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BRIEF COMMUNICATION

Synthesis of $LaMnO_{3+\delta}$ by Firing Gels with Poly(Acrylic Acid) in a Pure Argon Stream

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Perovskite-type $LaMnO_{3+\delta}$ was synthesized by firing the gels with 0.007–0.033 *M* of poly(acrylic acid) (PAA) in a pure argon stream. The oxygen content, crystallite size (D_{024}), specific surface area, and catalytic activity for CO oxidation on $LaMnO_{3+\delta}$ were measured to characterize the $LaMnO_{3+\delta}$ surface. In spite of a small specific surface area, the catalytic activity for CO oxidation on $LaMnO_{3+\delta}$ fired in the pure argon stream is twice that on $LaMnO_{3+\delta}$ fired in air. These results indicate that firing the gels in the pure argon stream improved the crystallinity (regularity of the ions) of the $LaMnO_{3+\delta}$ surface.

INTRODUCTION

Perovskite-type $LaMnO_{3+\delta}$ is available to be used as a catalyst that oxidizes hydrocarbons or carbon monoxide (CO) oxidation (1–3). $LaMnO_{3+\delta}$ is generally synthesized at high temperature using a standard ceramic technique. Therefore, the specific surface area of $LaMnO_{3+\delta}$ is less than 5 m^2/g (2–3). By using poly(acrylic acid) (PAA), Taguchi *et al.* synthesized $LaMnO_{3+\delta}$ with a large specific surface area and defined the conditions to synthesize $LaMnO_{3+\delta}$ in air (4). They measured the La/Mn ratio, specific surface area, and catalytic activity for CO oxidation on $LaMnO_{3+\delta}$ in order to characterize the $LaMnO_{3+\delta}$ surface (5).

PAA is an important chemical to make a gel from the solution, and to provide the heat of combustion for the synthesis of $LaMnO_{3+\delta}$. From the results of differential thermal analysis (DTA) of the gel, the gel gave the exthothermic peaks in the temperature range from 160 to 300°C, and these peaks correspond to the combustion of PAA (6). Because of the rapid combustion of PAA, the crystal structure of $LaMnO_{3+\delta}$ becomes orthorhombic. The rapid changes in temperature cause many cracks in $LaMnO_{3+\delta}$, resulting in a large specific surface area. Recently, we measured both the catalytic activity for CO oxidation and the amount of adsorbed oxygen on $(La_{1-x}Sr_x)MnO_3$ synthesized using PAA and the solid-state reaction (7). Then, it is apparent that the surface of the samples firing the gels using PAA has an insufficient crystallization and is lacking in adsorption sites in comparison with the samples synthesized using the solid-state reaction.

In order to improve the $LaMnO_{3+\delta}$ surface, it is necessary to control the combustion of PAA. In the present study, we tried to synthesize $LaMnO_{3+\delta}$ by firing the gels in a pure argon stream. Thereafter, the crystal structure, oxygen content, crystallite size, specific surface area, and catalytic CO oxidation on $LaMnO_{3+\delta}$ were measured. These results will provide some information about the stability of $LaMnO_{3+\delta}$ synthesized in the pure argon stream and the crystallinity (regularity of the ions) on the $LaMnO_{3+\delta}$ surface.

EXPERIMENTAL

The preparation of the gels using PAA has been described in detail elsewhere (4). Average molecular weight of PAA was 2000. In the present study, the PAA concentration was from 0.007 to 0.033 *M*. The gels were fired at 400–900°C in the pure argon stream for 6 h. The heating rate was 1°C/min up to 300°C, and then 10°/min.

The crystal phases of the samples were identified by X-ray powder diffraction (XRD) using monochromatic Cu*K*α radiation. The oxygen content in each sample was determined by an oxygen-reduction (redox) method (8). The crystallite size (D_{024}) of the samples was calculated from the half-width of a diffraction peak (024) using Scherrer's equation (9). The specific surface area of the samples was determined by the BET method for nitrogen adsorption. The catalytic activities for CO oxidation were measured at 195 to 300°C using a conventional flow system. The samples (0.1 g) were preheated at 300°C in a pure oxygen

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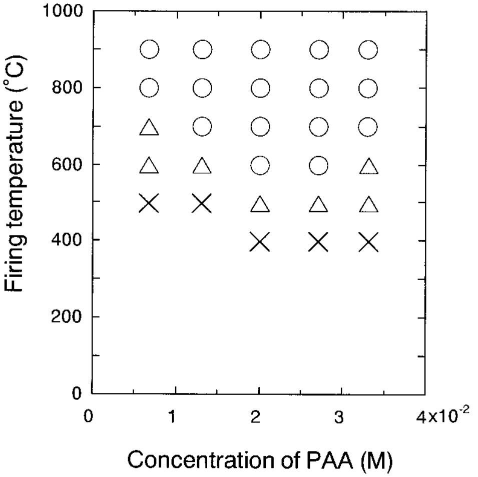

FIG. 1. The relationship between the crystal structure of the samples and the synthesis condition (PAA concentration and firing temperature). The samples were synthesized by firing the gels for 6 h in a pure argon stream. (○; hexagonal $LaMnO_{3+\delta}$; △, a mixture of hexagonal $LaMnO_{3+\delta}$ and La_2O_3; ×, amorphous).

stream for 3 h. A mixed gas of CO (1.0%), O_2 (2.0%), and He (balance) was fed in a flow reactor at a flow rate of 150 $cm^3 \cdot min^{-1}$. The products were analyzed by gas chromatography using a column (Molecular Sieve 5A) kept at 50°C during the measurements.

RESULTS AND DISCUSSION

Figure 1 shows the relationship between the crystal structure of the samples and the synthesis conditions (PAA concentration and firing temperature) in the pure argon stream. From the XRD patterns, it is obvious that the sample fired at low temperature is amorphous or is a mixture of hexagonal $LaMnO_{3+\delta}$ and La_2O_3. In the concentration range from 0.007 to 0.033 *M* of PAA, the sample fired at high temperature is indexed as a hexagonal perovskite-type structure. The region for the formation of $LaMnO_{3+\delta}$ in the pure argon stream is wide in comparison with the region for the formation of $LaMnO_{3+\delta}$ in air (4).

Table 1 shows the oxygen content ($3 + \delta$) of $LaMnO_{3+\delta}$ fired in the pure argon stream. From the results of Fig. 1, it is obvious that firing temperature in the pure argon stream is higher than the firing temperature in air. When the gels are fired in air, the oxygen content of $LaMnO_{3+\delta}$ increases with increasing firing temperature (4). However, the oxygen content of $LaMnO_{3+\delta}$ fired in the pure argon stream is ca. 3.18–3.21 and is independent of the synthesis condition. Table 1 also shows the crystallite size (D_{024}) and the specific surface area (*S*) of $LaMnO_{3+\delta}$ for gels fired in the pure argon stream. D_{024} increases with increasing PAA concentration and firing temperature. Although we can not understand the reason why the specific surface area of $LaMnO_{3+\delta}$ for the gel fired with 0.020 *M* of PAA at 700°C is very low, other values of the specific surface area decrease with increasing the PAA concentration and firing temperature. The variation in D_{024} and the specific surface area suggests the incrrease in the particle size of $LaMnO_{3+\delta}$.

TABLE 1
Oxygen Content ($3 + \delta$), Crystallite Size (D_{024}), Specific Surface Area (*S*), and Rate of Reaction (*R*) of $LaMnO_{3\pm\delta}$ for the Oxidation of CO at 270°C

Firing condition						
PAA Concentration (%)	Temp. (°C)	Atmosphere	$3 + \delta$	D_{024} (nm)	*S* (m^2/g)	*R* ($cm^3 \cdot min^{-1} \cdot m^{-2}$)
0.007	700	Ar	3.20	18.8	21.1	0.54
0.020	700	Ar	3.21	25.5	11.4	0.44
0.033	700	Ar	3.18	25.5	16.7	0.43
0.007	900	Ar	3.20	25.5	9.2	0.22
0.020	900	Ar	3.18	33.3	4.8	0.48
0.020	700	Air	3.18	18.0	23.5	0.21
0.020	900	Air	3.18	31.5	5.4	0.22

In order to investigate the stability of $LaMnO_{3+\delta}$, $LaMnO_{3+\delta}$ was fired at 700°C for 6–36 h in the pure argon stream. Figure 2 shows the XRD patterns of $LaMnO_{3+\delta}$ for the gel fired with 0.020 *M* at 700°C for 6, 12, 24, and 36 h. The XRD patterns of $LaMnO_{3+\delta}$ fired for 12, 24, and 36 h were indexed as the hexagonal perovskite-type structure (10). The diffraction peaks (300), (214), (220), and (208) were observed in hexagonal $LaMnO_{3+\delta}$ fired for 6 h. With increased firing time, the intensity of the peak (018) decreased the peaks (400) and (224) became one broad peak. The slight decrease in 2θ of each peak indicates

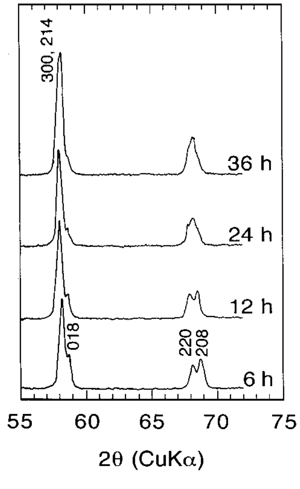

FIG. 2. XRD patterns of a $LaMnO_{3+\delta}$-fired gel with 0.020 *M* at 700°C for 6, 12, 24, and 36 h in a pure argon stream.

the increase in the cell constant with increasing firing time. From these results, it is obvious that hexagonal $LaMnO_{3+\delta}$ fired at 700°C for 6–36 h in the pure argon stream is stable.

The conversion from CO to CO_2 was measured for $LaMnO_{3+\delta}$ fired in the pure argon stream. The rate of reaction (R) at a given temperature is calculated using the following equation:

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

where F is the gas flow per minute, C the initial concentration of CO, C_V the conversion per gram from CO to CO_2, m is the mass of the sample, and S is the specific surface area of the sample (11). The rate of reaction at 270°C is shown in Table 1. Except the rate of reaction for $LaMnO_{3+\delta}$ for the gel fired with 0.007 M of PAA at 900°C, the rate of reaction is ca. 0.43–0.54 $cm^3 \cdot min^{-1} \cdot m^{-2}$. The oxygen content, the crystallite size (D_{024}), the specific surface area, the rate of reaction of $LaMnO_{3+\delta}$ for the gels fired in air are also shown in Table 1. The variation in D_{024} and the specific surface area suggests that the particle size of $LaMnO_{3+\delta}$ increases with change in the atmosphere. The rate of reaction for $LaMnO_{3+\delta}$ fired in air is ca. 0.21–0.22 $cm^3 \cdot min^{-1} \cdot m^{-2}$, and this value is half of the rate of reaction for $LaMnO_{3+\delta}$ fired in the pure argon stream (12).

The oxidation of CO occurs at the metal ions of the surface, and the catalytic activity is strongly influenced by both the metal ion content and the crystallinity of the surface (13). There are two kinds of oxygen at the surface; one is lattice-oxygen and the other is oxygen adsorbed on the metal ions. CO_2 is produced by the reaction of CO with oxygen adsorbed on the metal ions of the outermost surfce. After the desorption of CO_2 from the surface, oxygen is again adsorbed on the metal ions. When the gels were fired in air, the abrupt combustion of PAA made a large number of cracks in $LaMnO_{3+\delta}$. The low rate of reaction is due to the lack of the crystallinity or the adsorption sites. When the gels were fired in the pure argon stream, it is considered that the combustion of PAA was mild and oxygen was supplied from PAA. The nucleation of $LaMnO_{3+\delta}$ occurred slowly and the crystallinity of the $LaMnO_{3+\delta}$ surface was improved by firing the gels in the pure argon stream. Therefore, the atmosphere plays an important role in the control of the surface structure of $LaMnO_{3+\delta}$.

CONCLUSION

Perovskite-type $LaMnO_{3+\delta}$ was synthesized by firing the gels with 0.007–0.033 M of PAA in the pure argon stream. The variation in the crystallite size (D_{024}) and the specific surface area suggests that the particle size of $LaMnO_{3+\delta}$ fired in the pure argon stream is larger than that of $LaMnO_{3+\delta}$ fired in air. However, the rate of reaction for CO oxidation on $LaMnO_{3+\delta}$ fired in the pure argon stream is twice that on $LaMnO_{3+\delta}$ fired in air. These results indicate that the crystallinity of the $LaMnO_{3+\delta}$ surface is easily improved by changing the firing condition.

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