + $Mo_{21}S_8$ formed at 1000°C, 5 days; (d) $Mo_{21}S_8$ formed at 1000°C, 6 days; (e) $Mo_{14}S_5$ formed 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 pattern 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.

TABLE I

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

Product	Reaction conditions (°C/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, β = 102.4°
Mo_6S_8 + MoS_2	1000/3	—	—	—
Mo_6S_8 + $Mo_{21}S_8$	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

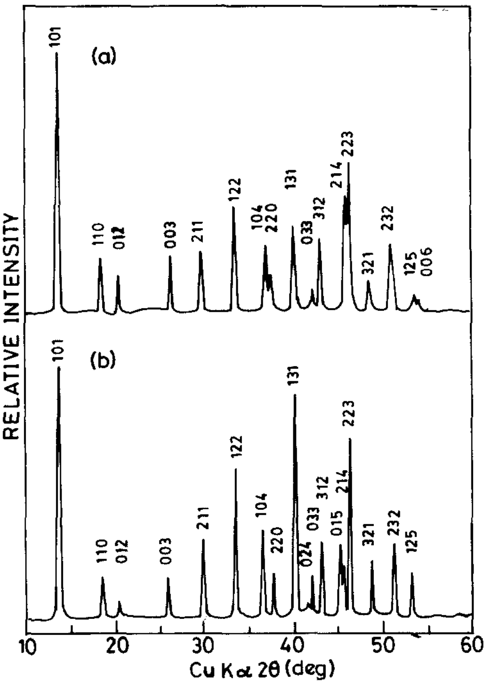

FIG. 2. X-ray powder diffraction patterns of (a) $Cu_{3.6}Mo_6S_8$ and (b) $Ni_2Mo_6S_8$.

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 $M_xMo_6S_8$ Chevrel phases by the hydrogen-reduction route. Accordingly, we could prepare $Cu_{3.6}Mo_6S_8$, $Cu_2Mo_6S_8$, and $Ni_2Mo_6S_8$ 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

We thank Professor C. N. R. Rao, F. R. S., for valuable advice and encouragement. Thanks are also due to the University Grants Commission, New Delhi, and the Department of Science and Technology, Government of India, for support of this research.

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