

Preparation and Characterization of Ultrafine Rare Earth Molybdenum Complex Oxide Particles

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Ultrafine rare earth molybdenum (La–Mo and Ce–Mo) complex oxide particles have been synthesized by the sol–gel process using citric acid as complexing agent. The influence of preparation conditions such as thermal treatment temperature (*T*), molar ratio of citric acid to metallic ions (*L/M*), and pH value of the starting solution on the oxide particle size has been studied. The formation of $\text{La}_2\text{Mo}_2\text{O}_9$ and $\text{Ce}_2\text{Mo}_3\text{O}_{12}$ has been investigated using XRD, DTA–TG, FT-IR, TEM, and BET surface area measurements. It is shown that the morphology and structure of the oxide particles are significantly dependent on the preparation conditions. The influence of different preparation methods on the particle size of La–Mo and Ce–Mo oxides is also discussed.

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INTRODUCTION

Selective oxidation of hydrocarbons to organic oxygenate compounds on metal oxide catalysts is one of the challenges in the field of catalysis which have been actively developed in recent years. As might be expected, the Mo-based and V-based oxides have been among the most widely used for selective oxidation of hydrocarbons (1). In the past decades, considerable attention has been devoted to the design of highly selective oxidation catalysts, and great efforts have been made in improving the catalytic selectivity by adding promoters to these oxides. It has been found that Bi, Fe, Sn, W, and rare earths are effective promoters of the Mo-based and V-based oxide catalysts for selective oxidation of toluene to benzaldehyde (2–7), and the preparation conditions, oxide composition, and catalyst structure exert great influences on the catalytic selectivity.

As reported in the literature, the synthesis of these catalytic systems is normally achieved by two classical methods, the coprecipitation process and the solid state reaction technique. However, because these conventional methods do not always produce molecularly homogenous distributions of various components, multicomponents oxide catalysts can be obtained only after thermal treatment at high temperature, resulting in oxide particles that are very large

and a BET surface area that is rather small. This obviously limits the catalytic activity of these catalysts.

It is well known that catalytic researchers have long been interested in the preparation of new catalytic materials, not only by refining and perfecting the traditional processing methods but also by developing that new and improved processing techniques. Among the new catalyst preparation methods, sol–gel synthesis has received increasing attention lately (8–16) due to its potential for delivering samples that are better mixed on a molecular scale, although it has been known since 1846 (17). The sol–gel process is a versatile solution technique used to obtain ultrafine, homogenous powders of a variety of glass and ceramic materials at low temperatures and in short times (18). By using this method, catalytic researchs have successfully prepared a variety of ultrafine particles whose catalytic properties were much better than those of large particles prepared by other methods (19–23). For instance, Lopez *et al.* have used the sol–gel process to synthesize supports and metallic catalysts with high surface areas, high temperature resistance, and good catalytic properties, as well as remarkable resistance of the active metal to self-deactivation in hydrogenation reactions (21–23).

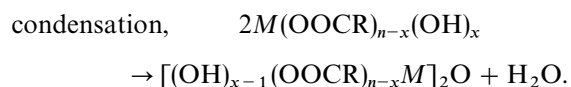
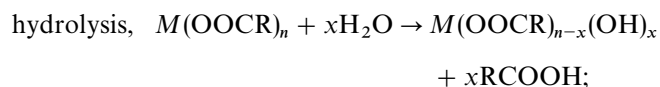
In our previous studies (24, 25), it has been found that by decreasing the particle size of La–Mo and Ce–Mo complex oxide to nanoscale, the reactivity of lattice oxygen ions and thus the selectivity for oxidation of toluene to benzaldehyde can be remarkably improved. In the present work, we report the preparation of ultrafine La–Mo and Ce–Mo complex oxide particles by the sol–gel technique using citric acid as complexing agent.

EXPERIMENTAL

Sample Preparation

In the conventional sol–gel process, alkoxides are often used as a precursor for preparation of metal oxides. In the present study, ultrafine La–Mo and Ce–Mo complex oxide particle catalysts were prepared by a modified sol–gel method, as reported in the literature (13, 20, 26), in which

citric acid was used as a complexing polyfunctional hydroxy acid. With a citrate ($M(\text{OOCR})_n$) as a precursor, sol-gel chemistry can be described in terms of two classes of reactions:



Lanthanum nitrate (AR, Shanghai) or cerium nitrate (AR, Shanghai) and ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 6\text{H}_2\text{O}$ (AR, Shanghai) solutions were prepared separately and then mixed with metallic ions in molar ratio 1:1 (La/Mo) and 2:3 (Ce/Mo). Citric acid (AR, Shanghai) solution was then added slowly to the mixture solution under constant stirring. The pH of the solution was adjusted to the required level with the addition of ammonia (2.0 mol/L) or nitric acid (2.0 mol/L) solution. The solution was kept in

a water bath at 333 K until gelation was completed, and then the as-prepared gels were dried at 393 K for 24 h. The gel samples were calcinated at various temperatures at air for 4 h. The heating rate for calcination was 10 K/min. For comparison, the conventional coprecipitation method, in which lanthanum nitrate or cerium nitrate aqueous solution was mixed with ammonium molybdate aqueous solution, was also used to prepare La-Mo and Ce-Mo oxides, and the precipitates formed were dried and calcinated.

Characterization

X-ray diffraction patterns were obtained in a Shimadzu 3A diffractometer with $\text{CuK}\alpha$ radiation (0.15418 nm). The particles' shape and size were elucidated by TEM with a JEM-100S transmission electron microscope. TG/DTA studies were taken with a Rigaku thermal analyzer by heating a 10- to 20-mg sample from room temperature to 873 K in air at a heating rate of 20 K/min. The BET surface area measurements were performed on a Micromeritics ASAP-2000 instrument (N_2 adsorption at 77 K). The IR spectra

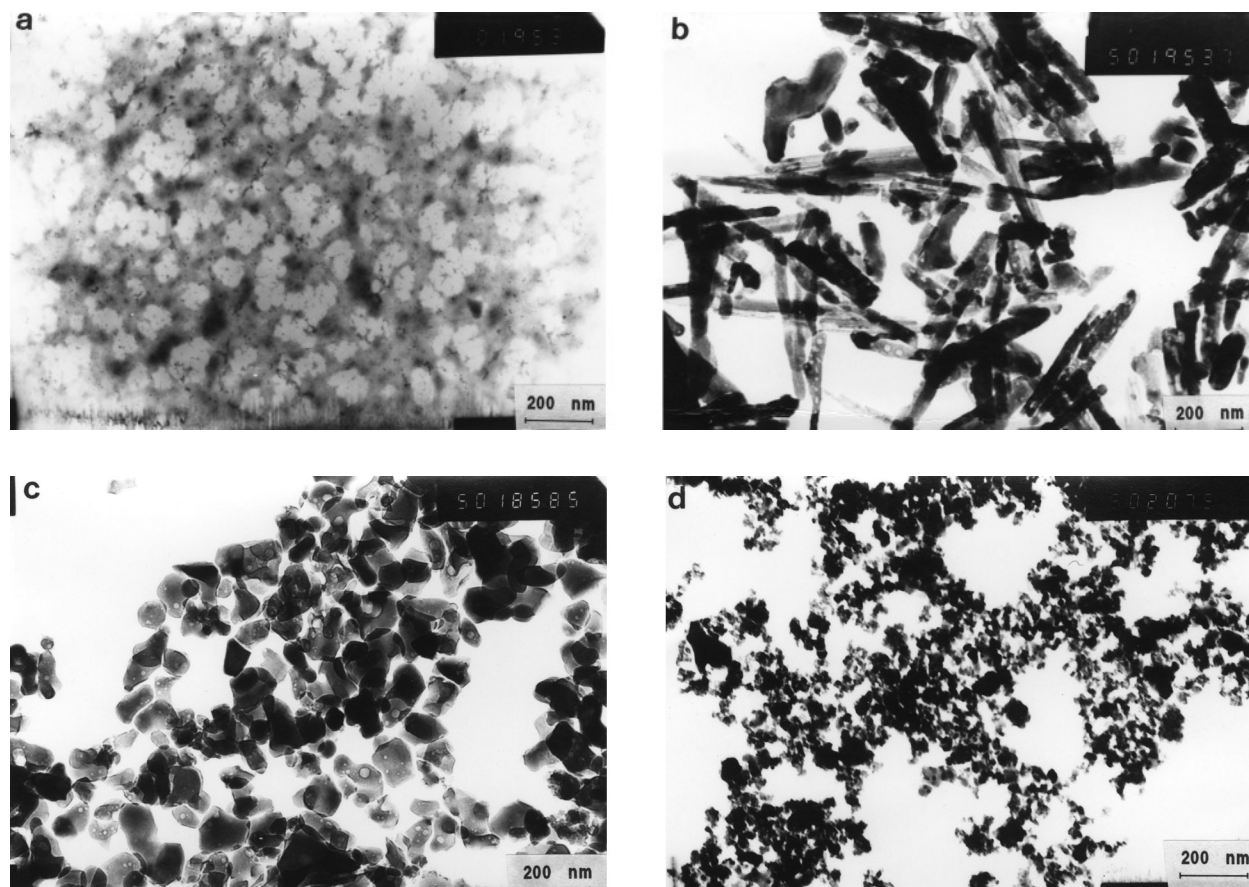


FIG. 1. TEM images of the gels after heat treatment: (a) La-Mo after treated at 393 K, (b) Ce-Mo after treated at 393 K, (c) La-Mo after treated at 773 K, (d) Ce-Mo after treated at 773 K.

were measured with a Nicolet 510P Fourier transform infrared spectrometer operated with special resolution $\pm 2 \text{ cm}^{-1}$.

RESULTS AND DISCUSSION

The TEM images of La–Mo and Ce–Mo gels after drying at 393 K are presented in Figs. 1a and 1b. It can be seen that the gels show relatively good homogeneity with a three-dimensional net structure for the La–Mo sample and a rod-shaped structure for the Ce–Mo sample. This reveals that the carboxylate groups of citric acid have attached to the metallic ions. XRD results indicate that the two gels are amorphous.

The composite DTA–TG curves of the two gels are shown in Fig. 2. For the La–Mo gel, an exothermic peak in the DTA trace is observed at 489 K, and accordingly, a significant weight loss (ca. 50 wt%) occurs in the TG curve. For the Ce–Mo gel, an endothermic peak is observed at 383 K, an exothermic peak in the DTA trace is observed at 441 K, and accordingly, a significant weight loss (ca. 42 wt%) occurs in the TG curve. The temperature of the endothermic peak is near the boiling point of water, so it can be assigned to desorption of physically adsorbed water from the gel. In order to define the exothermic peak and weight loss information in the DTA–TG traces of the two gels, FT-IR spectroscopy was performed.

The FT-IR spectra of the two gels after heat treatment at different temperatures are exhibited in Fig. 3. In the solid

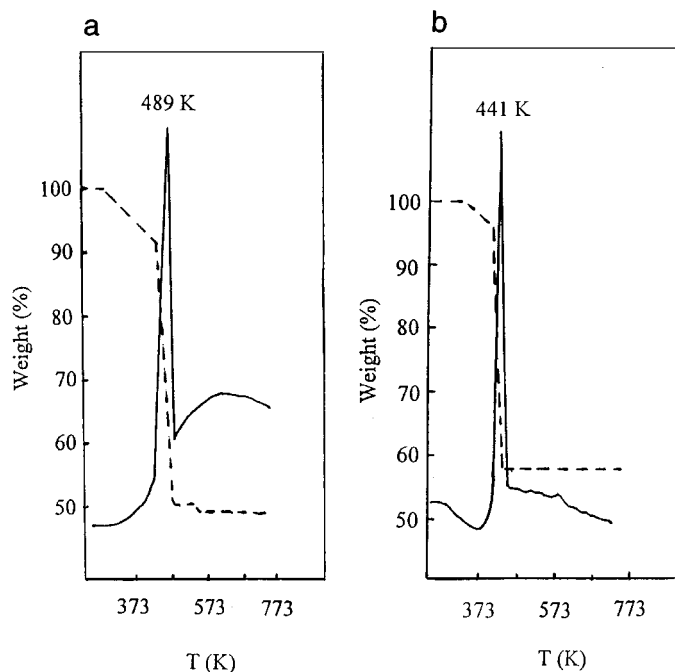


FIG. 2. DTA–TG curves of the gels: (a) La–Mo, (b) Ce–Mo.

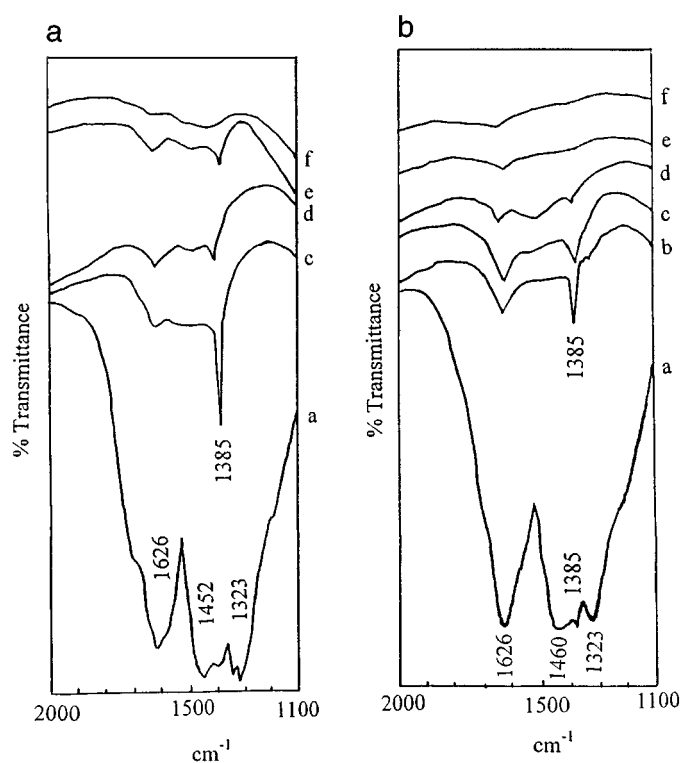
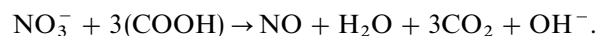


FIG. 3. FT-IR spectra of the La–Mo (A) and Ce–Mo (B) gels after heat treatment at different temperatures: (a) gel, (b) 441 K, (c) 473 K, (d) 573 K, (e) 673 K, (f) 773 K.

citrate the carboxyl groups are ionized. Compared with the principal absorption bands of the citric acid and citrate complex in the literature (27–33), the peak at 1626 cm^{-1} of the gel can be more characteristically assigned to the COO^- group vibration of citrate complex, and the peaks at 1460, 1452, and 1400 cm^{-1} can be attributed to the typical anti-symmetrical and symmetrical stretching vibrations of the carboxylate ion ($-\text{COO}^-$). The peaks at 1352 and 1323 cm^{-1} can be attributed to the C–O stretching vibrations. Finally, the peak at 1385 cm^{-1} can be assigned to the bending vibration of NO_3^- (34). These peaks suggest the existence of citrate and nitrate occluded in the gels after the gelation point.

After heat treatment at 473 K (for La–Mo) and 441 K (for Ce–Mo), the above peaks decrease significantly, indicating that the exothermic peak and weight loss information in the DTA–TG traces of the gels may be attributed to the decomposition of citrate and nitrate occluded in the gels. The exothermic reaction between free carboxyl groups and nitrates is considered to correspond to (35)



However, at 1385 cm^{-1} the peak typical of NO_3^- is decreased but still observed in Figs. 3a (trace c) and 3b

(trace b). After heat treatment at 773 K (for La–Mo) and 673 K (for Ce–Mo), the peak assigned to NO_3^- disappears, implying that the nitrate in the gels is completely decomposed.

Trifiro *et al.* (36) have reported that at ca. 850 cm^{-1} a broad absorption appears due to the piling up of Mo–O–Mo with Mo–O–Fe when Mo binds with Fe through a bridge oxygen. For the La–Mo and Ce–Mo complex oxide particles, after heat treatment, as shown in Fig. 4, the absorption peak at ca. 850 cm^{-1} is much broader than that of MoO_3 . This leads us to assume that the broad absorption peak may result from the piling up of Mo–O–Mo with Mo–O–La or Mo–O–Ce. The strong interaction between La (or Ce) atoms and Mo atoms may be the main difficulty for growth of Mo–O species in the heat treatment process. Thus ultrafine complex oxide particles can easily be formed.

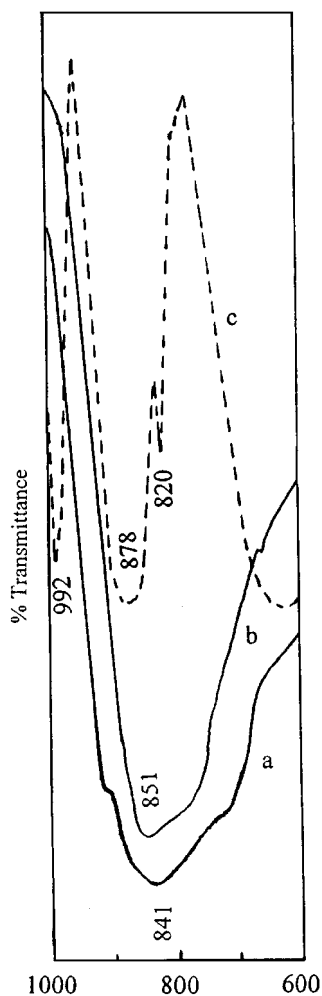


FIG. 4. FT-IR spectra of various samples: (a) Ce–Mo, (b) La–Mo, (c) MoO_3 .

The XRD patterns of the two samples after heat treatment at different temperatures are shown in Figs. 5 and 6, respectively. Only the XRD patterns of crystalline $\text{La}_2\text{Mo}_2\text{O}_9$ and $\text{Ce}_2\text{Mo}_3\text{O}_{12}$ are observed after heat treatment at 573 K (for La–Mo) and 441 K (for Ce–Mo), respectively. With an increase in the thermal treatment temperature, the peaks of the crystalline samples are gradually sharpened, indicating better crystallization of the particles and increase of the particle size.

The TEM images of La–Mo and Ce–Mo samples after calcination at 773 K (for La–Mo) or 673 K (for Ce–Mo) are exhibited in Fig. 1c and 1d. It can be observed that the morphology and structure of the gels have been changed to those of the corresponding oxides with particle size in the range of ultrafine scale ($<100\text{ nm}$). The size distribution of the particles is 40–80 nm (for La–Mo) and 20–40 nm (for Ce–Mo), respectively. The BET surface area of the two particles is $21.3\text{ m}^2/\text{g}$ (for La–Mo) and $20.3\text{ m}^2/\text{g}$ (for Ce–Mo), respectively. The BET surface area of the particles decreases with increased heat treatment temperatures (shown in Table 1). This is consistent with the above XRD results.

XRD results of La–Mo and Ce–Mo oxide prepared by the coprecipitation method show that forming crystalline $\text{La}_2\text{Mo}_2\text{O}_9$ and $\text{Ce}_2\text{Mo}_3\text{O}_{12}$ from their precipitates needs thermal treatment at 923 and 823 K, respectively. In contrast, in the sol–gel process, forming $\text{La}_2\text{Mo}_2\text{O}_9$ and $\text{Ce}_2\text{Mo}_3\text{O}_{12}$ only needs heat treatment at 573 and 441 K, respectively. The TEM images of La–Mo and Ce–Mo oxides prepared by the coprecipitation method are shown in Fig. 7. It can be seen that the size of La–Mo and Ce–Mo oxide particles prepared by coprecipitation method is rather larger than that prepared by sol–gel process. As a preparation method, coprecipitation does not favor molecular homogeneity because hydroxides of different metallic cations generally do not precipitate at the same pH (37). Thus crystalline $\text{La}_2\text{Mo}_2\text{O}_9$ and $\text{Ce}_2\text{Mo}_3\text{O}_{12}$ particles cannot easily be formed from their precipitates at low temperature. After heat treatment at high temperature, crystalline $\text{La}_2\text{Mo}_2\text{O}_9$ and $\text{Ce}_2\text{Mo}_3\text{O}_{12}$ can be formed; the particles, however, sinter and become larger, resulting in a smaller BET surface area. In contrast, in the sol–gel process, due to the molecular homogenous distribution of various components (8–16), it is possible to form crystalline $\text{La}_2\text{Mo}_2\text{O}_9$ and $\text{Ce}_2\text{Mo}_3\text{O}_{12}$ from La–Mo and Ce–Mo gels at low temperature. The particles forming at low temperature are easily of ultrafine size.

It is found that except for the heat treatment temperature, the quality of the final product prepared through the sol–gel process is also dependent on the process parameters, such as molar ratio of citric acid to metallic ions (L/M) and pH value of the starting solution (9, 10). As indicated by XRD patterns, crystalline $\text{La}_2\text{Mo}_2\text{O}_9$ can be formed at $L/M = 0.3, 1.0, \text{ and } 3.0$. The crystallization temperature is

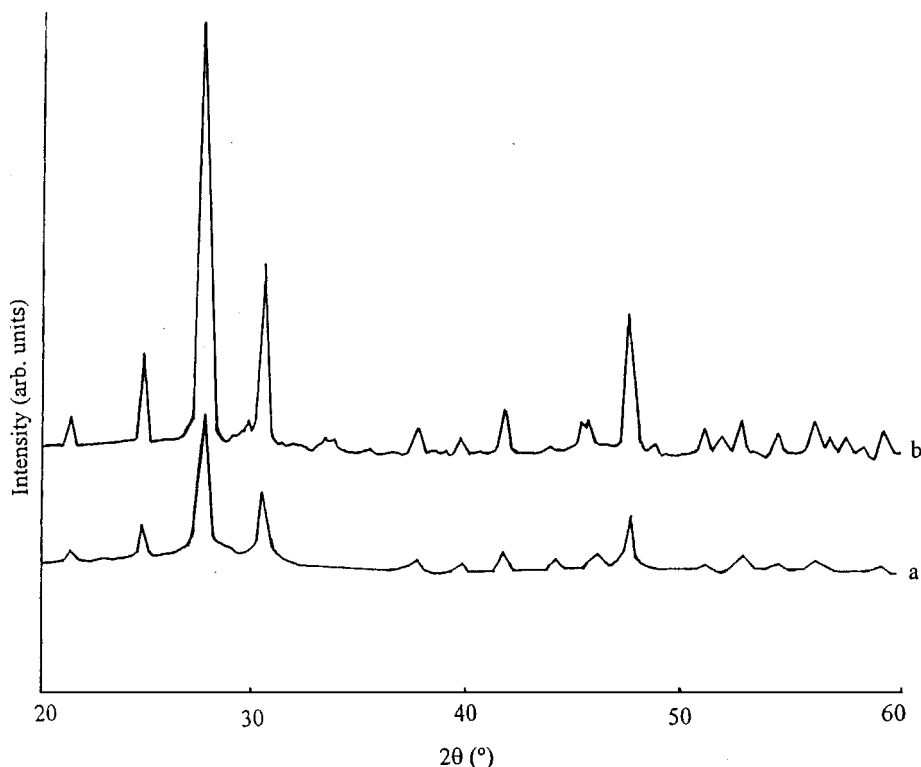


FIG. 5. XRD patterns of the La-Mo gel treated at different temperatures: (a) 573 K, (b) 873 K.

573, 773, and 873 K, respectively, for the above L/M , and the corresponding BET surface area is 21.3, 14.9, and $3.0 \text{ m}^2/\text{g}$, respectively. In contrast, it is found that only at $L/M = 0.3$ can crystalline $\text{Ce}_2\text{Mo}_3\text{O}_{12}$ be formed, and there are many peaks difficult to assign that appear in the XRD patterns at $L/M = 0.5, 1.0, \text{ and } 3.0$. The above results suggest that the molar ratio of citric acid to metallic ions (L/M) exerts a great influence on the structure and morphology of oxide particles. The excess of citric acid in gels may result in the heterogeneous distribution of metallic ions and further lead to the formation of different structure oxides or the decrease

of the BET surface area of the oxides. Similar results have also been reported in the literature (27, 32, 38). In conclusion, $L/M = 0.3$ is good for preparing ultrafine $\text{La}_2\text{Mo}_2\text{O}_9$ and $\text{Ce}_2\text{Mo}_3\text{O}_{12}$ particles.

The BET surface area of ultrafine $\text{La}_2\text{Mo}_2\text{O}_9$ and $\text{Ce}_2\text{Mo}_3\text{O}_{12}$ particles prepared at different pH values ($L/M = 0.3$) is listed in Table 2. XRD results show that the pH value of the starting solution has no effect on crystallization type. However, the BET surface area of the samples is obviously influenced by the pH value. For the preparation of the ultrafine oxide particles, the best pH is ca. 1.5 for $\text{La}_2\text{Mo}_2\text{O}_9$, and the appropriate pH is 0.5 for $\text{Ce}_2\text{Mo}_3\text{O}_{12}$.

TABLE 1
BET Surface Area of La-Mo and Ce-Mo Samples after Heat Treatment

Sample	Heat treatment temperature (K)	Surface area (m^2/g)
La-Mo	773	21.3
	823	16.7
	923	4.8
Ce-Mo	673	20.3
	773	13.2
	873	11.8

TABLE 2
Influence of pH Values on the BET Surface Area of the Samples

pH	Surface area (m^2/g)	
	La-Mo	Ce-Mo
0.5	10.9	20.3
1.5	21.3	12.7
2.5	11.8	15.0

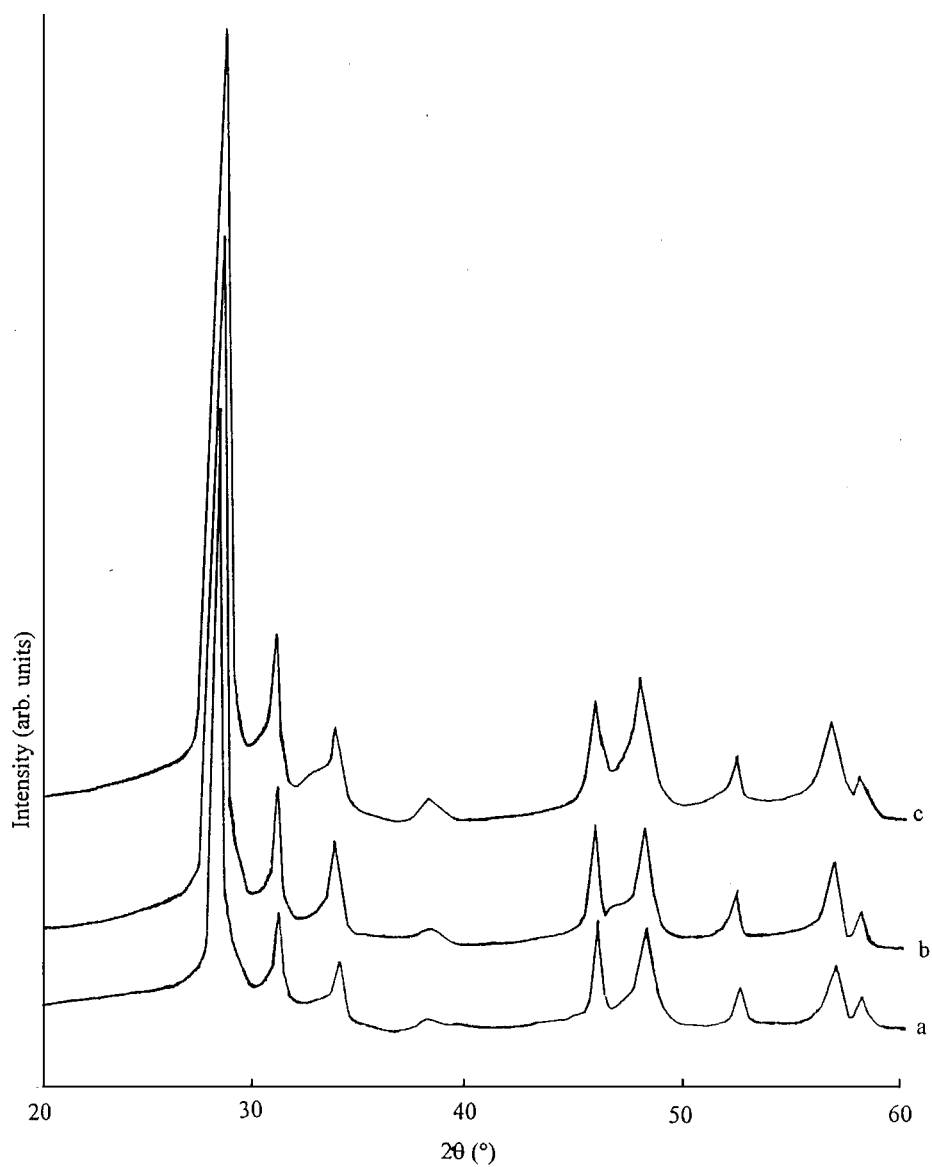


FIG. 6. XRD patterns of the Ce-Mo gel treated at different temperatures: (a) 441 K, (b) 573 K, (c) 773 K.

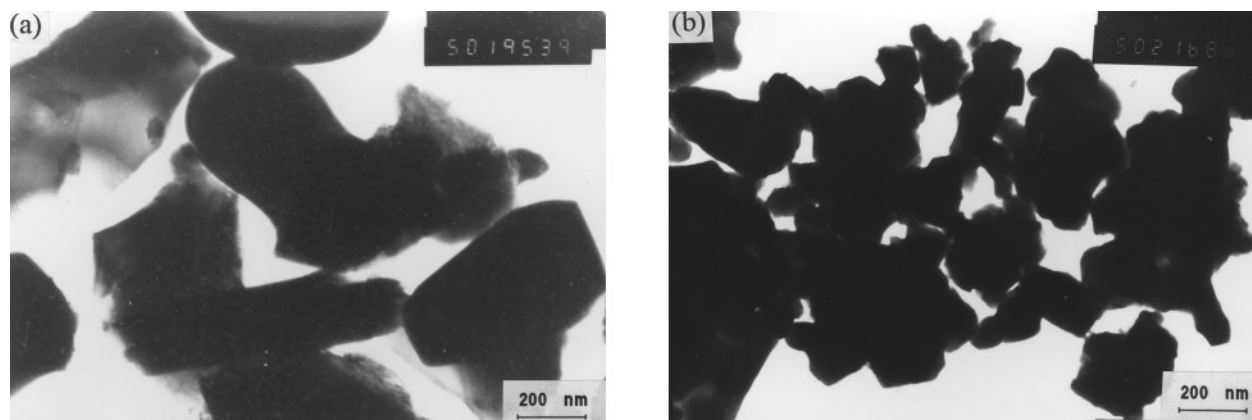


FIG. 7. TEM images of the oxides prepared by the coprecipitation method: (a) La-Mo, (b) Ce-Mo.

CONCLUSIONS

Rare earth molybdenum (La–Mo and Ce–Mo) complex oxides can be prepared under appropriate experimental conditions with the particle size in the range of ultrafine size (<100 nm) by the sol–gel method. It has been shown that La–Mo and Ce–Mo oxide particles prepared by the coprecipitation method are rather larger than those prepared by the sol–gel technique. Due to the molecular homogenous distribution of various components in the sol–gel process, crystalline $\text{La}_2\text{Mo}_2\text{O}_9$ and $\text{Ce}_2\text{Mo}_3\text{O}_{12}$ can be formed at low temperature. The particles forming at low temperature are of ultrafine size. It has been found that the gel preparation conditions such as heat treatment temperature (T), molar ratio of citric acid to metallic ions (L/M), and pH value of the starting solution exert a great influence on the morphology and structure of the oxide particles. For the preparation of ultrafine $\text{La}_2\text{Mo}_2\text{O}_9$ and $\text{Ce}_2\text{Mo}_3\text{O}_{12}$ particles, the appropriate conditions are $L/M = 0.3$; pH = 1.5 (for La–Mo), pH = 0.5 (for Ce–Mo); $T \leq 773$ K (for La–Mo), and $T \leq 673$ K (for Ce–Mo).

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