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SYNTHESIS OF MOLYBDENUM OXIDE BY THERMAL DECOMPOSITION OF MOLYBDENUM ACETYLACETONATE SOL-GEL

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Abstract

Synthesis of monophasic ultrafine molybdenum oxide at low temperatures by thermal decomposition of molybdenum acetylacetonate sol-gel is reported. The sol-gel is obtained through a solvent extraction technique from the organic solvent with the reduction in oxidation state of molybdenum. The thermal behaviour of the sol-gel is studied from the thermal analysis traces. The structural changes accompanying the thermal decomposition of the gel and the formation of monophasic molybdenum oxide is also reported with the help of X-ray diffraction and scanning electron microscopy techniques.

Keywords: molybdenum acetylacetonate, sol-gel, structure and morphology, thermal decomposition

Introduction

Ceramics and other materials with important electrical, magnetic and optical properties has 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., not too much work has been devoted to the synthesis of molybdenum oxides. MoO_3 and WO_3 are two well-known transition metal oxides that form the basis of several advances in solid State and Materials Sciences [1, 2]. Interest in molybdenum oxide (MoO_3) is centred on various directions *viz*., synthesis, structure-property relationship, and 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 electrochomic properties [1, 3]. The other application of MoO_3 is its function as electrochomic devices and it can be used for architectural energy conservation with automatic response to changes in environment.

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MoO_3 is the parent material for molybdenum bronzes [4] and for crystallographic shear phases [1]. 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 [5, 6] metathesis of olefins [7, 8]. High purity and fine molybdenum oxide are prepared and supported on anatase for studying the dispersive power of molybdena [9]. The chemical properties of oxidised Mo(110) serve as a bridge between single crystal studies of reactivity on metallic Mo(110) and catalytic MoO_3(110).

A metastable MoO_3 is isostructural with ReO_3 and has been synthesised by soft chemistry routes [10–13], Synthesis through ion exchange mechanism and also through deintercalating from Li_2MoO_3 lattice are reported [14, 15], however these synthetic routes involve stringent experimental conditions in the preparation of the precursor and as well as its deintercalation. This paper reports a novel route for the synthesis of molybdenum oxide through the thermal decomposition of the molybdenum acetylacetonate sol-gel. The stable oxidation state of molybdenum is Mo^{6+}. For a chemical reaction to take place in solution it is essential for the metals to be in their active oxidation states. The active oxidation state of molybdenum is Mo^{3+}/Mo^{5+}. To achieve this oxidation state Mo^{6+} has to be reduced to Mo^{3+}/Mo^{5+} using a proper reducing agent. Recently we have studied the low temperature synthesis of MoO_3 by thermal decomposition reduced ammonium molybdate precursor employing hydroxylamine hydrochloride as reducing agent [16]. It is envisaged in literature that, the synthesis of a crystalline material through thermal decomposition technique is achieved better, when during the decomposition of the precursor an amorphous to crystalline transition takes place [2, 17, 18a, 18b].

In this paper we report the importance of understanding the thermal behaviour of molybdenum acetylacetonate sol-gel under nitrogen atmosphere for obtaining monophasic molybdenum oxide (MoO_3). The infrared spectra of the gel, partially decomposed gel and MoO_3 are discussed. The morphology of MoO_3 particles is obtained employing scanning electron microscopy and X-ray diffraction technique is employed to understand the amorphous-crystalline transitions.

Experimental

A 0.25 M ammonium molybdate was prepared by dissolving 3.089 g of the salt in 100 mL of water in a beaker. Drops of dilute HCl were added to the ammonium molybdate solution until pH reached to about to 4. A 0.50 M ammoniated acetylacetonate was added. Upon addition of benzene, the ammonium molybdate solution separates into the organic and aqueous layers. This solution is kept under continuous stirring on a magnetic stirrer. To this continuously stirred solution, hydroxylamine hydrochloride solution was slowly added drop-wise while the pH of the solution was 4.0. After the addition of hydroxylamine hydrochloride the whole solution was transferred to the separating funnel. Organic layer was then extracted into the beaker, and on evaporation of the solvent a brown gel corresponding to Mo(III) was formed [19]. This gel was then allowed to settle overnight. The gel was washed with a minimal amount of water and allowed to dry in glass funnel for 10 h at ambient temperature and was then stored in a desiccator.

Results and discussion

Infrared spectra

Infrared spectra of three specimens derived from sample CM_1, CM_2 and CM_3 are shown in Figs 1a–c. Figure 1a corresponds to the as prepared gel (CM_1), Fig. 1b to that after heating the CM_1 sample at 300°C for 2 h and on cooling to room temperature (CM_2). Figure 1c shows the CM_1 sample after heating to 600°C for 2 h and on cooling to room temperature (CM_3).

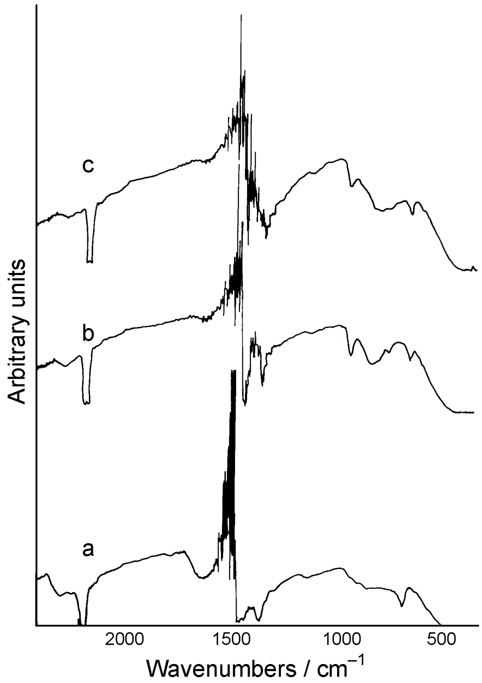

Fig. 1 IR spectra of a – CM_1 sample, b – CM_2 sample and c – CM_3 sample

The bands in the spectrum of the CM_1 sample (Fig. 1a) correspond essentially to those of acetylacetonate groups used in the preparation of molybdenum acetylacetonate. After heating the gel at 300°C (Fig. 1b), a band at 3400 cm^{-1} characteristic of O–H stretch belonging to water and at 1630 cm^{-1} bending mode of free water is observed. The broad band at 990 cm^{-1} is assigned to the Mo=O stretch; the sharp and strong band at around 720 cm^{-1} is characteristic of a Mo–O–Mo stretch [20]. The broad band at 880 and 810 cm^{-1} is typical of Mo–O stretch [5]. The sample heated at 600°C shown in Fig. 1c has similar features, but the peaks at 880 and 810 cm^{-1} disappeared.

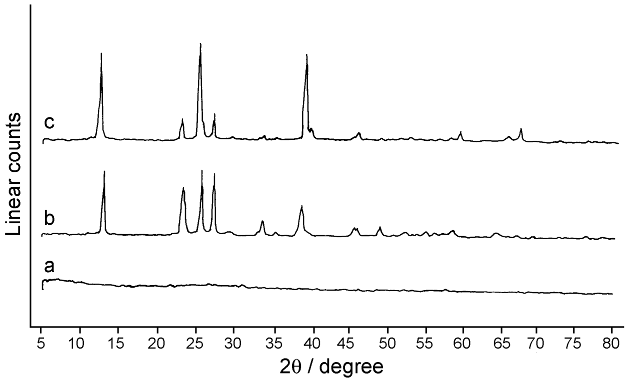

Fig. 2 X-ray diffraction pattern of a – CM_1 sample, b – CM_4 sample and c – CM_5 sample

A powder X-ray diffraction pattern of the CM_1 sample is recorded in the 2θ range 10–80° and is shown in Fig. 2(a). The X-ray diffraction pattern in this figure did not show any Bragg reflections, indicating that the sample was amorphous. A portion of this sample is oven dried at 120°C and the X-ray diffraction pattern is again collected. There was no significant change from the earlier X-ray diffraction pattern.

To understand the evolution of crystallisation on heating, the CM_1 sample is subjected to TG/DTA study with a heating rate of 10°C min^{-1}, in the temperature range 30–500°C in N_2 and air atmospheres. Figure 3a shows the thermal trace under N_2 atmosphere. This TG trace shows a two-step mass loss. The first step mass loss of 24% was observed from100–250°C and the second step of mass loss of 5.43% was observed from 250–450°C, and at higher temperatures (i.e., above 490°C), there is no appreciable mass loss. The presence of mass loss up to 250°C indicates the loss of bound water and other volatile impurities that are normally present in a gel. The second mass loss up to 450°C is due to decomposition of molybdenum acetylacetonate sol-gel. The DTA trace in Fig. 3a, shows the first endothermic peak at 205°C and an additional peaks at 250, 305 and 530°C (along with a shoulder). The first endothermic peak is due to desorption of water molecules on the surface of the gel. The endothermic peak at 250°C is due to partial decomposition of molybdenum acetylacetonate gel. The endothermic peak at 305°C is due to further decomposition of the partially decomposed gel. The endothermic peak at 530°C with its shoulder is due to the formation of MoO_3 oxide.

To understand the effect of atmosphere CM_1 sample is subjected to TG/DTA analysis in an air atmosphere with the same heating rate and temperature range as described for the thermal study under nitrogen atmosphere. Under air atmosphere shown in Fig. 3b the TG trace shows a gradual mass loss from 30–220°C and an additional mass loss from 260–430°C. At high temperature (above 430°C), there is no appreciable mass loss. The first mass loss was due to the loss of water molecules, the gradual mass loss clearly indicated the decomposition of gel. The exothermic peak at 420°C, is due to the formation of monophasic MoO_3 phase. The X-ray diffraction of the isothermally decomposed CM_1 sample at 420°C for 2 h, showed the confirmation of this phase, and the X-ray pattern is shown in Fig. 2c. $MoO_3 \cdot 2H_2O$ has intercalated water molecules [2, 21], and the dehydration takes place at room temperature under proper conditions. In the present study, MoO_3 was obtained on thermal decomposition of the gel at 420°C, and hence it may be understood here that the monophasic MoO_3 obtained was the dehydrated form, and is confirmed from the absence of OH peaks on the IR spectra and X-ray pattern which matches to that of pure MoO_3 (JCPDS 5-508).

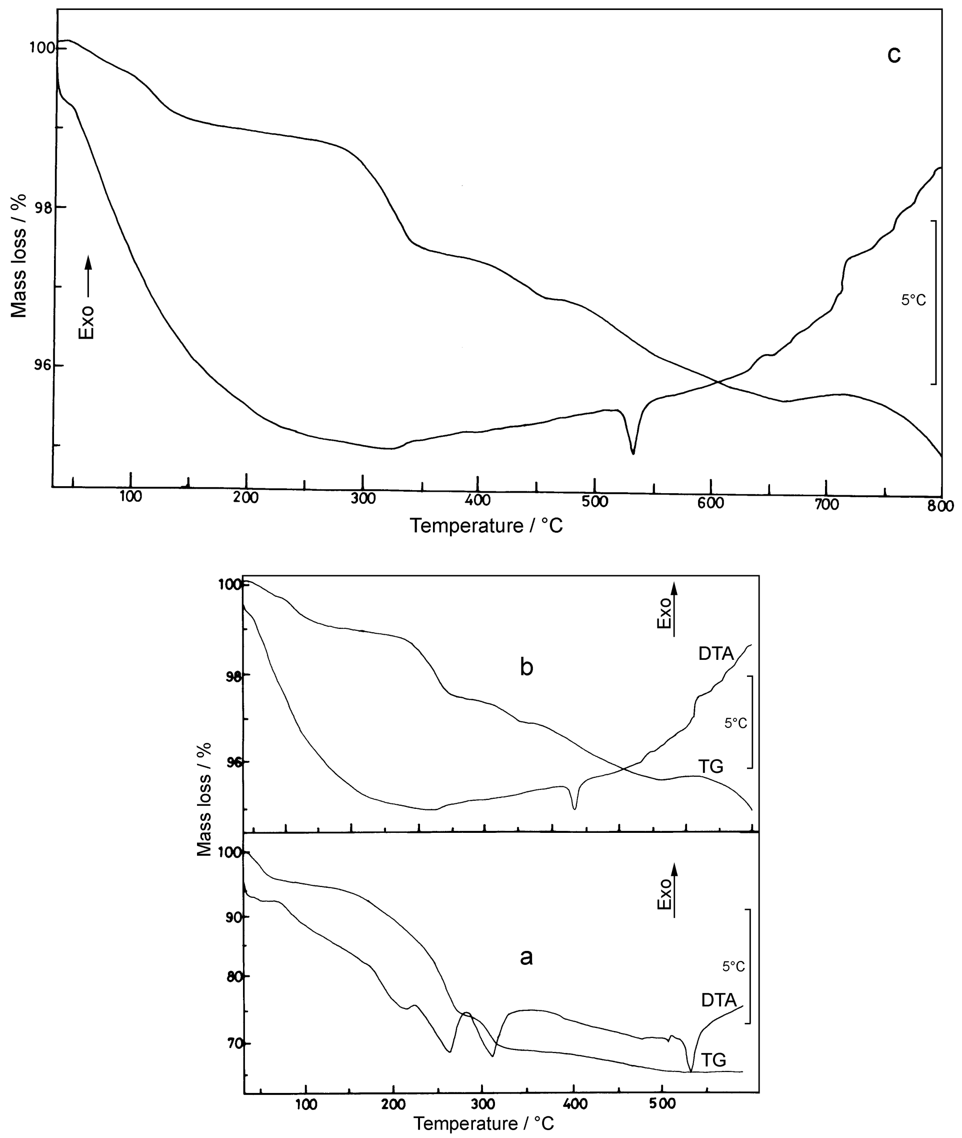

Fig. 3 TG/DTA trace of a – CM_1 sample under nitrogen atmosphere, b – CM_2 under air atmosphere and c – CM_4 sample under nitrogen atmosphere

In order to understand the formation of the oxide from the gel, it was necessary to remove the bound water molecules and the volatile impurities present in the gel (CM_1 sample). Hence a small portion of CM_1 sample was loaded into a 15 mm diameter evacuated quartz tube, and then gently heated with a flame to remove water and other volatile residues, and later this tube was sealed under vacuum. One portion of this vacuum dried CM_1 sample was heated to 300°C for 2 h and cooled to room temperature (hereafter called as CM_4) and was subjected to TG/DTA analysis under N_2 atmosphere. The thermal trace of this sample is shown in Fig. 3c and the X-ray diffraction pattern of this CM_4 sample is shown in Fig. 2b. Another portion of the CM_1 sample is heated at 600°C for 2 h and cooled to room temperature (hereafter named as CM_5), and the X-ray diffraction pattern is obtained for this sample.

The TG trace of the CM_4 sample heated at 300°C, showed a mass loss of 2% from 30–300°C and an additional mass loss of 2% from 300–600°C. The first mass loss was due to the decomposition of the gel partially. The second mass loss is due to decomposition of partially decomposed molybdenum acetylacetonate gel to form monophasic MoO_3. The DTA trace showed an endothermic peak at 520°C, which was due to the formation of monophasic MoO_3. The CM_4 sample had reflections in X-ray diffraction pattern as shown in Fig. 2b, corresponding to two different phases with presence of impurities. On the other hand, the sample heated at 600°C for 2 h and cooled to room temperature, shown in Fig. 2c, had well defined peaks corresponding to monophasic MoO_3. The X-ray diffraction pattern is indexed for a hexagonal system, the least square refined cell parameters were c=10.57 Å, a=3.70 Å. These values agree well with the reported value [22]. The X-ray diffraction pattern shown in Fig. 2c, has reflections corresponding to the MoO_3 phase and no other impurity peaks are detected.

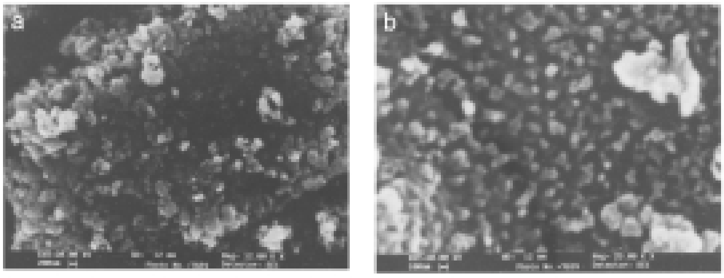

Fig. 4 SEM image of a – CM_2 sample and b – CM_3 sample

Figure 4a shows the SEM image of the CM_2 sample. The image shows a partially decomposed gel, nevertheless few particles of the nano size molybdenum oxide are also observed. Figure 4b shows the SEM image of the CM_3 sample, ultrafine spherical particles of molybdenum oxide of less than 100 nm diameter are observed.

Conclusions

A new synthetic approach to obtain transition metal oxide from the thermal decomposition of a gel via solvent extraction technique is achieved. Monophasic molybdenum oxide was obtained under the atmospheres of dynamic nitrogen and air, at 420 and 600°C respectively. These results indicate that the gel obtained from acetylacetonate precursor acts as a suitable precursor for the low temperature synthesis of monophasic molybdenum oxide with nano size dimensions.

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