

Low temperature synthesis of MoO_3 through the use of $\text{NH}_2\text{OH.HCl}$ as reducing agent

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This paper reports a novel technique for the synthesis of MoO_3 through the reduction of ammonium molybdate using hydroxylamine hydrochloride as a reductant. MoO_3 is formed upon thermal decomposition of the reduced ammonium molybdate. The progress of the formation of the oxide is understood on the basis of structure and thermal studies.

Ceramics and other materials with important electrical, magnetic and optical properties have become an area of intense research offering new approaches for the preparation of new materials. Although a great deal of research has been focussed on silica, alumina and some transition metal oxides, such as TiO_2 , ZrO_2 etc., much work has not been devoted to the synthesis of molybdenum oxides. MoO_3 and WO_3 are also two well-known transition metal oxides which form the basis of several advances in solid state and materials sciences^{1,2}. Interest in molybdenum oxide (MoO_3) is centered around various directions, viz., synthesis, structure-property relationship, role of topotactic dehydration, intercalation with metal and non-metals for various technological applications and in synthesis of new materials. Molybdenum oxides with its laminar oxide network provides a host structure in which small cations such as H^+ , Li^+ can be inserted, thus providing interesting electrochromic properties^{1,3}. The other application of MoO_3 is its function as electrochromic devices and it can be used for architectural energy conservation with automatic response to changes in the environment. H_xMoO_3 ⁴ and $\text{WO}_3\text{-MoO}_3$ ⁵ have been studied because of their on-off colours, yellow/purplish blue and generally amorphous MoO_3 films are substoichiometric $\text{MoO}_{0.26}$ ⁶.

MoO_3 is the parent material for molybdenum bronzes⁷ and for crystallographic shear phases¹. Even supported oxides of molybdenum are subjected to extensive investigation because of their significance in many industrially important reactions which include oxidation of alcohols and hydrocarbons^{8,9} metathesis of olefins^{10,11}. High purity and fine molyb-

denum oxides are prepared and supported on anatase for studying the dispersive power of molybdena¹². The chemical properties of oxidised $\text{Mo}(110)$ serve as a bridge between single crystal studies of reactivity on metallic $\text{Mo}(110)$ and catalytic $\text{MoO}_3(110)$.

MoO_3 adapts a unique layered structure consisting of double octahedral layers formed by edge and corner sharing of $\text{MoOO}_{2/2}\text{O}_{3/3}$ octahedra¹³. Interesting the hydrates of molybdenum oxide ($\text{MoO}_3\cdot 2\text{H}_2\text{O}$) is isotropic consisting of infinite $[\text{Mo}_{4/2}\text{O}(\text{H}_2\text{O})]$ layers. The crystal structure and the topotactic thermal decomposition of $\text{MoO}_3\cdot 2\text{H}_2\text{O}$, are reported in literature¹⁴⁻¹⁶.

A metastable MO_3 is isostructural with ReO_3 and has been synthesized by soft chemistry routes¹⁷⁻²⁰. Synthesis through ion exchange mechanism and also through deintercalating from Li_2MoO_3 lattice are reported^{21,22}, however, these synthetic routes involve stringent experimental conditions in the preparation of the precursor and as well as its deintercalation. In this paper, we report a novel route of employing a common organic reducing agent, viz. Hydroxyl amine hydrochloride ($\text{NH}_2\text{OH.HCl}$) for reducing the oxidation state of molybdenum in ammonium molybdate and the subsequent thermal decomposition of this reduced ammonium molybdate precursor to obtain monophasic molybdenum oxide ($\text{MoO}_3\cdot 2\text{H}_2\text{O}$) at a low temperature under both the atmospheres of dynamic air and nitrogen. The synthesis and characterisation of molybdenum oxide, MoO_3 using ammonium molybdate as a precursor have also been reported.

Experimental Procedure

A 0.25 M solution of hydroxylamine hydrochloride ($\text{NH}_2\text{OH.HCl}$) is prepared by dissolving 1.737 g of

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the salt in 100 mL of water and the pH of this solution is adjusted to about 10 adding NaOH. A 0.25 M ammonium molybdate is prepared by dissolving 3.089 g of the salt in 100 mL of water in another beaker. Drops of dilute HCl are added to the ammonium molybdate solution until the pH of this solution is maintained as 4 ± 0.3 . Immediately after the addition of $\text{NH}_2\text{OH} \cdot \text{HCl}$, the solution turns yellow, signalling the formation of ammonium molybdate with molybdenum in +5 oxidation state (i.e. a change from +6 to +5 in the oxidation state of molybdenum). Further addition of 100 mL of $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution within a period of 10 min resulted in a yellow precipitate. A decrease or increase in pH of the solution thereafter did not alter the yield of the precipitate, thereby indicating that the complete reduction in the oxidation state from Mo^{6+} to Mo^{5+} takes place at pH 4, and the reaction is pH sensitive. This precipitate is allowed to settle overnight and then it is carefully filtered through a sintered crucible. The precipitate is washed with minimal amount of water and allowed to dry in glass funnel for 10 h at ambient temperature, and later stored in vacuum desiccator.

The thermal data are obtained with Mettler Toledo Star instruments under the dynamic atmospheres of air and nitrogen with a heating rate of $10^\circ\text{C}/\text{min}$. The X-ray diffraction patterns are obtained with JEOL JDX-80 diffractometer in the theta range from 10° to 60° using $\text{CuK}\alpha$ as source.

Results and Discussion

Fig. 1 shows the X-ray diffraction pattern of the as synthesized (ammonium molybdate in reduced oxidation state). This sample does not show any Bragg's reflections indicating amorphous nature of the sample. A small portion of this sample is taken and oven dried at 120°C for four hours, and the X-ray pattern of this

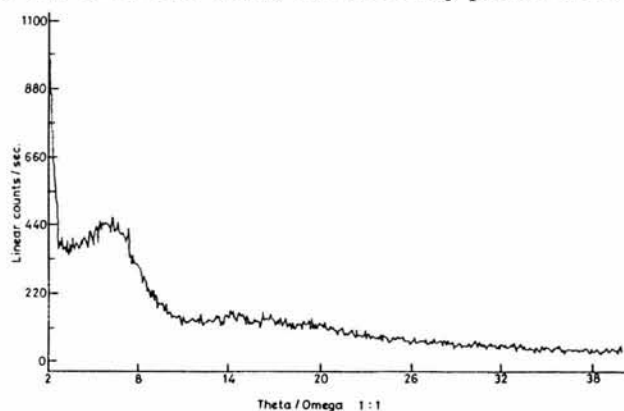


Fig. 1—X-ray diffraction pattern of the as prepared ammonium molybdate precursor

sample is again collected. There is no significant change in the X-ray pattern when compared with the earlier pattern (Fig. 1a).

To understand the process of crystallisation upon heating, the as prepared sample is subjected to thermal studies employing thermogravimetric analyser (TGA) and differential thermal analyser (DTA) under two different atmospheres, viz., air and nitrogen from 30 to 800°C and 30 to 700°C respectively. Fig. 2 shows the TGA/DTA trace of the sample under dynamic air atmosphere. The TGA trace in this figure shows a first weight loss of 33.93 weight % from 80 to 220°C , and a second step of weight loss of 22.86 weight % up to 250°C . On further heating there is no further weight loss. The first weight loss is understood to be due to the loss of two water molecules, and partial decomposition of the ammonium molybdate complex. Above 250°C , a complete decomposition of the partially decomposed ammonium molybdate to molybdenum oxide, MoO_3 takes place. The DTA trace in this figure shows a broad endothermic peak around 200°C and a strong exothermic peak at about 250°C . The endothermic peak supports the dehydration of the complex and the exothermic peak indicates the oxidative decomposition of the complex to form MoO_3 above 300°C .

A small portion of the precursor sample is placed in a silica crucible and gently heated in a flame to remove water and other volatile residues and then sealed under vacuum. One such sample is heated for 2 h at 300°C , and slowly cooled to room temperature, and the X-ray diffraction pattern shown in Fig. 3a for this heat treated sample had reflections corresponding to the impurities and the MoO_3 phase. However, this MoO_3 phase is not finely crystallised. The other sample from the sealed tube is heated for 2 h at 600°C , and cooled to room temperature. The X-ray diffrac-

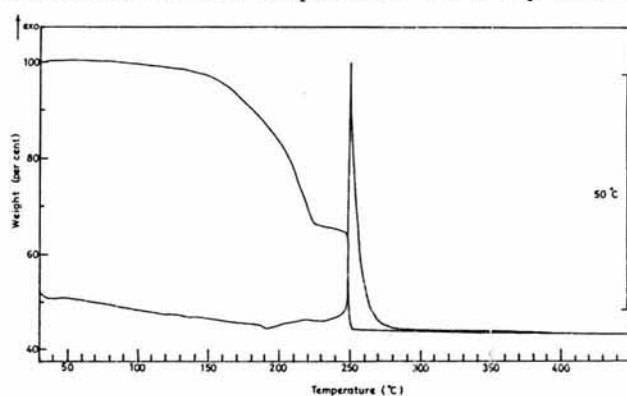


Fig. 2—Thermogram (TGA/DTA) of ammonium molybdate precursor under dynamic air atmosphere

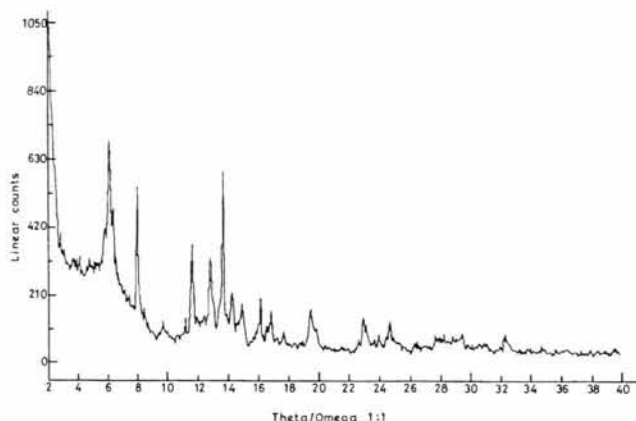


Fig. 3a—X-ray diffraction of ammonium molybdate precursor heated at 300°C

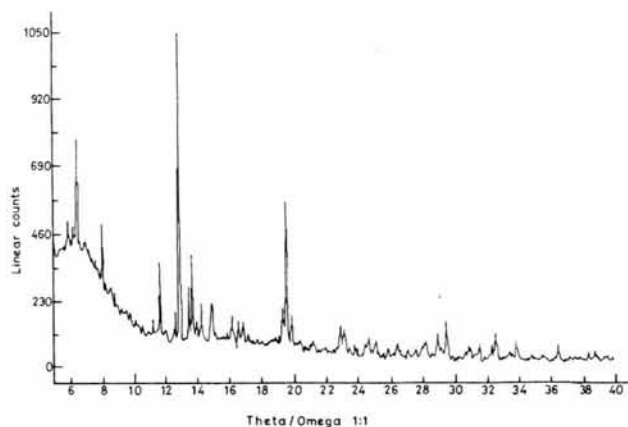


Fig. 3b—X-ray diffraction of ammonium molybdate precursor heated at 600°C.

tion pattern shown in Fig. 3b for this heat treated sample had reflections corresponding to monophasic MoO_3 phase. Accordingly the X-ray diffraction pattern is indexed on a hexagonal cell. The least square refined cell parameters were $a = 10.5 \text{ \AA}$, and $c = 3.72 \text{ \AA}$. These values agree well with the reported values²³.

To understand the effect of atmosphere in the synthesis of MoO_3 from the same precursor, the thermal analysis of this precursor is studied under dynamic nitrogen atmosphere. Fig. 4 shows the TGA/DTA trace for the precursor. The TGA trace shows a first step of weight loss of 5.3 weight % up to 200°C, indicating loss of adsorbed water molecules. The second step of weight loss of 8.15 weight % from 250 to 320°C is observed. This second step of weight loss indicates the decomposition of the partially decomposed complex to monophasic MoO_3 . The DTA trace shows a first endothermic peak at 210°C, and a second endothermic peak at 320°C. The second endothermic peak corresponds to the decomposition of the

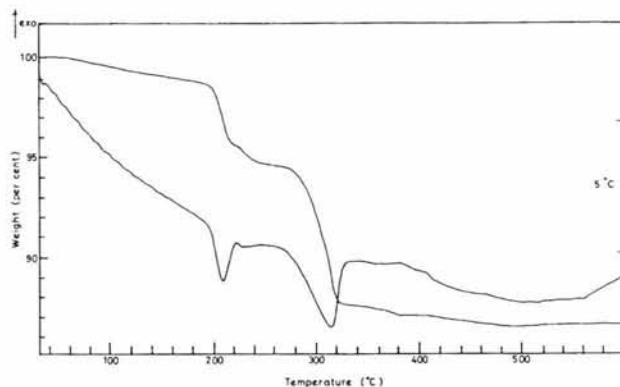


Fig. 4—Thermogram (TGA/DTA) of ammonium molybdate precursor under dynamic nitrogen atmosphere

complex and the crystallisation of MoO_3 . The X-ray diffraction pattern of the sample heated at 400°C, for two hours, resembles Fig. 3b, thereby indicating the formation of a monophasic MoO_3 , under nitrogen atmosphere around 400°C.

Conclusions

Hydroxylamine hydrochloride has been used as a reducing agent to obtain monophasic MoO_3 , through thermal decomposition of reduced ammonium molybdate precursor. This procedure represents a new and a convenient synthetic route to obtain a monophasic MoO_3 , and envisages the possibility of synthesising other transition metal oxides (WO_3 , V_2O_5 , etc.) which otherwise are difficult to synthesize.

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