

BRIEF COMMUNICATION

Soft Chemical Synthesis of a High-Pressure Phase of Molybdenum Trioxide: MoO₃-IIBonnie Baker, T. P. Feist, and E. M. McCarron III¹*Central Research and Development, The DuPont Company, Experimental Station, 356/341, Wilmington, Delaware 19880-0356*

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Topotactic dehydration of either the white molybdenum trioxide monohydrate, MoO₃ · H₂O, or the hemihydrate, MoO₃ · ½H₂O, provides a convenient synthetic route to a high-pressure phase of molybdenum trioxide, MoO₃-II. The structural filiations between the various molybdenum trioxide and trioxide hydrate phases are delineated, and simple mechanistic models for the transformations are proposed. © 1995 Academic Press, Inc.

INTRODUCTION

Our interest in understanding the mechanism of the selective oxidation of methanol to formaldehyde over molybdate catalysts (1) naturally led us to attempt the synthesis of model compounds which would hopefully mimic certain aspects of the heterogeneous catalytic process (2). One such compound was Mo₂O₅(OCH₃)₂ (3), made by the interaction of MoO₃ · 2H₂O with CH₃OH. Analogous to the catalytic process, this oxy-methoxide was observed to decompose with liberation of CH₂O. Mo₂O₅(OCH₃)₂ also was reported in this study to hydrolyze to give the hemihydrate MoO₃ · ½H₂O (4). Consequently, we noted that the hemihydrate dehydrated to give what appeared to be a monoclinically distorted variant of the layered orthorhombic α-MoO₃ structure (5). In a later related study, we reported on the synthesis and structure of a high-pressure form of molybdenum trioxide, MoO₃-II (6). In this paper, we show that the dehydration product of the hemihydrate and the high-pressure form of molybdenum trioxide are in fact the same phase.

Furthermore, the structure of the hemihydrate has just recently been determined (7), and we note a distinct structural similarity between the hemihydrate and the previously determined white monohydrate structure, MoO₃ · H₂O (8, 9). In the monohydrate studies, it was reported that dehydration resulted in the formation of

orthorhombic MoO₃. In this study, we show that the monohydrate dehydration product, like that of the hemihydrate, is in fact metastable MoO₃-II. Thus we demonstrate simple soft chemical syntheses of the high-pressure phase, and we propose topotactic mechanisms for the transformations based upon the structural filiation between the trioxides and the trioxide hydrates.

EXPERIMENTAL

Mo₂O₅(OCH₃)₂ and white MoO₃ · H₂O were prepared as previously described in the literature (3, 8, 9). Hydrolysis of Mo₂O₅(OCH₃)₂ at room temperature gave MoO₃ · ½H₂O. Dehydration of the hydrated phases was monitored by TGA. Phase identification was determined by X-ray powder diffraction and, in the case of the trioxides, by Raman spectroscopy.

DISCUSSION

The conversion of orthorhombic α-MoO₃ to its high-pressure monoclinic phase, MoO₃-II (6), is shown in Fig. 1. The phase transformation appears to involve little more than a change in the stacking sequence of the MoO_{1/1}O_{2/2}O_{3/3} layers from *aba* (ortho) to *aaa* (mono). The net result is a slightly more favorable packing of the layers at high pressure, the individual layers themselves remaining virtually unchanged (as can be inferred by a comparison of Raman spectra; Fig. 2). In actuality, the transition to monoclinic symmetry must involve a displacive motion of the molybdenum atoms of every other layer in the *a*-axial direction within the mirror plane (see Fig. 1). The fact that pressure alone will not bring about this transformation suggests that the transition barrier is substantial. MoO₃-II is metastable at ambient conditions and converts back to the orthorhombic form at moderate temperatures (Fig. 3).

In two separate structural studies (8, 9) of the white monohydrate, MoO₃ · H₂O, it was proposed that the de-

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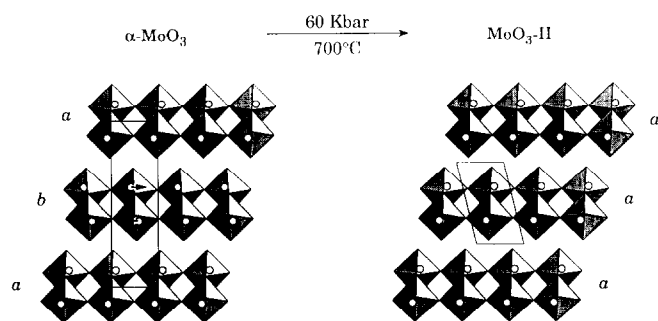


FIG. 1. Conversion of α - MoO_3 to MoO_3 -II. Displacement along the a -axial direction of the molybdenum atoms (in the mirror plane) of the b layer of α - MoO_3 generates the high-pressure monoclinic form.

hydration was topotactic in nature and resulted in the formation of orthorhombic MoO_3 . Similarly, in a study of the hemihydrate, $\text{MoO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ (4), orthorhombic MoO_3 was reported as the product of dehydration. We have also studied the dehydration of both the mono- and hemihydrates by careful TGA experiments. We find in agreement with the above studies water losses of 1 mole H_2O at $\sim 225^\circ\text{C}$ for the monohydrate and $\frac{1}{2}$ mole H_2O at $\sim 300^\circ\text{C}$ for the hemihydrate. However, by slowly heating to the point of initial water evolution and isothermally holding at that temperature until the water loss ceased, we find that the dehydration product in both cases is, by both X-ray powder diffraction and Raman spectroscopy, identical to monoclinic MoO_3 -II. The failure to detect the formation of a monoclinic phase in the previous studies most likely can be attributed to the metastability of the high-pressure form. Furthermore, formation of the metastable high-pressure phase implies the soft chemical nature of these topotactic transformations; i.e., the energy required for dehydration must be below that necessary for conversion to the stable orthorhombic form.

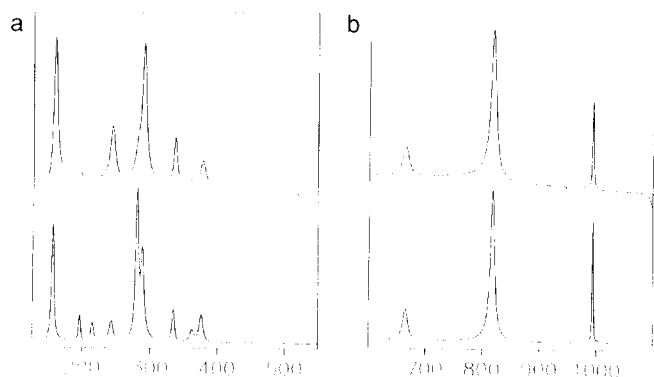


FIG. 2. Raman spectra of MoO_3 -II (top) and α - MoO_3 (bottom): (a) low-frequency (cm^{-1}) region indicative of lattice symmetry and (b) high-frequency (cm^{-1}) region indicative of MoO_6 octahedral coordination.

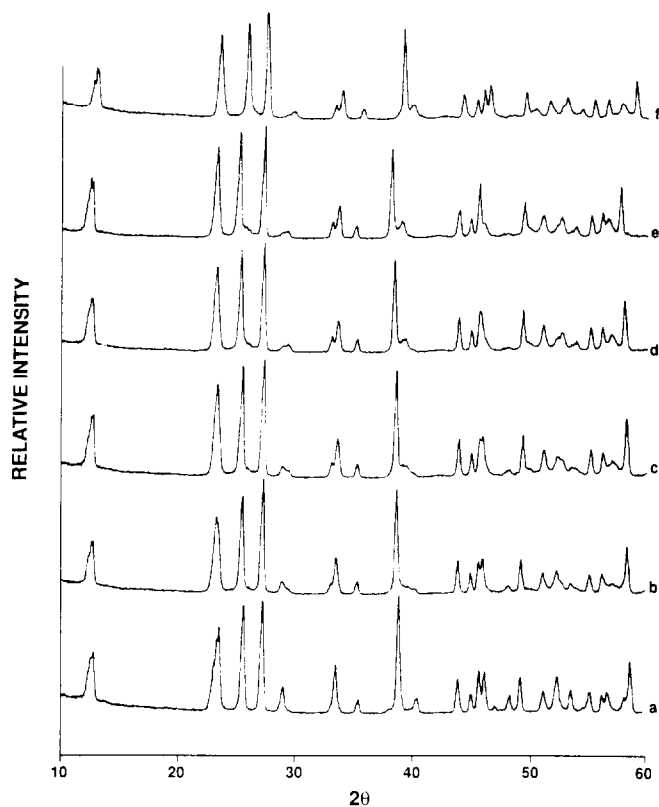


FIG. 3. X-ray powder diffraction data as a function of temperature showing the conversion of metastable MoO_3 -II to α - MoO_3 at: (a) RT, (b) 150°C , (c) 225°C , (d) 300°C , (e) 450°C , and (f) RT after heating.

Consequently, the implied soft chemical nature of the dehydrations along with the structural filiation between the trioxides and the mono- and hemihydrates allows us to propose topotactic mechanisms for the conversions. In both instances, it can be seen that the molybdenum atoms displacements within the individual MoO_6 octahedra in the direction of the edge-shared double chains are such that condensation of the chains to form layers will result in the aaa stacking of the high-pressure form as opposed to the aba stacking of the stable orthorhombic form (see Fig. 4). In the case the monohydrate, only weak $\text{Mo}-\text{OH}_2$ bonds need be broken and weak $\text{Mo}-\text{O}$ bonds reformed by a small translation of the edge-shared chains along the a -axis of the parent structure. In contrast, the case of the hemihydrate is somewhat more complicated. Not only must weak $\text{Mo}-\text{OH}_2$ bonds be broken but also the strong opposing $\text{Mo}-\text{O}$ bond must be broken as well (followed by rotation about and translation ($\frac{1}{2}$ unit cell) along the b -axis of the hemihydrate). That a strong $\text{Mo}-\text{O}$ bond must be broken is reflected in the higher dehydration temperature of the hemihydrate relative to that of the monohydrate. Fortunately, this higher temperature is still below that necessary for conversion to α - MoO_3 .

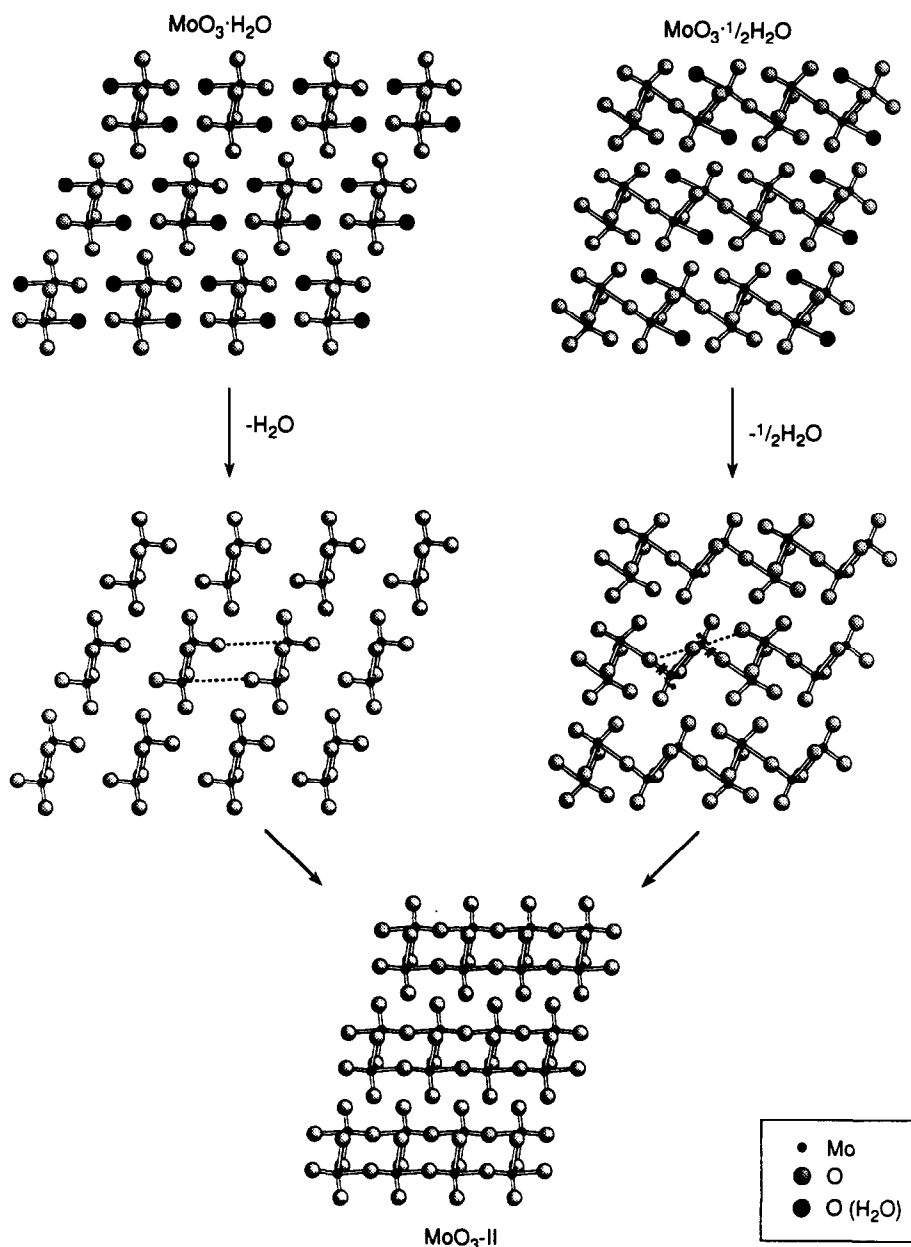


FIG. 4. Proposed topotactic mechanisms for the dehydration of the mono- and hemihydrates to $\text{MoO}_3\text{-II}$.

Other molybdenum trioxide hydrates, namely, yellow $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ (10) and white $\text{MoO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ (11), which do not possess edge-shared octahedral chains and are more closely related to $\beta\text{-MoO}_3$ (12), dehydrate to form this ReO_3 -type structure.

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