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Hydroxy Acid-Aided Synthesis of Perovskite-Type Oxides of Cobalt and Manganese

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The hydroxy acid-aided process using citric or malic acid produced a perovskite phase at relatively low calcination temperatures. The adjustment of the starting solution to an appropriate pH value in the malic acid-aided process resulted in reducing the temperature for the formation of single-phase perovskite-type oxides and in producing large surface-area oxides.

Perovskite-type oxides of cobalt and manganese have been known to be highly active catalysts for the gas phase reaction involved in the exhaust treatment (complete oxidation of CO and light hydrocarbons, NO_x removal) as well as for the electrochemical reduction of oxygen. Since in such catalytic applications perovskite-type oxides are mostly used in a pulverized form, the production of oxides with large surface areas (or in a fine particle form) is of essential importance. One method to produce large surface-area oxides is the amorphous organic precursor process developed by Marcilly et al.,[1] which is characterized by the use of complexing polyfunctional hydroxy acids, especially citric acid. In this process which is referred to as the hydroxy acid-aided process here, the formation of an amorphous precursor, in which a homogeneous mixing of the metal components is attained, makes easier the formation of perovskite-type oxides at lower temperatures. It was reported that the citric acid-aided process produced perovskite-type oxides with large specific surface areas[2] or with high homogeneity and purity[3] and that the large surface-area perovskite-type oxides prepared by this method showed excellent catalytic activity for combustion reaction[4] and electrochemical reduction of oxygen.[5] This letter reports the effects of hydroxy acids and the pH of the starting solution in the hydroxy acid-aided synthesis of $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.8}Sr_{0.2}MnO_3$.

$La(NO_3)_3 \cdot 6H_2O$ (42.0 mmol), $Sr(NO_3)_2$ (10.5 mmol), and $M(NO_3)_2 \cdot 6H_2O$ (M=Co and Mn, 52.5 mmol) were dissolved in water (1.5 dm^3), to which one of the following acids was added: citric, malic, lactic, succinic and tartaric acids. In all cases, a molar ratio of an acid to total metal ions was set at 3/n, where n is the number of -COOH groups in one acid molecule. The mixed aqueous solution of an acid and metal nitrates was adjusted to various pH values by the addition of aqueous ammonia (28%) with vigorous stirring. The starting solution was evaporated to dryness, followed by calcination in air at various temperatures. The calcination products were characterized by powder X-ray diffraction (XRD) analysis using Cu Kα radiation. The specific surface area was measured by N_2 adsorption (BET method). Perovskite-type oxides were also synthesized by evaporating an aqueous solution of metal nitrates or acetates followed by calcination (nitrate or acetate process). If necessary, the preparation processes were abbreviated to "**cit**" (citric acid-aided), "**mal**" (malic acid-aided), "**nit**" (nitrate), and "**ace**" (acetate).

When precursors of perovskite-type oxides were calcined at 850 °C, the single-phase perovskite-type oxides were obtained irrespective of preparation methods. At lower calcination temperatures, however, the formation of a perovskite phase was strongly dependent on preparation methods as shown in Fig. 1 for $La_{0.8}Sr_{0.2}CoO_3$. After calcination at 550 °C for 5 h, the formation of a perovskite phase, the strongest diffraction peak of which is at ca. 33°, was scarcely observed in nitrate and acetate processes. It is seen that the perovskite formation by the hydroxy acid-aided processes fairly depends on utilized acids and that citric acid- and malic acid-aided processes give a well-crystallized perovskite phase with a minor impurity compound of $SrCO_3$. When citric acid- and malic acid-aided processes were started from a mixed aqueous solution of metal acetates or chlorides, the perovskite formation was not observed even after calcination at 850 °C for 5 h. It follows that the production of the perovskite phase at lower calcination temperatures is realized successfully when using metal nitrates as metal sources and citric and malic acids as complexing acids. In accordance with a previous report on the citric acid-aided synthesis of perovskite-type oxides,[2] calcination at 850 °C was required to obtain a single-phase $La_{0.8}Sr_{0.2}CoO_3$ free from $SrCO_3$ impurity even when citric acid- and malic acid-aided processes were applied, whereas well-crystallized $La_{0.8}Sr_{0.2}MnO_3$ was obtained above 550 °C (cit) and 600 °C (mal).

Specific surface areas of single-phase $La_{0.8}Sr_{0.2}CoO_3$ prepared at 850 °C were almost equal irrespective of preparation methods; 4.4 (**cit**), 4.6 (**mal**), 3.5 (**nit**), and 4.1 (**ace**) $m^2 \cdot g^{-1}$ after calcination at 850 °C for 10 h. Figure 2 shows the dependence of specific surface areas of $La_{0.8}Sr_{0.2}MnO_3$ on calcination temperature. In citric acid- and malic acid-aided processes, specific surface areas of single-phase oxides decreased monotonically with increasing calcination temperature. This clearly shows that in the hydroxy acid-aided processes the lowering of calcina-

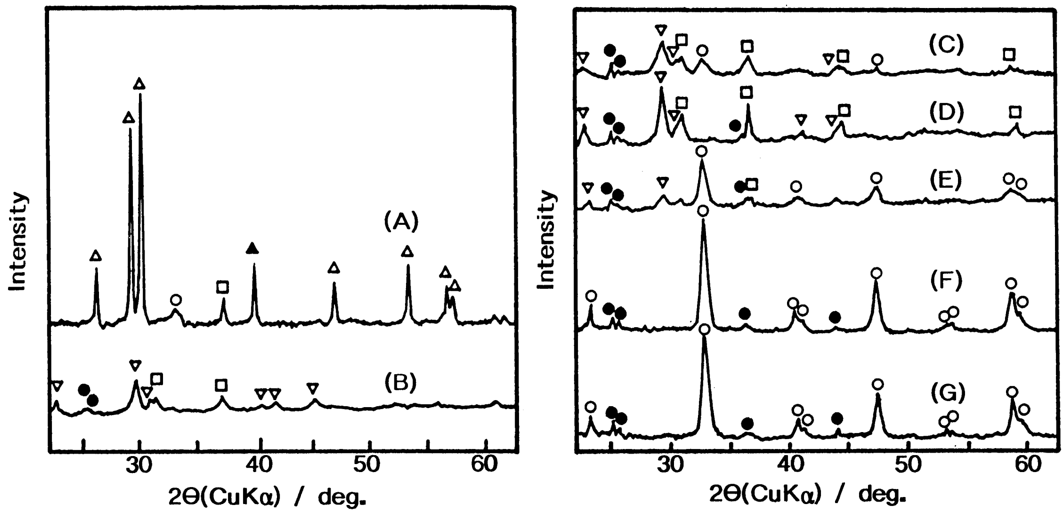

Fig. 1. XRD patterns of calcination products of precursors for $La_{0.8}Sr_{0.2}CoO_3$ at 550 °C for 5 h. Nitrate process (**A**), Acetate process (**B**), Hydroxy acid-aided process using lactic (**C**), tartaric (**D**), succinic (**E**), citric (**F**) or malic (**G**) acid. ▲ : $La(OH)_3$, △ : La_2O_3, ▽: $La_2O_2CO_3$, ● : $SrCO_3$, □ : Co_3O_4, ○ : perovskite-type oxide

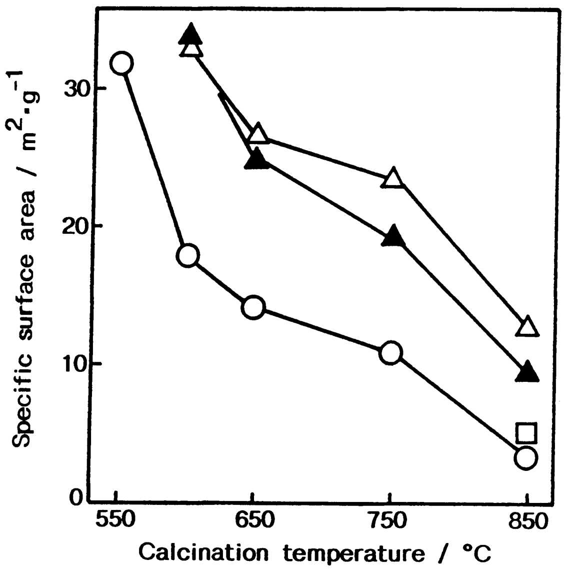

Fig. 2. Calcination temperature dependence of specific surface areas of $La_{0.8}Sr_{0.2}MnO_3$ prepared by nitrate (□), citric acid-aided (○) and malic acid-aided (△,▲) processes. Calcination period: 5 h (□,○,△), 10 h (▲)

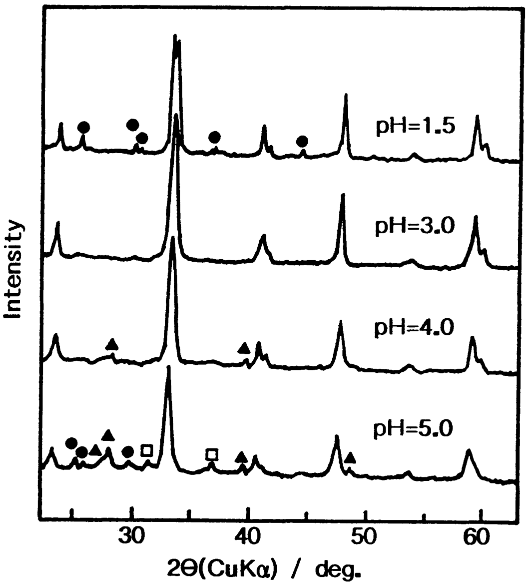

Fig. 3. Effect of the pH of the starting solution in the malic acid-aided synthesis of $La_{0.8}Sr_{0.2}CoO_3$ at 650 °C. Calcination period: 5h
▲: $La(OH)_3$, ●: $SrCO_3$, □: Co_3O_4

tion temperature for the formation of the single-phase perovskite-type oxides results in the production of larger surface-area oxides.[2,4] It should be noted that the malic acid-aided process gives larger surface-area $La_{0.8}Sr_{0.2}MnO_3$ than the citric acid-aided process at any calcination temperature. These results imply that which complexing hydroxy acid is utilized is the important factor for producing large surface-area oxides as well as for lowering temperature for the perovskite formation as shown in Fig. 1.

In the malic acid-aided process, the adjustment of the pH of the starting solution was found to be effective in producing single-phase perovskite-type oxides having large surface area (Fig. 3 and Table 1). Figure 3 shows how the adjustment of the pH of the starting solution is effective in producing single-phase $La_{0.8}Sr_{0.2}CoO_3$ after calcination at 650 °C. At pH=1.5 (pH-unadjusted), the product was a mixture of a perovskite-type oxide and $SrCO_3$ as described above. At pH=3.0 a single-phase perovskite-type oxide free from impurity compounds was obtained; the same was true at pH=2.5 and 3.5. At pH=4.0 and 5.0, precipitation took place by the addition of aqueous ammonia, and in such unfavorable cases a single-phase perovskite-type oxide was not obtained even after calcination at 850 °C for 5 h. As shown in Table 1, a single-phase $La_{0.8}Sr_{0.2}CoO_3$ prepared from the starting solutions of pH=2.5, 3.0, and 3.5 had large surface areas at each calcination temperature. In the case of $La_{0.8}Sr_{0.2}MnO_3$, when the pH of the starting solution was adjusted to 3.0 and 4.0, a well-crystallized perovskite-type oxide of a single phase was obtained at 550 °C which is 100 °C lower than at pH=1.5 (pH-unadjusted). Specific surface areas of $La_{0.8}Sr_{0.2}MnO_3$ changed in a complicated manner with changing the pH of the solution; with increasing the pH, specific surface areas first decreased at pH=3.0 and then increased to be maximum at pH= 4.0. It is noteworthy that the pH

Table 1. Specific surface areas of single-phase $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.8}Sr_{0.2}MnO_3$ prepared by the malic acid-aided process at various pH of starting solutions

Perovskite-type oxide	pH	Specific surface area a)/$m^2 \cdot g^{-1}$			
		550 b)	650 b)	750 b)	850 b)
$La_{0.8}Sr_{0.2}CoO_3$	1.5 c)	----	----	----	4.3
	2.0	----	----	8.1	5.4
	2.5	----	15.1	13.8	9.4
	3.0	19.9	17.0	16.6	10.2
	3.5	19.7	18.4	16.1	9.9
	4.0 d)	----	----	----	----
	5.0 d)	----	----	----	----
$La_{0.8}Sr_{0.2}MnO_3$	1.8 c)	----	26.6	23.4	12.8
	3.0	32.4	21.0	13.5	10.0
	4.0	36.8	31.6	27.5	16.2
	5.0 d)	----	----	----	----

a) ----: Calcination product was not a single-phase perovskite-type oxide. b) Calcination temperature (°C). Calcination period: 5 h. c) pH-unadjusted. d) Precipitation was observed.

region producing large surface-area oxides, pH=2.5-3.5 for $La_{0.8}Sr_{0.2}CoO_3$ and pH=4.0 for $La_{0.8}Sr_{0.2}MnO_3$, is coincident with that producing single-phase oxides at lower temperatures.

In the citric acid-aided process, on the other hand, the addition of aqueous ammonia to the mixed aqueous solution of citric acid and metal nitrates (pH=1.7 for $La_{0.8}Sr_{0.2}MO_3$ (M=Co and Mn)) brought about the precipitation even at pH=2.0, and the formation of perovskite-type oxides at lower calcination temperatures was not realized. Thus it is concluded that the malic acid-aided process combined with the pH adjustment of the starting solution is promising to produce large surface-area perovskite-type oxides of a single phase. In the hydroxy acid-aided processes, the formation of a homogeneous precursor is essential and if a metal component is separated from the precursor, it is detected as an impurity compound in the resulting oxide.[4] The effects of the utilized acid, metal components and the pH of the starting solution in the hydroxy acid-aided synthesis of perovskite-type oxides seem to originate from changing the precursor state of the corresponding metal complexes in the solution. It is likely that the pH of the solution controls not only the dissociation of carboxylic acid groups but also the formation of metal-acid complexes. Although the pH of the solution changes during the evaporation process, the formation of a homogeneous precursor in the starting solution of an appropriate pH value may be responsible for lowering the temperature for the formation of single-phase perovskite-type oxides as well as for producing large surface-area oxides.

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