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Hydrothermal phase relations in molybdenum oxide–water systems

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Molybdenum oxides are important for materials scientists as they show good semiconducting properties. Study of stability relations in molybdenum oxide system is interesting from the point of view of syntheses of pure phases of the oxides or of mixed oxides with other cations. We have studied phase stability in molybdenum oxide–water systems using Tuttle-type pressure vessels. MoO_3 on the low-temperature side and MoO_2 on the high-temperature side were the stable oxides. A metastable blue phase found between the MoO_3 and MoO_2 fields was a hydrated nonstoichiometric molybdenum oxide.

MOLYBDENUM has tetravalent (MoO_2) and hexavalent (MoO_3) stable oxidation states, but many nonstoichiometric 'magneli' phases with composition MoO_n ($2 < n < 3$) have been reported because of its mixed valence states^{1–3}. Preparation of such oxides by high-temperature methods usually involves uncertainty with regard to oxygen stoichiometry, particularly when the process involved is high-temperature sintering with or without control of oxygen fugacity in the atmosphere. One of the promising techniques of synthesis and

growth of single crystals of oxides is the hydrothermal method, which has not received extensive attention from materials scientists. We have been studying the phase relations in several transition metal oxide–water systems in steel or stellite reactor vessels under hydrothermal conditions^{4–7}. The intrinsic oxygen fugacity developed in steel or stellite reactors with water

Table 1. Experimental details for the H_2MoO_4 – H_2O system.

Temp. (°C)	Pressure (bar)	Duration (h.)	Product
175	350	68	$\text{MoO}_3 \cdot n\text{H}_2\text{O}$
200	350	59	$\text{MoO}_3 \cdot n\text{H}_2\text{O}$
225	350	69	$\text{MoO}_3 \cdot n\text{H}_2\text{O} + \text{MoO}_2$
300	350	72	MoO_2
400	350	68	MoO_2
150	700	84	$\text{MoO}_3 \cdot n\text{H}_2\text{O}$
200	700	66	$\text{MoO}_3 \cdot n\text{H}_2\text{O}$
250	700	86	MoO_2
350	700	58	MoO_2
450	700	94	MoO_2
550	700	56	MoO_2
150	1050	68	$\text{MoO}_3 \cdot n\text{H}_2\text{O}$
225	1050	86	$\text{MoO}_3 \cdot n\text{H}_2\text{O}$
300	1050	99	MoO_2
400	1050	56	MoO_2
150	1750	78	$\text{MoO}_3 \cdot n\text{H}_2\text{O} + *$
220	1750	86	$\text{MoO}_3 \cdot n\text{H}_2\text{O} + *$
350	1750	77	$\text{MoO}_2 + *$
110	2100	85	$\text{MoO}_3 \cdot n\text{H}_2\text{O}$
175	2100	94	$\text{MoO}_3 \cdot n\text{H}_2\text{O} + *$
250	2100	58	$\text{MoO}_3 \cdot n\text{H}_2\text{O} + *$
350	2100	58	*
450	2100	69	MoO_2
550	2100	89	MoO_2

*Blue oxide phase

Table 2. Experimental details for the MoO_3 – H_2O system.

Temp. (°C)	Pressure (bar)	Duration (h.)	Product
150	350	78	MoO_3
250	350	69	MoO_3
350	350	79	MoO_3
400	350	88	MoO_3
450	350	86	*
500	350	48	MoO_2
600	350	72	MoO_2
675	350	54	MoO_2
750	350	84	MoO_2
400	850	68	$* + \text{MoO}_3$
200	1050	64	MoO_3
300	1050	94	$\text{MoO}_3 + *$
350	1050	69	$\text{MoO}_3 + *$
450	1050	65	*
550	1050	64	*
600	1050	59	MoO_2
700	1050	95	MoO_2
200	1750	85	MoO_3
250	1750	77	MoO_3
300	1750	56	$\text{MoO}_3 + *$
400	1750	78	*
500	1750	88	*
600	1750	73	$\text{MoO}_2 + *$
700	1750	94	MoO_2

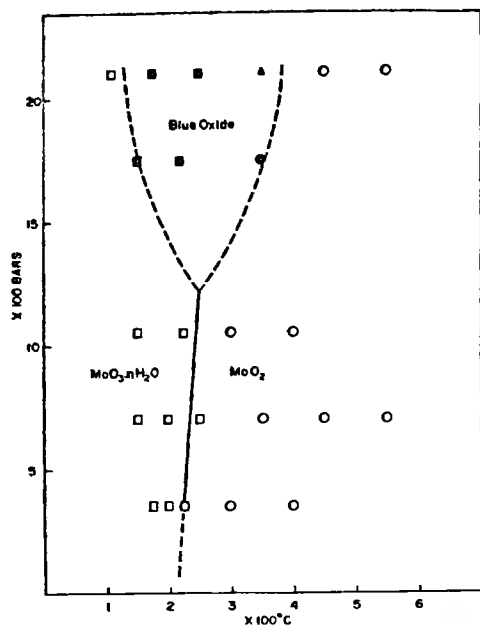


Figure 1. Phase diagram for the $\text{H}_2\text{MoO}_4\text{-H}_2\text{O}$ system.

vapour corresponds to Ni-NiO buffer⁸ and therefore the material is under consistent oxygen fugacity. Here we report the nature of stable molybdenum oxide phases under different conditions of water-vapour pressure (up to 2.5 kbar) and temperature (up to 750°C).

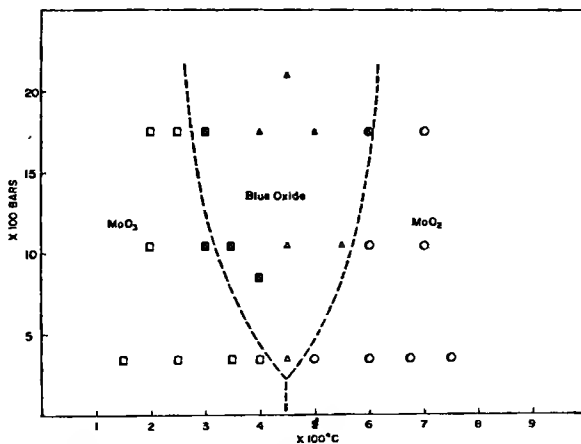


Figure 2. Phase diagram for the $\text{MoO}_3\text{-H}_2\text{O}$ system.



Figure 3. Scanning electron micrographs of (a & b) radiating crystals of MoO_3 in $\text{H}_2\text{MoO}_4\text{-H}_2\text{O}$ system; (c) isolated stubby crystal of MoO_2 in $\text{MoO}_3\text{-H}_2\text{O}$ system.

The technical details of the hydrothermal method were reported earlier⁹⁻¹¹. In the present study, the two starting solids used were molybdic acid H_2MoO_4 (Analar, Wilson) and molybdenum trioxide MoO_3 (Analar, Glaxo). The fluid used with the solids was distilled water. The charge was sealed in platinum capsules. Details of the experimental runs are given in Tables 1 and 2, and the corresponding plots for $\text{H}_2\text{MoO}_4\text{-H}_2\text{O}$ and $\text{MoO}_3\text{-H}_2\text{O}$ systems are given in Figures 1 and 2 respectively. In the $\text{H}_2\text{MoO}_4\text{-H}_2\text{O}$ system, molybdic acid directly decomposes to MoO_2 at low pressures (< 1.5 kbar), but in the high-pressure region (> 1.5 kbar) the white molybdic acid transforms into a blue oxide phase and then to MoO_2 . The blue oxide phase was slightly soluble in water, hence yield was poor. Besides it was admixed with a white molybdic acid phase and therefore identification and analysis of this phase were unsuccessful. Both molybdic acid and blue oxide phases, when directly heated in air, transform to MoO_2 , which, further, sublimates at 800°C . The MoO_2 in this system invariably appeared as radiating tabular crystal aggregates. In the $\text{MoO}_3\text{-H}_2\text{O}$ system, the blue phase is found at pressures lower than 0.5 kbar. There is a progressive change in colour of the blue phase as well as in the relative intensities of certain reflections in the X-ray powder diffraction data with increasing temperature of the run. These changes may be due to the varying valence state of molybdenum in the blue oxide with the corresponding oxygen nonstoichiometry. Attempts to determine the oxygen content of the blue oxide by heating it under oxygen atmosphere until it converted to MoO_3 were unsuccessful because of the minute oxygen deficiency which is beyond the measuring accuracy of the normal thermogravimetric methods. MoO_2 in this system appeared as good stubby crystals. Scanning electron micrographs of MoO_2 crystals obtained in the two systems are shown in Figure 3.

We feel that phase diagrams provide useful information for synthesis of molybdenum-based mixed oxides with both 6^+ and 4^+ valence states of molybdenum with well-controlled oxygen stoichiometry, because of the constant intrinsic oxygen fugacity in the hydrothermal system and the relatively low temperatures involved.

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A study on Palamau vermiculite with special reference to its metal-adsorption properties

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Vermiculite-hydrobiotite is a hydrated magnesium aluminium iron sheet silicate of variable chemical composition. X-ray diffraction study of samples of mineral deposit shows that the material consists of unaltered biotite, hydrobiotite and vermiculite. We also present chemical composition determined by microprobe analysis. Vermiculite also has useful metal-adsorption properties and can be used as a low-cost adsorbent. Zinc removal by vermiculite is pH-dependent and is higher in alkaline medium. Vermiculite may also be useful as an adsorbent for removal of other metal pollutants.

THE mineral is flaky and yellowish-brown to brownish-grey, with a subpearly to submetallic lustre. It occurs as soft, pliable, inelastic laminae, often showing negative optical character and small axial angle. The hardness (Moh's scale) ranges between 1 and 2, while the specific gravity varies between 2.36 and 3.20. Vermiculite mostly resembles the low-grade micas, but differs by its characteristic of being expanded at an angle of 90° to the cleavage plane when heated above 200°C . Expansion or exfoliation occurs when vermiculite is rapidly heated to about 1000°C and maintained at that temperature for a few seconds so that part of its combined water is expelled. The most striking characteristic is that, when exfoliated, the colour changes from brown to glittering gold, silver tint or bronze, which confers insulation against radiation. Vermiculite exfoliates without any change of colour when treated with hydrogen peroxide. When vermiculites are refluxed for about three hours with a 1:2 mixture of sulphuric acid and water, milky-white pure silica flakes are liberated, confirming that the sample is vermiculite and not biotite. Thus vermiculite can be differentiated from biotite by the exfoliation and refluxing test and by treatment with hydrogen peroxide. The rate of