Formation of Uniform Lanthanum(III) Carbonate Hydroxide Particles in the Presence of 1,2-Ethanediamine and Their Conversion into Oxides

Shuichi HAMADA,* Yoshiyuki KUDO, and Hiroaki MATSUDA
Department of Applied Chemistry, Faculty of Science, and Institute of Colloid and Surface Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162
(Received February 15, 1993)

Synopsis. Uniform spherical particles of crystalline lanthanum(III) carbonate hydroxide were prepared by aging at 100 °C the corresponding 1,2-ethanediamine complex solution in the presence of carbonate ion under specified conditions. The latter anions were generated from a mild oxidation of the ligand with nitrate ions present. The carbonate hydroxide particles were completely converted into the oxides at 900 °C without deformation.

Lanthanide compounds, especially its oxides, are interesting regarding their electric, catalytic, and ceramic properties.[1,2] Lanthanum(III) carbonates were produced by the hydrolysis of the corresponding trichloroacetate,[3,4] and by the hydrothermal reaction of lanthanum(III) salt and carbon dioxide,[5,6] whereas their particle shapes were irregular. Recently, uniform carbonate hydroxide particles of lanthanum(III) and yttrium(III), as well as mixed lanthanide, were produced using urea at elevated temperatures under specified conditions.[7,8]

Slow formation of solutes, such as OH^-, CO_3^{2-}, and S^{2-}, by the decomposition of certain inorganic and organic compounds[7—10] in electrolyte solutions can be used to produce uniform particles of metal compounds, as well as to release free metal ions from the corresponding metal complexes of exothermic formation at elevated temperatures.[11,12] In the present work, the preparation of uniform lanthanum(III) carbonate hydroxide particles from the 1,2-ethanediamine complexes and conversion into oxides are described.

Experimental

Mixed solutions of lanthanum(III) nitrate and 1,2-ethanediamine were prepared in concentration ranges from 5.0×10^{-3} to 3.0×10^{-2} mol dm^{-3} for lanthanum(III) ions ($[La^{3+}]_t$) and from 7.0×10^{-1} to 2.8 mol dm^{-3} for 1,2-ethanediamine ($[en]_t$), followed by filtration through a membrane filter of 0.2 μm in pore size. The concentration ratio ($[en]_t/[La^{3+}]_t$) in the mixed solutions was fixed at 140. The pH was adjusted to between 7.6 and 8.8 using nitric acid. An aliquot of the mixed solution (40 cm^3) tightly sealed in a screw-capped Pyrex glass tube, after bubbling nitrogen, was initially heated at a heating rate of 1 °C min^{-1} in an oil bath and then kept at 100±0.5°C for a given period of time up to 6 h. The particles, thus produced, were centrifuged at 3000 rpm and repeatedly washed with doubly distilled water.

The concentration of lanthanum(III) species in the solution was assayed spectrophotometrically using arsenazo III[13] at regular time intervals after the solids were removed from the suspension by centrifugation at 10000 rpm, followed by filtration through a membrane filter of 0.1 μm in pore size. The filtrate did not show any Tyndall cone. The solid phase was further separated into amorphous-like and crystalline fractions due to a difference in their solubilities in 4×10^{-4} mol dm^{-3} nitric acid. The total concentration of carbonate ions was determined by isotachophoresis at 20 °C.

Results and Discussion

Spherical particles of a reasonably narrow size distribution were obtained over a fairly narrow range of $[La^{3+}]_t$ from 1.0×10^{-2} to 2.0×10^{-2} mol dm^{-3} at an $[en]_t/[La^{3+}]_t$ ratio of 140 with an initial pH_i of 8.0—8.2 (resulting in almost the same final pH_f) at 100 °C for 2 h. Figure 1 shows, as an example, uniform spherical particles with an average modal size of 2.8 μm and a relative standard deviation of 0.12. These particles were identified as being well-crystallized lanthanum(III) carbonate hydroxide, $La(CO_3)(OH)$,[14] by X-ray powder diffractometry.

However, since the mixed solution had already become turbid, even at room temperature when the pH_i was greater than 8.5, particle preparation was not carried out under these conditions. No particles appeared

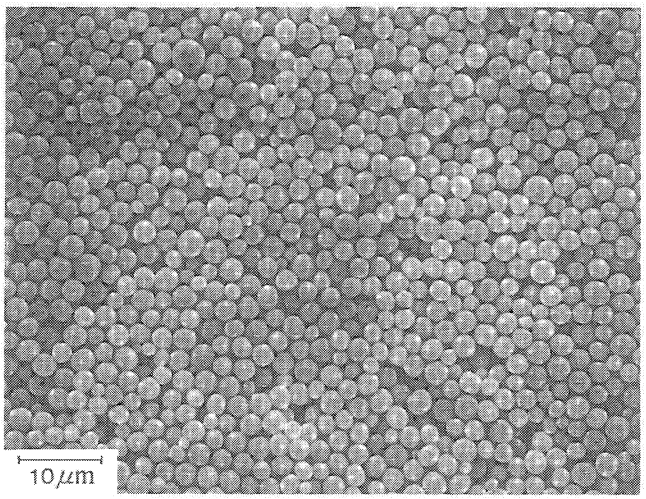

Fig. 1. Scanning electron micrograph of spherical lanthanum(III) carbonate hydroxide particles obtained by aging at 100 °C for 2 h a solution of $[La^{3+}]_t=1.0\times10^{-2}$ mol dm^{-3}, $[en]_t=1.4$ mol dm^{-3}, $[HNO_3]_{add}=1.7$ mol dm^{-3}, and initial $pH_i=8.1$ (final $pH_f=8.1$).

at $[en]_t/[La^{3+}]_t$ ratios of less than 100, whereas small and irregularly shaped particles were generated at ratios greater than 140, even at almost the same pH_i.

Matijevic et al.[9] also prepared uniform spherical lanthanide (Gd, Eu, Tb, and Sm) carbonate hydroxide particles by forced hydrolysis of the corresponding metal salt solution in the presence of urea at elevated temperatures. However, these particles were amorphous and much smaller (0.05—0.5 μm) than those obtained in the present system, except for crystalline ellipsoidal platelets of cerium(III) carbonate hydroxide.

Figure 2 illustrates the change in the fractions(F) of soluble lanthanum(III) species, as well as amorphous-like and crystalline fractions, as a function of the aging time under the conditions given in Fig. 1. The soluble lanthanum(III) species (○) in the supernatant solution decreased steeply after 56 min, following precipitation of flocks identified as lanthanum(III) hydroxide[15] of very low crystallinity. The crystalline lanthanum (III) carbonate hydroxides (□) were produced through dissolution and recrystallization of the amorphous-like lanthanum(III) hydroxides (△), as judged from almost the same rates of appearance and disappearance of the respective solids, and from sharp X-ray powder diffraction peaks of the resulting carbonate hydroxides. The fraction of the crystalline phase increased until all of the amorphous-like hydroxides had disappeared. The lanthanum(III) carbonate hydroxide particles grew linearly up to around 90 min at a radial growth rate of 2.2 $\mu m\,h^{-1}$ and more slowly after that, while uniformity of the particles became rather poor.

Under the optimum conditions for making the uniform carbonate hydroxide particles (Fig. 1), the fraction

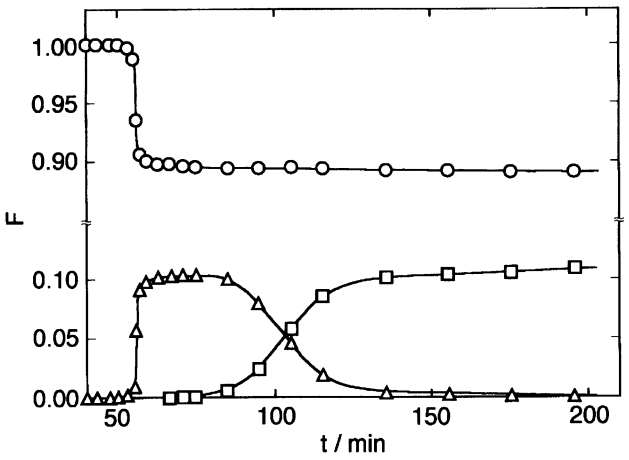

Fig. 2. Fractional changes in soluble lanthanum (III) species and solids as a function of aging time under the conditions given in Fig. 1. Symbols: ○; soluble lanthanum(III) species, △; amorphous-like lanthanum(III) hydroxide, and □; crystalline lanthanum(III) carbonate hydroxide. The latter two fractions were determined after resolving the solid mixture using 4×10^{-4} mol dm^{-3} nitric acid.

of free lanthanum(III) ions is greatly decreased from 0.91 in the absence of the ligand at 25 °C to 9.7×10^{-6} by complexation, as calculated using the formation constants.[16—20] However, the amorphous-like hydroxides are produced by the hydrolysis of lanthanum(III) ions released from the 1,2-ethanediamine complexes at elevated temperatures due to their exothermic formations ($\Delta H_1=-11.5$ kJ mol^{-1} for $[La(en)]^{3+}$ and $\Delta H_2=-10.3$ kJ mol^{-1} for $[La(en)_2]^{3+}$)[19] in the absence of a sufficient amount of carbonate ions. Therefore, the concentration of free lanthanum(III) ions was determined by the solubility product of lanthanum(III) hydroxide at a given temperature ($K_{sp}=4.1\times10^{-19}$ $mol^4\,dm^{-12}$ at 25 °C and $\Delta H_s=12.9$ kJ mol^{-1}).[21,22]

A mixed solution of 1,2-ethanediamine and nitric acid ($[en]_t=1.4$ mol dm^{-3} and $[HNO_3]_{add}=1.7$ mol dm^{-3}, pH 8.2) without lanthanum(III) ions was aged at 100 °C for 1 h to verify an origin of carbonate ions. Aldehyde was clearly detected in this aged solution by a chromotropic acid test.[23,24] The generation of aldehyde from 1,2-ethanediamine has been confirmed during the course of formation of uniform metallic silver particles by the reduction of corresponding metal ions at 100 °C.[25] In the present case, a further oxidation of aldehyde to the carbonate ion led to carbonate hydroxide particles. The total concentration of carbonate ions increased to 4.2×10^{-4} mol dm^{-3} in the same mixed solution with the heating time, and remained nearly constant after around 150 min, although carbonate ions were originally included as a very small amount (4×10^{-5} mol dm^{-3}). This fact indicates that the carbonate ions are supplied by a mild oxidation of 1,2-ethanediamine via formaldehyde with nitrate ions present at elevated temperatures. However, an initial heating rate of 1—2 °C min^{-1} was required to produce uniform particles. This means that an appropriate degradation rate of 1,2-ethanediamine is essential for producing uniform particles.

Uniform lanthanum(III) oxide particles were prepared by calcination in air at 900 °C for 12 h, while keeping their original morphology. However, the average modal size of the oxides decreased from 2.8 to 2.4 μm with almost the same relative standard deviation as the original dispersion. The BET specific surface area determined by nitrogen adsorption increased form 3.6 to 5.1 $m^2\,g^{-1}$ due to the formed porosity.

Figure 3 illustrates the X-ray powder diffraction patterns of the original carbonate hydroxide particles and the same powders heat-treated at 600, 700, and 900 °C for 12 h in air, respectively. The conversion of the carbonate hydroxides clearly took place through an intermediate, $La_2(CO_3)O_2$,[26] as shown in the pattern at around 600 °C, and finally to the oxides, La_2O_3.[27] This fact agreed well with the following proposed pyrolyses[28] through this intermediate. However, the

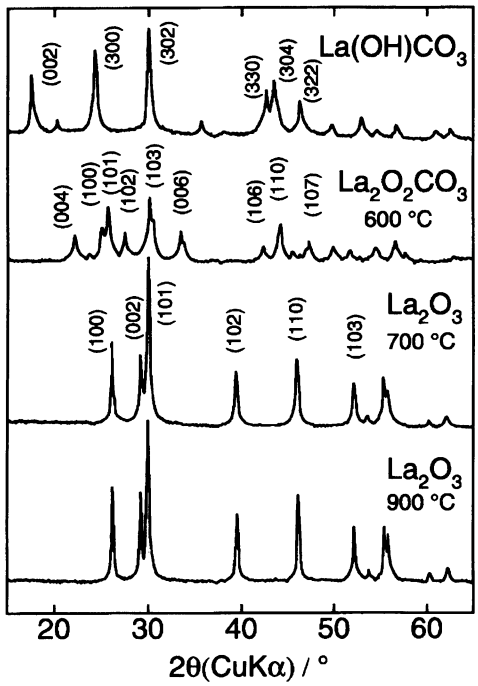

Fig. 3. X- Ray powder diffraction patterns of lanthanum(III) carbonate hydroxide and those heat-treated at 600, 700, and 900 °C for 12 h.

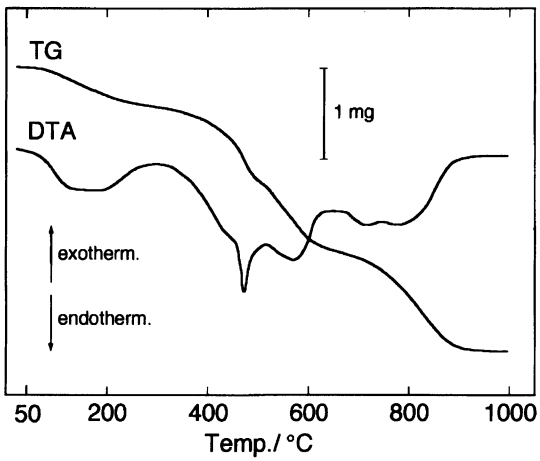

Fig. 4. Differential thermal analysis (DTA) and thermogravimetry (TG) on lanthanum(III) carbonate hydroxide particles at a heating rate of 20 °C min^{-1} in nitrogen atmosphere. Sample weight=11.6 mg.

$$La_2(CO_3)_2(OH)_2 \cdot H_2O = La_2(CO_3)O_2 + CO_2 + 2H_2O. \quad (1)$$

$$La_2(CO_3)O_2 = La_2O_3 + CO_2. \quad (2)$$

dehydration of the water of crystallization separately took place at around 140 °C prior to conversion to $La_2(CO_3)O_2$, as judged from a differential thermal analysis (DTA) and thermogravimetry (TG) of the original particles (Fig. 4), although no modification for the water of hydration was described in the literature.[14] The weight loss at the final stage corresponds to the pyrolysis of $La_2(CO_3)O_2$ to La_2O_3 through Eq. 2, whereas no cause could be offered for the splitting of the endothermic peaks at around 720 and 780 °C.

On the other hand, the degradation to $La_2(CO_3)O_2$ after dehydration would be more complicated, as judged from the sharp and broad endothermic DTA peaks at 473 and 570 °C, respectively. An inflective change in the TG curve at 493 °C also suggests a complex degradation into the intermediate, $La_2(CO_3)O_2$, although no detailed process is clear.

References

1) G. V. Rao, S. Ramdes, P. N. Mehrotra, and C. N. R. Rao, *J. Solid State Chem.*, **2**, 377 (1970).
2) E. R. S. Winter, *J. Chem. Soc.*, **1968**, 2889.
3) M. L. Salutsky and L. L. Quill, *J. Am. Chem. Soc.*, **72**, 3306 (1950).
4) R. G. Charles, *J. Inorg. Chem.*, **27**, 1489 (1965).
5) J. A. K. Tareen and T. R. N. Kutty, *Cryst. Growth*, **50**, 527 (1980).
6) T. R. N. Kutty, J. A. K. Tareen, and I. Mohammed, *J. Less-Common Met.*, **105**, 197 (1985).
7) B. Aiken, W. P. Hsu, and E. Matijević, *J. Am. Ceram. Soc.*, **71**, 845 (1988).
8) M. Akinc, D. J. Sordelet, and M. Munson, *Adv. Ceram. Mater.*, **3**, 211 (1988).
9) E. Matijević and W. P. Hsu, *J. Colloid Interface Sci.*, **118**, 506 (1987).
10) D. M. Wilhelmy and E. Matijević, *J. Chem. Soc., Faraday Trans. 1*, **80**, 563 (1984).
11) S. Hamada, S. Niizeki, and Y. Kudo, *Bull. Chem. Soc. Jpn.*, **59**, 3443 (1986).
12) S. Hamada, Y. Kudo, and T. Matsumoto, *Bull. Chem. Soc. Jpn.*, **62**, 1017 (1989).
13) H. Flaschka and A. J. Barnard, "Chelate in Analytical Chemistry," Marcel Dekker, New York (1969), Vol. 2, pp. 1—91.
14) A. N. Christensen, *Acta Chem. Scand.*, **27**, 2973 (1973).
15) R. Roy and H. A. McKinstry, *Acta Crystallogr.*, **6**, 365 (1953).
16) R. M. Smith and A. E. Martell, "Critical Stability Constants," Plenum, New York (1989), Vol. 4, p. 2.
17) S. Kotrlý and L. Šůcha, "Handbook of Chemical Equilibria in Analytical Chemistry," Halsted, New York (1985), p. 125.
18) G. Biedermann and L. Ciavatta, *Acta Chem. Scand.*, **15**, 1347 (1961).
19) G. V. Narayana, S. J. Swamy, and P. Lingaiah, *Indian J. Chem.*, **25A**, 491 (1986).
20) R. M. Smith and A. E. Martell, "Critical Stability Constants," Plenum, New York (1989), Vol. 2, p. 36.
21) J. Kragten and L. G. Decnop-Weever, *Talanta*, **34**, 861 (1987).
22) D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, S. M. Bailey, I. Halow, K. L. Churney, and R. L. Nutall, "Handbook of Chemistry and Physics," 64th ed, ed by R. C. Weast, CRC Press, Boca Raton, FL (1988), p. D-55.
23) F. E. Critchfield and J. B. Johnson, *Anal. Chem.*, **29**,

797 (1957).
24) B. Klein and M. Weissman, *Anal. Chem.*, **25**, 771 (1953).
25) S. Hamada, Y. Kudo, and S. Ichikawa, *Colloid Polym. Sci.*, **269**, 187 (1991).
26) J. P. Attfield and G. Férey, *J. Solid State Chem.*, **82**, 132 (1989).
27) C. E. Hamrin, Jr., W. D. Arnett, R. J. De Angelis, X. X. Ding, and W. D. Ehmann, *Solid State Commun.*, **69**, 1063 (1989).
28) L. M. D' Assunção, I. Giolito, and M. Ionashiro, *Thermochim. Acta*, **137**, 319 (1989).