Synthesis of Manganite Perovskites by Reverse Homogeneous Precipitation Method in the Presence of Alkylammonium Cations

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A single-phase $LaMnO_{3+\delta}$ perovskite with high surface area could be synthesized after air-calcining the hydroxide precursor at 650 °C and above. The precursor was easily obtained by dropping a mixed aqueous solution of La and Mn nitrates into highly basic aq NH_3 with and without the presence of $N(CH_3)_4Br$. The addition of $N(CH_3)_4Br$ was effective in increasing the specific surface area of the products as well as in stabilizing the colloidal solution of the hydroxide precursor.

Perovskite-type oxides (ABO_3) containing transition metals, especially Co and Mn, are recognized to be potential catalytic materials for gas-phase reactions such as complete oxidation and NOx removal as well as for electrode processes.[1] Since the powders of these oxides synthesized by conventional methods have rather small specific surface areas, development of the preparation methods which give high surface-area oxides is indispensable for full use of their catalytic potential. More advanced methods based on wet chemistry, such as sol–gel, coprecipitation and complexing methods, have been developed to prepare homogeneous, high surface-area oxides.[2,3] In the complexing methods which have been frequently used,[3] complexing/gelation agents such as a citric acid–ethylene glycol couple,[3] hydroxyl acids,[4–6] and EDTA,[7,8] are used to form a homogeneous precursor maintaining metal components in a highly dispersed state. However, the use of organic agents by large amount often causes serious problems, e.g., unexpected explosion during heating and low ceramic yield, making it difficult to obtain large quantities of product powders. From this standpoint, the hydroxide precursor seems to be attractive. In an ordinary hydroxide coprecipitation process, a basic solution like aq NH_3 is added to an acidic solution containing component metal cations of the target mixed oxides. If the pH dependence of solubility of each hydroxide formed is not the same, preferential precipitation would occur, giving an inhomogeneous mixture of metal hydroxides. This happens sometimes even when the homogeneous coprecipitation method using urea is applied. On the other hand, when the mixed acidic solution is added dropwise to a large amount of the basic solution, pH of the reaction medium can be kept high enough until all the components are precipitated completely as hydroxides, allowing homogeneous coprecipitation to take place within individual droplets. This method is thus called here a reverse homogeneous precipitation (RHP) method. It was reported that the RHP method gave $PbZr_{1-x}Ti_xO_3$[9] with compositional homogeneity and $La_{0.8}Sr_{0.2}MnO_3$ (M = Co, Mn)[10] with large specific surface areas. We have been investigating the effect of the addition of alkylammonium cations in the RHP synthesis solutions under the assumption that they would adsorb on the surface of the hydroxide precursor particles to hinder the agglomeration and this would result in further increases in surface areas of the products. As reported here on the synthesis of $LaMnO_{3+\delta}$, the presence of $N(CH_3)_4^+$ cation is remarkably effective not only in increasing the surface areas but also in stabilizing the colloidal solution of the hydroxide precursor.

Lanthanum and manganese nitrates (9 mmol for each) were dissolved in 90 mL of deionized water. The mixed nitrate solution was then dropped through a burette at a rate of 1.0–1.5 mL min^{-1} into aq NH_3 (300 mL, pH=13.1) with and without $N(CH_3)_4Br$ (9 mmol) under vigorous stirring. The preparation methods with and without $N(CH_3)_4Br$ are named as Me-RHP and RHP methods, respectively. The final pH of the reaction medium was about 10.6.[11] The suspension was further stirred for 1 h, kept standing for 30 min, and filtrated to collect the solid precursor (hydroxide). The precursor was dried at 110 °C for 12 h, and calcined for 5 h at 550–850 °C. Products were characterized by X-ray diffraction (XRD, Rigaku RINT2200, Cu Kα), N_2 adsorption at –196 °C (Micromeritics Gemini 2370, BET method) and transmission microscopy (JEOL JEM- 2010HT, 200 kV).

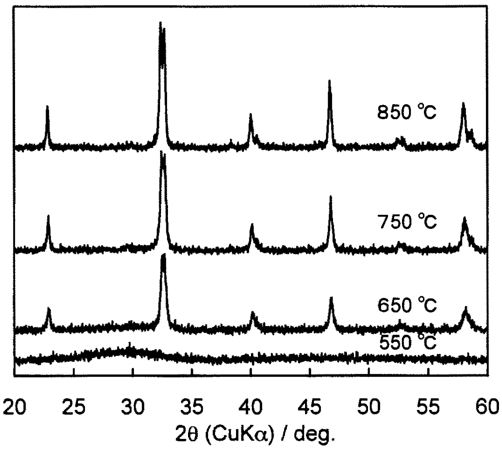

Figure 1. XRD patterns of $LaMnO_{3+\delta}$ prepared by the Me-RHP method.

XRD patterns of the lanthanum manganite samples prepared by the Me-RHP method are shown in Figure 1. The product calcined at 550 °C was X-ray amorphous, while all the other products calcined at 650 °C and above were assigned to oxygen-excess $LaMnO_{3+\delta}$ (JCPDS 32-484) free from any apparent impurity phases. The same results were also obtained with the RHP method. For comparison, the conventional nitrate decomposition (NIT) method[12] required calcination at 850 °C or above to form a single phase of $LaMnO_{3+\delta}$. Accordingly, both Me-RHP and RHP methods can reduce the lowest calcination temperature by 200 °C as compared with the conventional NIT method. Such lowering in calcination temperature resulted in an increase in the specific surface area (Sa). As shown in Table 1, the Sa value of

$LaMnO_{3+\delta}$ became larger as the calcination temperature lowered. It is noted that the Me-RHP method gave larger Sa values than the RHP method at any calcination temperatures.[13] As seen from the TEM image (Figure 2), the $LaMnO_{3+\delta}$ particles prepared by the Me-RHP method and calcined at 700 ºC were fairly uniform in size with a narrow distribution centered around 25 nm. It is also seen that the particles are kept from being heavily agglomerated. Since the particle sizes of $LaMnO_{3+\delta}$ estimated by Scherrer's equation were comparable between the two methods, it seems that the difference in Sa originates from the difference in the degree of agglomeration of the particles. The high surface-area product of $LaMnO_{3+\delta}$ thus prepared showed high catalytic activity for the combustion of C_3H_8.[14]

Table 1. Specific surface areas (m^2 g^{-1}) of $LaMnO_{3+\delta}$ prepared by the Me-RHP and RHP methods

Calcination Temp.	650 ºC	750 ºC	850 ºC
Me-RHP	27	19	6
RHP	18	12	5

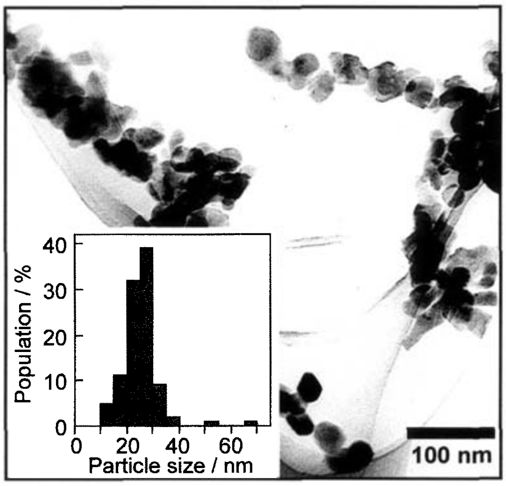

Figure 2. TEM image of $LaMnO_{3+\delta}$ prepared by the Me-RHP method (700 ºC). Inset: Particle size distribution.

Another superiority of the Me-RHP method over the RHP was the stability of the colloidal solution of the hydroxide precursor. The wet hydroxide precursors just after the filtration were suspended in pure water under the irradiation of supersonic waves for 1 h. For the suspension containing the RHP precursor, sedimentation became noticeable after 2 weeks and completed within one month (Figure 3A). On the other hand, the suspension containing the Me-RHP precursor was quite stable from sedimentation even after one month (Figure 3B) or more.[15] The colloidal solution appears to be applicable for preparing supported perovskite oxide catalysts on alumina, silica, carbon etc. as well as for thin/thick film preparation.

In the present methods, the precipitation reaction takes place immediately when each nitrate droplet reaches the surface of the basic solution, so that the metal compositions of each hydroxide precursor particle formed are expected to be the same as those of the starting solution. Such compositional homogeneity of the precursor would make the low-temperature synthesis possible. Since the apparent isoelectric point of the RHP hydroxide precursor was roughly 9.0 as determined by titration, the surface of the precursor is negatively charged in the basic solution (pH > 10.6 in the present condition). In the Me-RHP method, $(CH_3)_4N^+$ cations are adsorbed electrostatically on the precursor to neutralize the surface negative charges, which would supposedly hinder the precursor particles to agglomerate together. This may account for why the presence of $(CH_3)_4N^+$ results in the stabilization of the colloid solution and in an increase in the specific surface area of the calcined product.

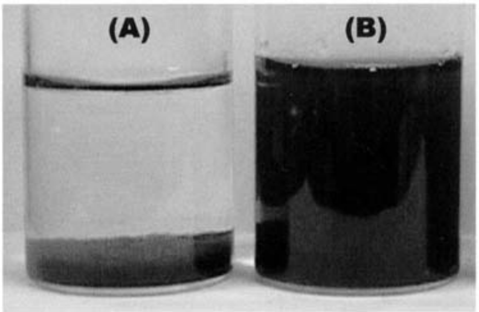

Figure 3. Colloidal solutions of the (A) RHP and (B) Me-RHP hydroxide precursors after passing one month (*ca.* 0.9 g L^{-1}).

References and Notes

1 For reviews, see: M. Misono and E. A. Lombardo, "Perovskites," (Special issue of Catalysis Today, Vol. 8, No. 2), Elsevier, Amsterdam (1990); L.J. Tejuca and J. L. G. Fierro, "Properties and Applications of Perovskite-type Oxides," Marcel Dekker, Inc., New York (1993).

2 J. Twu and P. K. Gallagher, in "Properties and Applications of Perovskite-type Oxides," ed. by L. J. Tejuca and J. L. G. Fierro, Marcel Dekker, Inc., New York (1993), p. 1.

3 M. Kakihana and M. Yoshimura, *Bull. Chem. Soc. Jpn.*, **72**, 1427 (1999).

4 C. Marcilly, P. Courty, and B. Delmon, *J. Am. Ceram. Soc.*, **53**, 56 (1970).

5 H. M. Zhang, Y. Teraoka, and N. Yamazoe, *Chem. Lett.*, **1987**, 665.

6 Y. Teraoka, H. Kakebayashi, I. Moriguchi, and S. Kagawa, *Chem. Lett.*, **1991**, 673.

7 F. H. Chen, H. S. Koo, and T. Y. Tseng, *J. Am. Ceram. Soc.*, **75**, 96 (1992).

8 R. H. E. van Doorn, H. Kruidhof, A. Nijmeijer, L. Winnubst, and A. J. Burggraaf, *J. Mater. Chem.*, **8**, 2109 (1998).

9 V. M. McNamara, *J. Can. Ceram. Soc.*, **34**, 103 (1965).

10 Y. Teraoka, Y. Taura, I. Moriguchi, and S. Kagawa, *Kagaku Kogaku Ronbunshu*, **21**, 1032 (1995).

11 Solubility of $La(OH)_3$ and $Mn(OH)_2$ at pH=10.6 are 6.3×10^{-10} and 1.2×10^{-6} mol L^{-1}, respectively, and the final concentration of La or Mn is 2.3×10^{-2} mol L^{-1}. Accordingly, the assumption of the complete precipitation of the hydroxides is practically true.

12 A mixed aqueous solution of metal nitrates was evaporated to dryness, followed by calcination in air.

13 The similar results were also observed with $(C_2H_5)_4N^+$ and $(C_3H_7)_4N^+$ cations.

14 The weight-normalized activity of $LaMnO_{3+\delta}$ at a fixed temperature, e.g., 250 ºC, increased almost linearly with the Sa value. Reaction condition: C_3H_8 (0.8%)–O_2(25%)–He(balance). W/F = 0.5 g s cm^{-3}.

15 The suspension containing the Me-RHP precursor are stable more than 1 year. The average particle size of the Me-RHP precursor colloids was ca. 8 nm (light scattering method, Otsuka Electronics, DLS-700).