

Characterization of La_2MoO_6 prepared by the cation complexation technique

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Abstract

The La_2MoO_6 mixed oxide was prepared by the cation complexation technique using citric acid as complexant agent. The main purpose of this work was to obtain a mesoporous powder with relatively high specific surface area. The thermal decomposition behavior of the metal complex was studied by thermal analysis and Fourier transform infrared spectroscopy. A specific surface area value of $\sim 15 \text{ m}^2 \text{ g}^{-1}$ was obtained by nitrogen adsorption/desorption measurements. X-ray diffraction patterns of calcined mesoporous materials reveal that even though a low degree of crystallinity is attained, this phase may be obtained at low temperatures.

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1. Introduction

The lanthanum molybdate compounds form a group of ceramic materials whose properties are dependent upon the crystalline structure and on the molybdenum valence. The phase diagram of this system exhibits several phases with $\text{La}_2\text{O}_3\text{--MoO}_3$ molar ratios 1:1, 1:2, 1:3, 1:4, 1:6, 2:1, 3:1 and 9:4 [1].

Earlier crystallographic studies [1,2] of the La_2MoO_6 mixed oxide have shown that it crystallizes in the tetragonal structure, space group $I\bar{4}2m$ (no. 121). However, the X-ray diffraction pattern exhibited extra low-intensity peaks, which could not be indexed according to the unit cell reported [3,4]. Further investigations of this ceramic material presented evidence that the space group $I4_1/acd$ (no. 142) would better describe the unit cell configuration [4]. Neutron diffraction results revealed that the crystalline structure of the La_2MoO_6 phase might be described as constituted by two La_2O_2 layers intercalated between layers of MoO_4 tetrahedra. The lanthanum ions are coordinated by

eight oxygen ions, whereas each molybdenum ion is four-coordinated with oxygen ions, in the first coordination sphere [5].

Potential applications of MoO_3 and Mo-mixed oxides as catalysts in the selective oxidation of hydrocarbons and oxidative dehydrogenation of methanol have been recognized [6–10]. Relevant material properties for this application are relatively high specific surface area and pore size distribution in the mesopore range.

Most of the experimental works on lanthanum molybdate compounds have been carried out on powders prepared by solid state reactions or by the coprecipitation techniques. For MoO_3 -based catalysts, values of specific surface area obtained by these methods are lower than $10 \text{ m}^2 \text{ g}^{-1}$ [6–8]. Recently the $\text{La}_2\text{Mo}_2\text{O}_9$ phase and other molybdate-based mixed oxides prepared by a modified sol–gel route were shown to be obtained at relatively low temperature [11,12] and this finding was attributed to a size-dependent effect of the powder particles. In addition, the selectivity of these materials to benzaldehyde and toluene conversion was found to be higher than those of larger oxide particles obtained by conventional methods of synthesis [12].

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In this work, the La_2MoO_6 mixed oxide was synthesized by the cation complexation technique aiming to obtain a high specific surface area material with a mesopore structure. The thermal decomposition of the precursor material was studied by thermal analyses. Surface and microstructural characterization of the precursor and thermally treated materials were carried out by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and scanning electron microscopy (SEM).

2. Experimental

Lanthanum nitrate, La_2O_3 (99.9%, IPEN) and molybdenum oxide, MoO_2 (99%, Alfa Aesar) were used as starting materials. Other reagents were anhydrous citric acid (99.5%), and nitric acid (65%, P.A.). The lanthanum oxide was synthesized at our Institute from a rich-cerium concentrate by the ion exchange resin and the fractioned precipitation techniques. A lanthanum nitrate solution was prepared by dissolution of the La_2O_3 in a hot nitric acid solution. The molybdenum nitrate solution was prepared in a similar way to that of lanthanum nitrate, except by the addition of a suitable amount of hydrogen peroxide to promote the oxidation of molybdenum. A mixed nitrate solution was then prepared by mixing the individual nitrate solutions in the stoichiometric proportion under vigorous stirring. Another solution containing citric acid as a complexant agent was added to the mixed cation solution. The molar ratio metal: citric acid was set to 1:2. After homogenization of this solution, the temperature was raised to 80 °C, and maintained under stirring to remove excess water and to convert it to a transparent gel. While raising the temperature, the solution became more viscous with evolution of foam, and finally it gelled without any visible formation of precipitation or turbidity. Keeping the solution at this temperature, there is an increase of the viscosity with simultaneous elimination of water and NO_2 . This method of synthesis was initially proposed for the preparation of dispersed mixed oxides or solid solutions [13]. The initial thermal decomposition of the precursor was carried out at 200 °C for 1 h. The resulting ash-like material was afterwards pyrolyzed at 500 or 600 °C for 5 h.

The thermal decomposition of the organic precursor was studied by simultaneous thermogravimetry, TG, and differential thermal analysis, DTA (STA 409, Netzsch) up to 720 °C, heating at a rate of 5 °C min^{-1} in synthetic air (~20% O_2). Alumina (Alumalux, Alcoa) was used as reference material. Fourier transform infrared spectroscopy (Magna IR560, Nicolet) was also used to follow the decomposition of the precursor material. Transparent pellets were prepared by mixing the powder specimen and KBr. The specific surface area of the powder calcined at 600 °C was analyzed using five-point Brunauer, Emmett and Teller, BET, analysis by nitrogen adsorption (ASAP 2010, Micromeritics) after degassing at 300 °C. The X-ray diffraction (D8 Advance, Bruker-AXS) method was used for phase analysis. Typical experimental

conditions were 40 kV and 40 mA, using a Ni-filtered $\text{Cu K}\alpha$ radiation source. Scans were conducted in the 15–75° 2θ range at 0.05°/10 s counting time. The morphology of powder particles was observed by scanning electron microscopy (XL30, Philips), using secondary electrons.

3. Results and discussion

The differential thermal analysis curve of the precursor material is shown in Fig. 1. Three exothermic peaks and one endothermic peak were detected. The first exothermic peak at 140 °C and the endothermic peak at 265 °C were identified with the decomposition reaction of free citric acid [14], since an excess of citric acid was used to ensure the complexation of all metal cations. Exothermic peaks at 505 and 535 °C were related to the decomposition of metal citrates, and to the oxidation reaction of decomposition products, which are usually observed to occur in this temperature range during the thermal decomposition of these complexes [15]. The DTA curve during cooling down the specimen to room temperature did not show any thermal event that could be attributed to a phase transition. Therefore, it may be concluded that a single-phase powder was obtained by thermal decomposition of the precursor material, and that this phase is thermally stable in the temperature range of measurements.

The DTA curve of Fig. 1 evidences an intimate mixing of cations in the precursor material allowing for obtaining a lanthanum molybdate compound with the desired stoichiometry upon thermal decomposition.

Fig. 2 shows the thermogravimetric and its derivative (DTG) curves of the precursor material. The weight loss may be divided into two steps with a total weight loss of 71.5% up to 600 °C. Assuming that a mixture of simple metal–citrates was formed during the complexation reaction, a calculated weight loss of 70.8% would be expected in good agreement with TG results. The DTG curve exhibits peaks at 135 and 190 °C related to the elimination of free citric acid and resid-

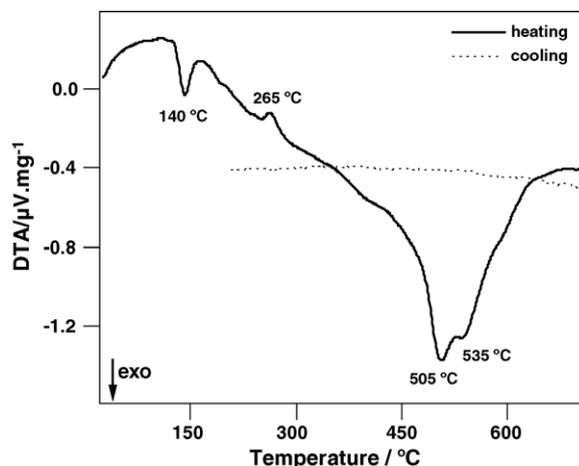


Fig. 1. DTA curve of the lanthanum molybdate complex.

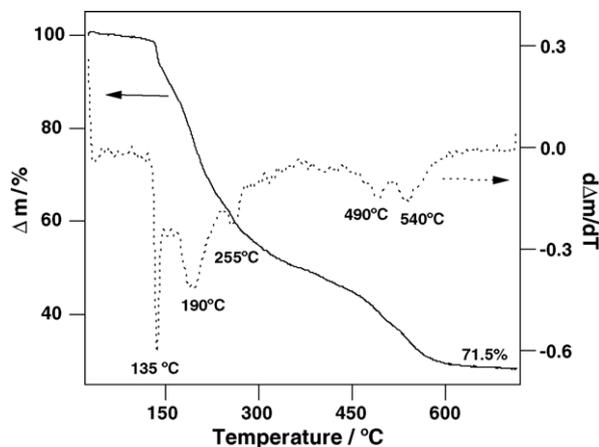


Fig. 2. TG and DTG curves of the lanthanum molybdate complex.

ual water, due to the hygroscopic nature of the precursor material. The DTG peak at 255 °C correlates with the endothermic peak at 265 °C (Fig. 1) and may be also attributed to the decomposition of citric acid. The last two DTG peaks at 490 and 540 °C are related to the elimination of organic matter resulting from the decomposition reaction.

FT-IR spectra of as-prepared complex, partially decomposed material (200 °C), and after pyrolysis (500 and 600 °C) are shown in Fig. 3. In the spectrum of the as-prepared material the main observed bands are related to [16] free citric acid ($\sim 1724\text{ cm}^{-1}$), COO^- vibration of a metal complex and/or O–H bend vibration ($\sim 1630\text{ cm}^{-1}$), and other vibrations (~ 1394 , 1230 and 1076 cm^{-1}) due to carbon–oxygen bonds.

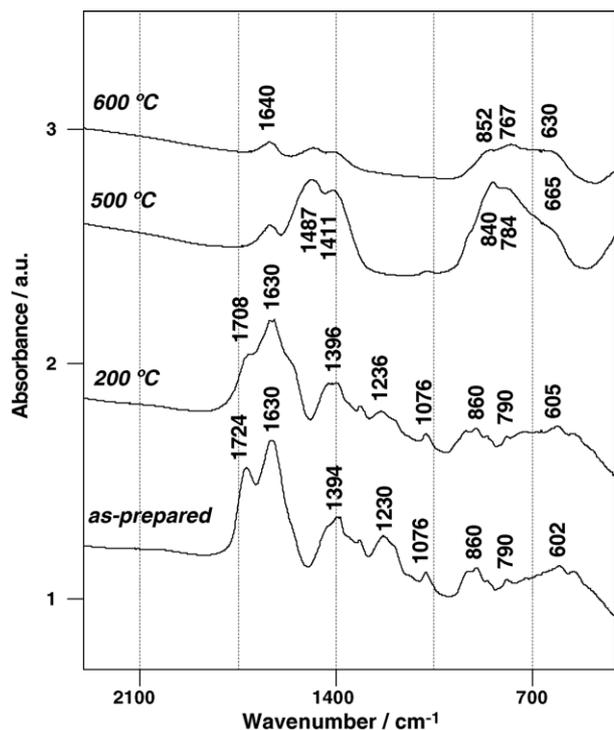


Fig. 3. FT-IR spectra of the lanthanum molybdate complex and after thermal treatment at 200 °C/1 h, 500 °C/5 h and 600 °C/5 h.

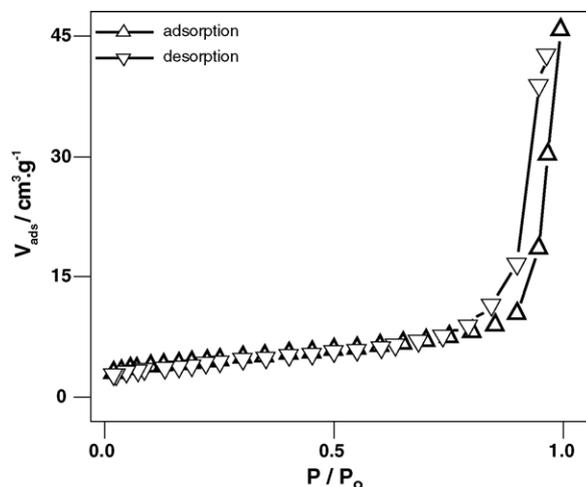


Fig. 4. Adsorption/desorption isotherm of La_2MoO_6 pyrolyzed at 600 °C.

Vibrations characteristic of NO_3^- (~ 1385 and 840 cm^{-1}) were not detected. The FT-IR spectrum of the specimen thermally treated at 200 °C for 1 h exhibits almost the same absorption bands of the as-prepared material. However, there is

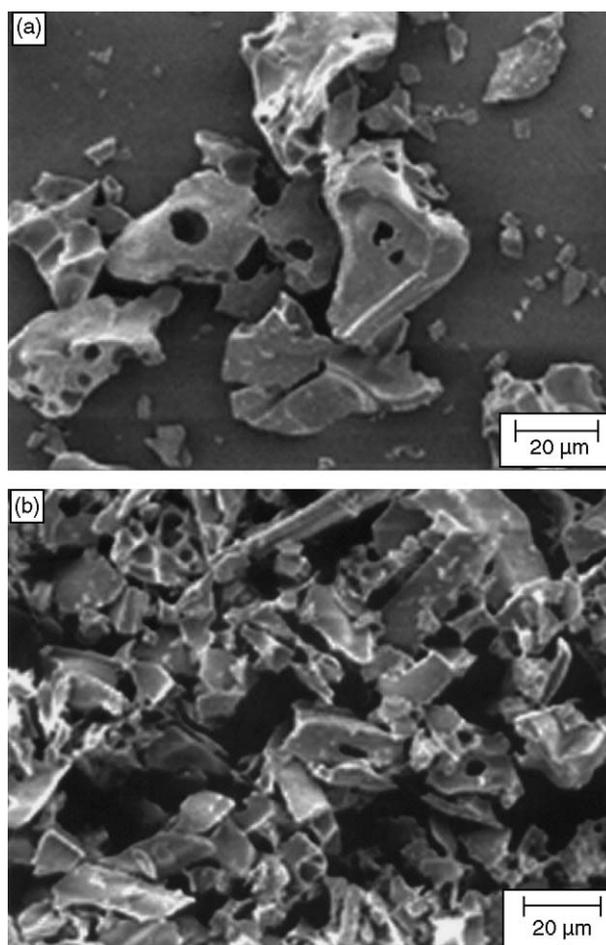


Fig. 5. SEM micrographs of La_2MoO_6 powders pyrolyzed at 500 °C (a) and 600 °C (b).

a small shift in the peak position and a slight decrease in the relative intensity of these absorption bands. After pyrolysis at 500 or 600 °C, most of the infrared absorption bands disappeared, except those at low wavenumber, which are attributed to metal–oxygen bonds.

These results on thermal analysis and FT-IR suggest that during synthesis of the metal complex, La and Mo cations are complexed as a compound with a specific decomposition behavior. This type of result was observed to occur during the chelation and polyesterification reactions of metallic cations [17].

Nitrogen physisorption measurements were performed also on pyrolyzed powders. As an example, in Fig. 4 an adsorption/desorption isotherm of the powder thermally treated at 600 °C is shown. This isotherm is characteristic of type IV in the IUPAC classification [18], typical of a well-developed mesopore system. The specific surface area determined by the BET method is $15.1 \text{ m}^2 \text{ g}^{-1}$. The pore size distribution calculated from the desorption branch curve by using the BJH method indicates that 100% of porous have a size lower than 60 nm.

SEM micrographs of powders after pyrolysis at 500 and 600 °C are shown in Fig. 5. The morphology of powders shows a very porous structure. In addition, large particles were formed as shown in Fig. 5a (pyrolyzed at 500 °C). These large particles are porous and were probably formed

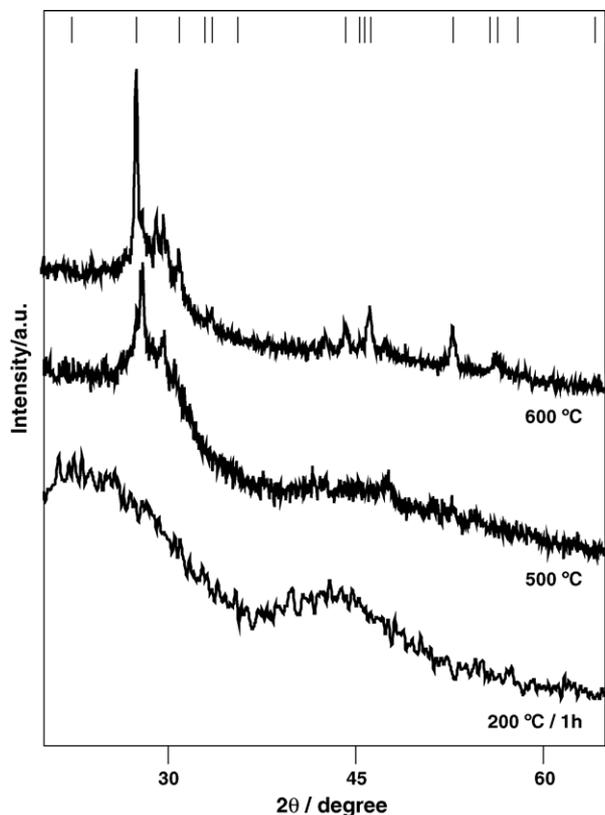


Fig. 6. X-ray diffraction patterns of lanthanum molybdate powders pyrolyzed at different temperatures. Vertical lines identify diffraction peaks of the tetragonal La_2MoO_6 phase according to ICDD—24-0550.

by the liberation of CO_2 and water from the decomposition of citric acid. Increasing the temperature of thermal treatment to 600 °C, the morphology of powder particles (Fig. 5b) changed slightly. The magnification in Fig. 5a and b are the same, so it can be seen that the particle size decreases with increasing the pyrolysis temperature. This feature may be explained as a result of the liberation of residual carbon entrapped into the porous structure. The pressure exercised by gaseous species should be responsible for the break up of the porous structure of large particles.

X-ray diffraction patterns obtained for the partially decomposed material and after pyrolysis at 500 or 600 °C are shown in Fig. 6. The material thermally treated at 200 °C is amorphous to X-rays, whereas after decomposition it is crystalline. However, the diffraction peaks are broad and there is a relatively high background in these patterns indicating that these powders are composed of very small crystallites. In these patterns the high-intensity reflections of the tetragonal phase (ICDD—24-0550) are identified.

4. Conclusions

Ultrafine powders resulting from the thermal decomposition of a metal complex precursor of the La_2MoO_6 composition was successfully prepared by the cation complexation technique. Results on thermal analyses support the direct formation of a single-phase lanthanum molybdate compound. The tetragonal phase of La_2MoO_6 could be obtained by calcination of the precursor material at relatively low-temperatures. The cation complexation technique proved to be an alternative and suitable route for the preparation of lanthanum molybdate mixed oxides.

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