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Surface Characterization of $LaMnO_{3+\delta}$ Powder Synthesized Using Poly(Acrylic Acid)

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The La/Mn ratio, specific surface area, and catalytic activity for CO oxidation on perovskite-type $LaMnO_{3+\delta}$ synthesized by firing gels with poly(acrylic acid) (PAA) were measured to characterize the $LaMnO_{3+\delta}$ surface. $LaMnO_{3+\delta}$ synthesized by gel firing with low PAA concentration had a large specific surface area, but a Mn ion content lower than that of $LaMnO_{3+\delta}$ synthesized using acetates. Increasing the PAA concentration or the firing temperature improved the surface state of $LaMnO_{3+\delta}$. At $5 \times 10^{-2} M$ PAA, the catalytic activity was better than that of $LaMnO_{3+\delta}$ synthesized using acetates.

INTRODUCTION

The catalytic properties of perovskite-type oxides (ABO_3) have been widely reported (1–5). $LaMO_3$ (M: Cr, Mn, Fe, Co, and Ni) shows high activity for carbon monoxide (CO) oxidation. The catalytic activity for CO oxidation on $LaNiO_3$ is higher than that of NiO (6). $LaMO_3$ is generally synthesized using a standard ceramic technique. Since the mixtures of metal acetates or metal nitrates were used as starting materials and fired above 850°C, the specific surface area is less than 5 m^2/g (2, 3). To improve the catalytic activity, it is necessary to synthesize $LaMO_3$ with a large specific surface area.

Taguchi *et al.* synthesized perovskite-type $(La_{1-x}Sr_x)MnO_3$ using poly(acrylic acid) (PAA) (7). Because of the low firing temperature, the specific surface area of $(La_{1-x}Sr_x)MnO_3$ was about 17.5–23.5 m^2/g. Recently, we have noted that the crystal structure or the oxygen content of $(La_{1-x}Sr_x)MnO_3$ depends strongly on the PAA concentration. Therefore, we synthesized $LaMnO_{3+\delta}$ at low temperature using gels with various PAA concentrations and examined the crystal structure and oxygen content (8). The crystal structure of $LaMnO_{3+\delta}$ changes from hexagonal to orthorhombic with increasing PAA concentration. At $5 \times 10^{-2} M$ PAA, the crystal structure of $LaMnO_{3+\delta}$ changes from orthorhombic to hexagonal with increasing firing temperature. At $5 \times 10^{-2} M$ of PAA, the crystal structure of $LaMnO_{3+\delta}$ changes from orthorhombic to hexagonal. When $3 + \delta$ is near 3.00, $LaMnO_{3+\delta}$ is orthorhombic. But, in the range ca. $3.12 \leq 3 + \delta \leq 3.17$, $LaMnO_{3+\delta}$ is orthorhombic.

In the present study, induced coupling plasma (ICP) and X-ray photoelectron spectroscopy (XPS) measurements were performed to determine the chemical composition for $LaMnO_{3+\delta}$ synthesized by gel firing with various PAA concentrations. Then the specific surface area and catalytic activity for CO oxidation were measured. These results will provide some information toward characterizing the $LaMnO_{3+\delta}$ surface and the mechanism of CO oxidation on $LaMnO_{3+\delta}$.

EXPERIMENTAL

The preparation of $LaMnO_{3+\delta}$ using PAA has been described in detail elsewhere (8). In the present study, the PAA concentration was 3, 4, and $5 \times 10^{-2} M$. The gel was fired at 400, 700, and 900°C in air for 6 hr. For comparison, a sample was also synthesized using a standard ceramic technique. Powders of $La(CH_3COO)_3 \cdot \frac{3}{2} H_2O$ and $Mn(CH_3COO)_3 \cdot 4H_2O$ were weighed and milled for a few hours with acetone. After the mixed powder had been dried at 100°C, it was calcined in air at 400°C for several hours and then fired at 900°C in air for 6 hr.

The crystal structure of the samples was identified by X-ray powder diffraction (XRD) using monochromatic Cu$K\alpha$ radiation (RAD-1C, Rigaku, Japan). We prepared an aqueous lanthanum nitrate (67 and 135 ppm) and manganese nitrate (28 and 58 ppm) as a standard solution and

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then dissolved the samples by hydrochloric acid. First we made a calibration curve from the intensity of the standard solution using ICP (SPS-7000, Seiko, Japan) and then measured the concentration of La and Mn in the samples. XPS measurements (ESCA-750, Shimadzu, Japan) were carried out for La 3*d* and Mn 2*p* levels of the samples using Al*Kα* radiation at room temperature. The energy was calibrated using C 1*s* peak from the usual contamination. The specific surface area of the samples was determined by the BET method for nitrogen adsorption.

Catalytic activities for CO oxidation were measured at 195 to 300°C using the conventional flow system. The samples (0.1 g) were preheated at 300°C in a pure oxygen stream for 3 hr. A mixed gas of CO (1.0%), O_2 (2.0%), and He (balance) was fed into the flow reactor at a flow rate of 300 $cm^3 \cdot min^{-1}$. The products were analyzed by gas chromatography (D-2500, Hitachi, Japan) using a column (WG-100, GL Sciences, Japan) kept at 50°C during measurement.

RESULTS AND DISCUSSION

XRD patterns of the samples fired at 400, 700, and 900°C were indexed as the hexagonal perovskite-type structure, except for the sample fired with 3×10^{-2} *M* PAA at 400°C, which was an orthorhombic perovskite. The diffraction peaks of all samples sharpened with increasing PAA concentration or firing temperature. The sample synthesized using acetates also had the hexagonal perovskite-type structure. Therefore, the oxygen content of most $LaMnO_{3+\delta}$ synthesized was $3.12 \leq 3+\delta \leq 3.17$.

The La/Mn ratios from the concentration of La and Mn in all samples, as measured by ICP, were about 1.03 and independent of the PAA concentration or the firing temperature. These values show that the La/Mn ratio of the bulk $LaMnO_{3+\delta}$ is near stoichiometric. No difference was found between the La/Mn ratios of the bulk $LaMnO_{3+\delta}$ synthesized using PAA and those synthesized using acetates. XPS measurements were used to determine the surface composition of the sample (3). Figure 1 shows the XPS spectra of the La $3d_{5/2}$ and Mn $2p_{3/2}$ levels. A satellite peak was observed ~4 eV forward the high binding energy side of the La $3d_{5/2}$ peak. This satellite is interpreted as the excitation of an electron from the anion valence band into the lanthanum *f* band (9, 10). We calculated the La and Mn contents of the $LaMnO_{3+\delta}$ surface from the intensities of the La $3d_{5/2}$ and Mn $2p_{3/2}$ peaks of XPS using the equation

$$C = \frac{X_A/q_A}{\Sigma X_j/q_j},$$

where *C* is the molar fraction content of element *A* in the sample, X_A the intensity (or area) of the peak for *A*, and q_A the sensitive factor for *A* (11, 12). According to Seah's report of measurement X_{Cu} for Cu $2p_{3/2}$ of CuO, he included the intensity of the satellite peak in X_{Cu} (11). Therefore, we did not resolve the main La $3d_{5/2}$ and the satellite peak. Figure 2 shows the relation between the La/Mn ratios of the $LaMnO_{3+\delta}$ surface and the PAA concentration. The La/Mn ratio of the $LaMnO_{3+\delta}$ surface synthesized using acetates is ca. 1.45. As for $LaMnO_{3+\delta}$ synthesized with 4×10^{-2} and 5×10^{-2} *M* PAA, the La/Mn ratio of the $LaMnO_{3+\delta}$ surface is independent of the PAA concentration and the firing temperature.

Figure 3 shows the relation between the specific surface area of $LaMnO_{3+\delta}$ and the PAA concentration. The specific surface area of $LaMnO_{3+\delta}$ synthesized using acetates is shown at 0 *M*. $LaMnO_{3+\delta}$ synthesized with 3×10^{-2} *M* PAA at 400°C exhibited a specific surface area of ca.

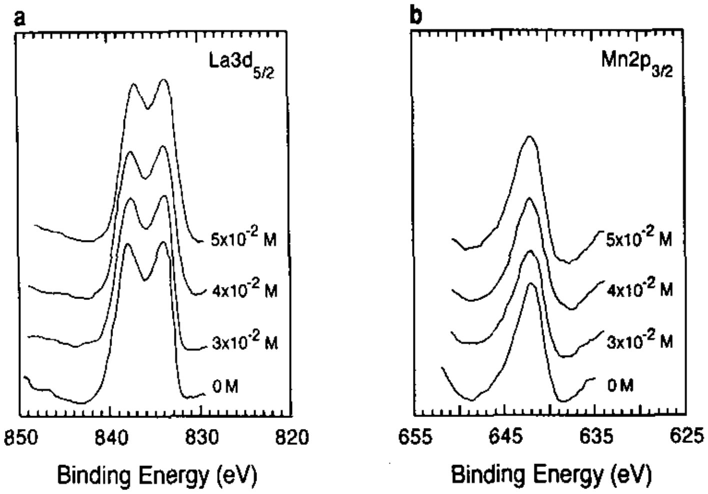

FIG. 1. XPS spectra of the La 3*d* and Mn 2*p* levels of $LaMnO_{3+\delta}$. $LaMnO_{3+\delta}$ was synthesized by firing the gels at 900°C for 6 hr. The PAA concentration of the gels was 0, 3, 4, and 5×10^{-2} *M*.

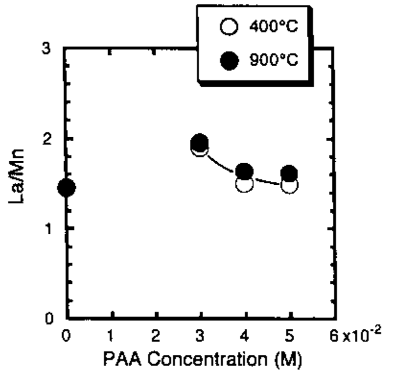

FIG. 2. The PAA concentration of the gels vs the La/Mn ratio of the $LaMnO_{3+\delta}$ surface. The La/Mn ratio was calculated from the intensities of La $3d_{5/2}$ and Mn $2p_{3/2}$ peaks of XPS. $LaMnO_{3+\delta}$ was synthesized by firing the gels at 400 and 900°C for 6 hr.

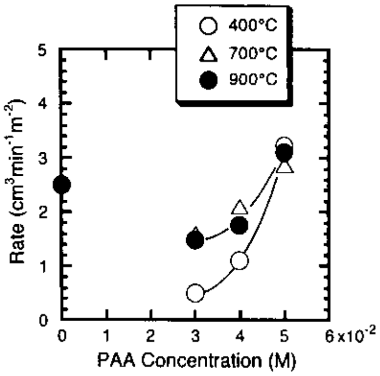

FIG. 4. The PAA concentration of the gels vs the catalytic activity of $LaMnO_{3+\delta}$. The rate of reaction was calculated from the conversion at 270°C. $LaMnO_{3+\delta}$ was synthesized by firing the gels at 400, 700, and 900°C for 6 hr.

19 m^2/g. The specific surface area decreased to ca. 2 m^2/g with increasing firing temperature or PAA concentration. The specific surface area of $LaMnO_{3+\delta}$ synthesized with 5×10^{-2} *M* PAA was independent of the firing temperature and less than the surface area of $LaMnO_{3+\delta}$ synthesized using acetates.

The conversion from CO to CO_2 was measured for various $LaMnO_{3+\delta}$ samples. The conversion per gram was less than 10% below 200°C and increased abruptly above 240°C. We calculated the rate of reaction (R) at a given temperature using the equation (13).

$$R = \frac{F \times C \times Cv}{m \times S},$$

where F is the gas flow per minute, C the initial concentration of CO, Cv the conversion per gram from CO to CO_2, m is the mass of the sample, and S the specific surface area of the sample. Figure 4 shows the rate of reaction measured at 270°C. The rate of reaction for $LaMnO_{3+\delta}$ synthesized using acetates is ca. 2.5 cm^3 · min^{-1} · m^{-2}. The rate of reaction increases with increasing PAA concentration. No significant difference was found in the rate of reaction for $LaMnO_{3+\delta}$ synthesized at 700 and 900°C. On the other hand, the rate of reaction for $LaMnO_{3+\delta}$ synthesized at 400°C was small in the low PAA concentration. At 5×10^{-2} *M* PAA, the reaction rate was independent of the firing temperature and slightly higher than that for $LaMnO_{3+\delta}$ synthesized using acetates.

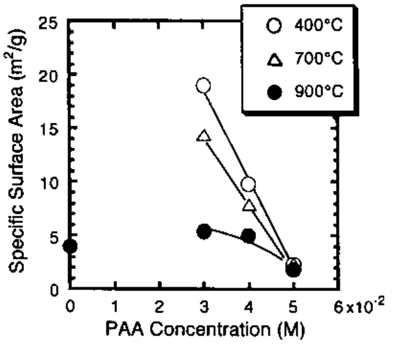

FIG. 3. The PAA concentration of the gels vs the specific surface area of $LaMnO_{3+\delta}$. $LaMnO_{3+\delta}$ was synthesized by firing the gels at 400, 700, and 900°C for 6 hr.

Voorhoeve *et al.* reported the catalytic activity for CO oxidation on perovskite-type oxides (14). CO oxidation occurs at the metal ions of the surface. Their report indicates that both the Mn ion content and the surface crystallinity play an important role in the catalytic activity. For $LaMnO_{3+\delta}$ synthesized with 3×10^{-2} *M* PAA, although the specific surface area is large, the Mn ion content at the surface is less than the La ion content as seen in Fig. 2. Therefore, the catalytic activity of $LaMnO_{3+\delta}$ is less than that of $LaMnO_{3+\delta}$ synthesized using acetates. The increased catalytic activity with firing temperature is caused by the surface crystallinity. With increasing PAA concentration of the gels, although the specific surface area of $LaMnO_{3+\delta}$ decreases, both the surface Mn ion content and the surface crystallinity increased. Therefore, the catalytic activity increases with PAA concentration as seen in Fig. 4.

From the results of XRD, the La/Mn ratio, the specific surface area, and catalytic oxidation of CO for $LaMnO_{3+\delta}$, we propose the model shown in Fig. 5 for the synthesis of $LaMnO_{3+\delta}$ using PAA. PAA is important to synthesize $LaMnO_{3+\delta}$, both to make the gel from the solution and to provide the heat of combustion for the synthesis. According to this model, the gel is heated at a rate of 10°C/min and the temperature of the sample increases rapidly near 200°C as PAA burns (7). The $LaMnO_{3+\delta}$ nucleates when the PAA burns. Because of the rapid combustion of PAA, the partial pressure of oxygen near $LaMnO_{3+\delta}$ nuclei is low, and the crystal structure of $LaMnO_{3+\delta}$ be-

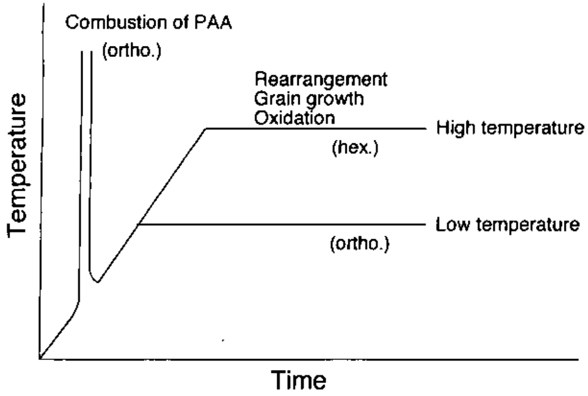

FIG. 5. The model for the synthesis of $LaMnO_{3+\delta}$ using PAA.

comes orthorhombic (8). The rapid changes in temperature cause many cracks in $LaMnO_{3+\delta}$, resulting in a large specific surface area. With increasing PAA concentration, the heat of combustion increases and the $LaMnO_{3+\delta}$ particles sinter one another. Therefore, $LaMnO_{3+\delta}$ was annealed at 400, 700, or 900°C for 6 hr. When the firing temperature is low, rearrangement of $LaMnO_{3+\delta}$, particle grain growth, or oxidation of $LaMnO_{3+\delta}$ is difficult to achieve. Consequently, the crystal structure of $LaMnO_{3+\delta}$ remains orthorhombic. On the other hand, at high firing temperature, rearrangement, grain growth, or oxidation of $LaMnO_{3+\delta}$ occurs more quickly, so that the specific surface area of $LaMnO_{3+\delta}$ decreases and the crystal structure of $LaMnO_{3+\delta}$ changes from orthorhombic to hexagonal.

CONCLUSION

A study of the La/Mn ratio, specific surface area, and catalytic activity for CO oxidation on $LaMnO_{3+\delta}$ provides the following conclusions. Although $LaMnO_{3+\delta}$ synthesized by gel firing with low PAA concentration has a large specific surface area, both the Mn ion content of the surface and catalytic activity are less than those of $LaMnO_{3+\delta}$ synthesized with acetates. With increasing PAA concentration or firing temperature, however, the surface state of $LaMnO_{3+\delta}$ improved. At $5 \times 10^{-2} M$ PAA, the catalytic activity is better than that of $LaMnO_{3+\delta}$ synthesized using acetates. To obtain good catalytic activity for $LaMnO_{3+\delta}$, it is necessary to synthesize $LaMnO_{3+\delta}$ with a large specific surface area, a rich Mn ion content, and good surface crystallinity.

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