Preparative Method of Fine Powder of Yttrium(III) Oxide by Thermal Decomposition of $NH_4Y(C_2O_4)_2 \cdot H_2O$ Fine Crystals Obtained by New Reaction of Yttrium(III) Hydroxide Slurry with Oxalic Acid Solution

Yukinori MINAGAWA* and Fumikazu YAJIMA
Department of Inorganic Chemistry, Mitsubishi Kasei Corporation Research Center, 1000, Kamoshida-cho, Midori-ku, Yokohama 227
(Received August 3, 1989)

Synopsis. A fine powder of yttrium (III) oxide used for an additive of new ceramics, such as Si_3N_4, ZrO_2 etc, has been obtained by thermal decomposition (at 750 °C for 1.5 h) of $NH_4Y(C_2O_4)_2 \cdot H_2O$ prepared by the reaction of yttrium hydroxide slurry and an oxalic acid solution. This process has facilitated a scale-up for the production of $NH_4Y(C_2O_4)_2 \cdot H_2O$ fine crystals, resulting in low production costs. The formation mechanism of the crystals via $Y(OH)_3$ slurry is discussed.

In our previous paper,[1] a fine powder of yttrium oxide, Y_2O_3, for new ceramics was obtained by the thermal decomposition of fine crystals of $NH_4Y(C_2O_4)_2 \cdot H_2O$ precipitated by the reaction of a strongly acidic yttrium oxalate solution and an aqueous ammonia solution. In order to obtain fine crystals of $NH_4Y(C_2O_4)_2 \cdot H_2O$, it was necessary to mix these solutions rapidly (within 2 s) and, furthermore, to use large amounts of nitric acid and ammonia solutions. From an industrial viewpoint, a procedure which includes rapid mixing and the consumption of a large amount of acid and base (ammonia) does not seem feasible. It was therefore, expected that a more feasible process could be developed by the use of the worthy and interesting precipitate, $NH_4Y(C_2O_4)_2 \cdot H_2O$, from an industrial viewpoint. However, there is no mention in the literature regarding the formation conditions of the precipitate, exept for a report by Barrett el al.[2] and our previous paper.[1] We have found that the precipitate can be obtained by a reaction of yttrium hydroxide slurry and an oxalic acid solution. Thus, in the present work, the effect of the precipitation conditions for $NH_4Y(C_2O_4)_2 \cdot H_2O$ from the reaction of yttrium hydroxide slurry and an oxalic acid solution on the particle-size distribution of Y_2O_3 fine powder is examined from an industrial viewpoint.

Experimental

Preparation of $NH_4Y(C_2O_4)_2 \cdot H_2O$ Precipitate. Yttrium nitrate ($Y(NO_3)_3$ solution, 1 mol dm^{-3}) was prepared by dissolving Y_2O_3 powder (Rhone Poulence, 99.9%) into concd nitric acid (S.G. 1.38, 60%); an excess of nitric acid was removed by the usual heating method. Into a glass vessel (Volume; 1.5 dm^3), 105 cm^3 of a 1 mol dm^{-3} $Y(NO_3)_3$ solution and 500 cm^3 of water were taken and 300 cm^3 of a 1.48 mol dm^{-3} aqueous ammonia solution was added within one minute under agitation at 250 rpm with a paddle mixer having four blades (HEIDON Suri-Wan-Motor, G5). Into the $Y(OH)_3$ slurry, thus obtained, 200 cm^3 of a 0.9 mol dm^{-3} oxalic acid solution was added; the mixture was agitated for 10 minutes as the same agitation speed (250 rpm). The slurry was filtered by vacuum suction (from the filtrate, no precipitate was observed upon the addition of a large amount of oxalic acid solution; thus, the recovery of yttrium ion was estimated to be almost 100%), washed with 200 cm^3 of water, and then dried on a hot plate. The product was identified as being almost $NH_4Y(C_2O_4)_2 \cdot H_2O$ by a X-ray diffraction method (Rigaku-Denki, model RAD-3A).

Preparation of Y_2O_3 Powder and Measurement of Its Particle Size. Fine powder of Y_2O_3 was obtained by the calcination of $NH_4Y(C_2O_4)_2 \cdot H_2O$ fine precipitate in a platinum crucible at 750 °C for 1.5 h. The particle-size distribution of Y_2O_3 powder was measured by a Micron Photo Sizer (Seishin Kigyo, model SK). About 2 mg of Y_2O_3 powder was well dispersed in 10—20 cm^3 methanol by using a supersonic disperser. Particle having a diameter larger than 4 μm ϕ were measured by natural sedimentation, and those under 4 μm ϕ were measured by centrifugal sedimentation at 25±1 °C.

Results and Discussion

Preparative Conditions for Y_2O_3 Fine Powder. Table 1 shows the relationship between the addition time (time used for addition) of the aqueous ammonia solution and the particle-size distribution of Y_2O_3 powder. A faster addition of the aqueous ammonia solution seems to produce finer particles of $Y(OH)_3$, since finer particles may bring finer particles of Y_2O_3 via $NH_4Y(C_2O_4)_2 \cdot H_2O$ finer crystals. Therefore, the

Table 1. Effect of Addition Time of Aqueous Ammonia Solution for Obtaining $Y(OH)_3$ Slurry on Particle Size Distribution of Y_2O_3 Powder

Addition time	Particle size distribution/%				
min	0—1	1—2	2—3	3—4	4—6/μm
1[a)]	85	9	3	2.5	0.5
5	84	10	3	1.5	1.5
15	78	13	4.5	1.5	3
30	74	14	4.5	2	5.5

a) Standard conditions. Conditions: Charged molar ratio of oxalic acid to yttrium hydroxide; 1.75.

Table 2. Effect of Concentration of $Y(OH)_3$ Slurry on Particle Size Distribution of Y_2O_3 Powder

Concentration of $Y(OH)_3$ slurry	Particle size distribution/%				
mol dm^{-3}	0—1	1—2	2—3	3—4	4—6/μm
0.1[a)]	85	9	2	2.5	1.5
0.2	85	8	2	2.5	2.5
0.4	85	8	2	2	3

a) Standard conditions. Conditions: Charged molar ratio of oxalic acid to yttrium hydroxide; 1.75.

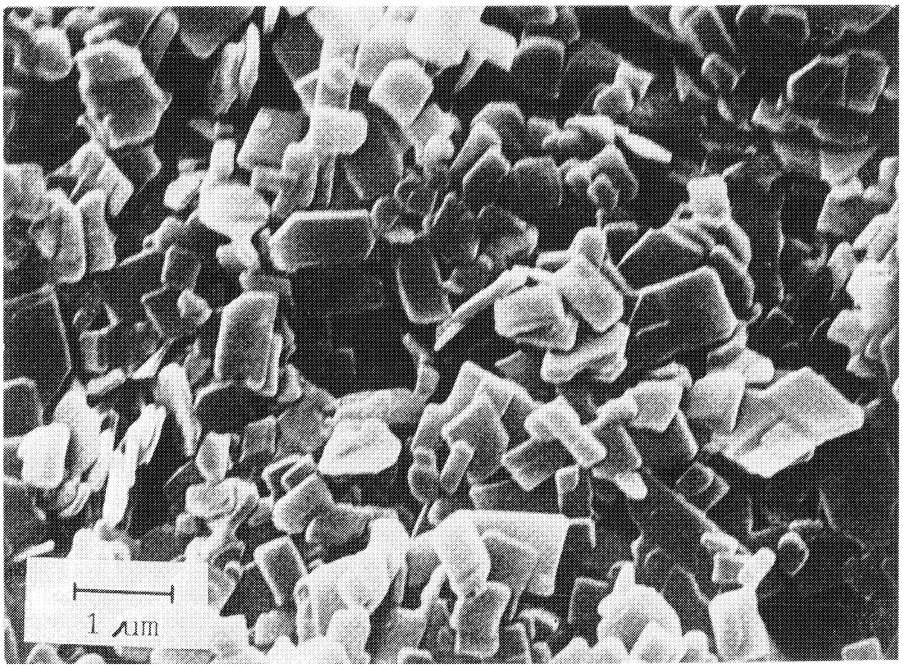

Fig. 1. Dried precipitate obtained at the standard conditions. ($H_2C_2O_4$/$Y(OH)_3$ molar ratio, 1.75): Magnification 12500×.

Table 3. Effect of Charged Molar Ratio of Oxalic Acid to Yttrium Hydroxide on Particles Size Distribution of Y_2O_3 Powder and Relationship between the Molar Ratio and Weight of Dried Precipitate Obtained by Preliminary Experiments[b)]

$H_2C_2O_4$/$Y(OH)_3$ molar ratio	Particle size distribution/%		Weight of dried precipitate[b)]
	0—1	1—6/μm	g
0.5	35	65	6.2
1.0	68	32	7.7
1.5	82	18	8.1
1.75[a)]	85	15	9.6
2.0	88	12	10.2

a) Standard conditions. b) All precipitates were obtained under the condition of amount of charged yttrium hydroxide being about 3.8 g as Y_2O_3 (in a small scale).

standard time for the addition of the aqueous ammonia solution, was determined as being one minute from an industrial viewpoint. The relationship between the concentration of $Y(OH)_3$ slurry and the particle-size distribution of Y_2O_3 powder is shown in Table 2. The concentration of the slurry from 0.1 to 0.4 mol dm^{-3} had no effect on the particle-size distribution of Y_2O_3 powder. This result is very important from an industrial viewpoint, because a large amount of $NH_4Y(C_2O_4)_2 \cdot H_2O$ crystals can be produced by the use of a small reactor. The relationship between the charged molar ratio of $H_2C_2O_4$ to $Y(OH)_3$ and the wt% of Y_2O_3 particles of diameter less than 1 μm and 1—6 μm is shown in Table 3. When the molar ratio is larger than 1.5, the particle-size distribution of Y_2O_3 powder is almost constant. From an industrial viewpoint, 1.75 is suitable to produce Y_2O_3 fine powder; the precipitate was identified as being almost $NH_4Y(C_2O_4)_2 \cdot H_2O$ by the X-ray diffraction method. Furthermore, in order to indirectly estimate the composition of the precipitate, the relationship between the molar ratio and the weight of the dried precipitate obtained by the preliminary experiments (in a small scale), is also shown in Table 3. The composition of the precipitate obtained under the molar ratio, 1.75, is easily estimated to be $NH_4Y(C_2O_4)_2 \cdot H_2O$, 89% and $Y(OH)C_2O_4$, 11%, respectively, from the material balance equation regarding yttrium and oxalate ions and supposing the main species to be $NH_4Y(C_2O_4)_2 \cdot H_2O$ and $Y(OH)C_2O_4$ crystals. The existence of these compounds was deduced by the use of the molar fraction of yttrium oxalate complexes ions in solution, calculated in our previous paper.[1)] All of the precipitates have good crystal form, with diameters less than 1 μm. Thus, there seems to be no amorphous substances as shown in Fig. 1. The relationship between the addition time of oxalic acid solution and the particle-size distribution of Y_2O_3 powder is shown in Table 4. Since a rapid addition of oxalic acid solution makes Y_2O_3 powder finer, the standard time used for the addition was selected to be 10 seconds. Suitable calcination conditions for the fine precipitate were determined at 750 °C for 1.5 h, as discussed in our previous paper.[1)] Based on the above results, the standard preparative conditions for Y_2O_3 fine powder with an average diameter, D_{50}, less than 1 μm, were selected as follows: Addition time of aqueous ammonia solution: 1 min. Concentration of $Y(OH)_3$ slurry: 0.1 mol dm^{-3}. Charged molar ratio

Table 4. Effect of Addition Time of Oxalic Acid Solution into the $Y(OH)_3$ Slurry on Particle Size Distribution of Y_2O_3 Powder

Addition time of oxalic acid soln	Particle size distribution/%				
s	0—1	1—2	2—3	3—4	4—6/μm
10[a)]	85	9	3	2.5	0.5
20	82	10	2	3	3
30	81	14	2	1	2

a) Standard conditions. Conditions: Addition time of NH_3 aqueous solution; 1 min. Concentration of $Y(OH)_3$ slurry; 0.1 mol dm^{-3}. Charged molar ratio, $H_2C_2O_4/Y(OH)_3$; 1.75.

$H_2C_2O_4$ to $Y(OH)_3$: 1.75. Addition time of oxalic acid solution: 10 s. Calcination conditions: 750 °C for 1.5 h.

Formation Process of $NH_4Y(C_2O_4)_2 \cdot H_2O$ Fine Crystals from the Reaction of $Y(OH)_3$ Slurry and the Oxalic Acid Solution. $Y(OH)_3$ slurry, prepared from the reaction of a $Y(NO_3)_3$ solution and an aqueous ammonia solution consists of very fine particles. Therefore, $Y(OH)_3$ particles are easily dissolved in an oxalic acid solution due to the formation of yttrium oxalate complexes, such as $Y(C_2O_4)^+$, $Y(C_2O_4)_2^-$ etc., as shown in Eqs. 1 and 2:

$$Y(OH)_3 + H_2C_2O_4 \longrightarrow Y(C_2O_4)^+ + OH^- + 2H_2O, \quad (1)$$

$$Y(OH)_3 + 2H_2C_2O_4 \longrightarrow Y(C_2O_4)_2^- + H^+ + 3H_2O. \quad (2)$$

Feibush et al.[3] reported the formation constants for $Y(C_2O_4)^+$, $Y(C_2O_4)_2^-$, and $Y(C_2O_4)_3^{3-}$ complex ions. As discussed in our previous paper,[1] the $Y(C_2O_4)_2^-$ ion is the main species in the present system; it reacts rapidly with NH_4^+ ion, which exists as a dominant species, to form an ion pair in the solution:

$$Y(C_2O_4)_2^- + NH_4^+ \rightleftharpoons NH_4Y(C_2O_4)_2 \longrightarrow NH_4Y(C_2O_4)_2 \cdot H_2O. \quad (3)$$

The ion-pair formation is so fast that $NH_4Y(C_2O_4)_2 \cdot H_2O$ predominantly precipitates from the solution. Thus, the Y_2O_3 particle size does not depend on the concentration of $Y(OH)_3$ slurry, but slightly depends on the addition time of oxalic acid solution into the $Y(OH)_3$ slurry. Therefore, this preparative method is very useful for the production of Y_2O_3 fine powder.

The authors are indebted to prof. Dr. T. Yotsuyanagi of Tohoku University at Sendai, Japan, Dr. K. Yoshida, president of our research center, Drs. T. Onoda and K. Wada who are our bosses, and Messrs. K. Kojima, T. Kaneko, K. Yamaguchi, and S. Kasuya, our teammate, for their kind encouragement and helpful discussions.

References

1) Y. Minagawa and F. Yajima, *Bull. Chem. Soc. Jpn.*, **63**, 378 (1990).
2) M. F. Barrett, T. R. R. McDonald, and N. E. Topp, *J. Inorg. Nucl. Chem.*, **26**, 931 (1964).
3) A. M. Feibush, Keith Rowley, and Louis Gordon, *Anal. Chem.*, **30**, 1610 (1958).