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New Preparative Method of Fine Powder of Yttrium(III) Oxide by Thermal Decomposition of $NH_4Y(C_2O_4)_2 \cdot H_2O$ Fine Crystal Obtained by Reaction of a Strongly Acidic Solution of Yttrium Oxalate and an Aqueous Ammonia Solution

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A fine powder of yttrium(III) oxide has been obtained by calcination of a quasi-stable salt of $NH_4Y(C_2O_4)_2 \cdot H_2O$, which was prepared by the rapid addition of an aqueous ammonia solution into a strongly acidic yttrium oxalate solution. The particle size distribution weakly depends on the addition time of the aqueous ammonia solution and the agitation speed, and strongly depends on the washing times with pure water and on the calcination temperature of $NH_4Y(C_2O_4)_2 \cdot H_2O$ crystal. The precipitation mechanism of $NH_4Y(C_2O_4)_2 \cdot H_2O$ is discussed in terms of kinetics in the solution.

A fine powder of yttrium(III) oxide Y_2O_3, has been demanded as an additive of new ceramics, such as Si_3N_4 and ZrO_2. Usually, Y_2O_3 fine powder was obtained by the calcination of a fine crystal of yttrium oxalate $Y_2(C_2O_4)_3$. However, it was difficult to obtain Y_2O_3 fine powder with an average diameter, D_{50}, less than 2μm by the thermal decomposition of $Y_2(C_2O_4)_3$, which was obtained by conventional mixing of a yttrium ion solution and an oxalic acid solution, since the size strongly depends on the mixing method. On a laboratory scale it is fairly easy to obtain $Y_2(C_2O_4)_3$ fine crystals, but on an industrial scale, it is difficult to mix the two solutions rapidly and to obtain a homogeneous nucleation which makes it possible to precipitate the fine crystals. From an industrial viewpoint, new methods have been demanded for obtaining Y_2O_3 fine powder. In the present work, a method for Y_2O_3 fine powder via $NH_4Y(C_2O_4)_2 \cdot H_2O$ is proposed.

Experimental

Materials: A yttrium(III) nitrate solution 1 mol dm^{-3} was prepared by dissolving 250 g of Y_2O_3 powder (composition was Y_2O_3 99.1%, Gd_2O_3 0.01%, Tb_4O_7 0.01%, Dy_2O_3 0.42%, Ho_2O_3 0.14%, Er_2O_3 0.28%, and Yb_2O_3 0.05%.) in concd nitric acid (S.G. 1.38, 60%). The solution was heated so as to eliminate any excess nitric acid, and diluted to 1 dm^3 with water. An oxalic acid solution 0.9 mol dm^{-3} was prepared by dissolving 228 g of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) into 2 dm^3 of water in 20 dm^3 polyethylene vessel with agitation.

Preparation of a Strongly Acidic Yttrium Oxalate Solution:[1] Two cubic decimeter aliquots of concd nitric acid was added to 2 dm^3 of 0.9 mol dm^{-3} oxalic acid solution in a 20 dm^3 polyethylene vessel. A 1.05 dm^3 of 1 mol dm^{-3} yttrium nitrate solution and 3 dm^3 of water were added to the mixture with agitation. This strongly acidic yttrium oxalate solution did not form any precipitate.

Preparation of Ammonium Dioxalatoyttrate(III): A 2.3 dm^3 volume of concd aqueous ammonia (S.G. 0.9, 28%) was diluted with 1.7 dm^3 of water in a 5 dm^3 polyethylene beaker. This solution was rapidly poured into the yttrium oxalate solution in the 20 dm^3 polyethylene vessel. The standard addition time was less than 2 seconds and the agitation speed was 245 rpm with a paddle mixer having four blades (HEIDON, Suri-wan-Moter, model G5). After the precipitate was formed, the slurry was allowed to stand for an hour. The pH value of the slurry was in the range of 8.0 to 8.2.

Standard Preparation of Y_2O_3 Powder: The slurry of the precipitate was filtered and washed two times with 210 cm^3 of water by suction. Then, the cake was washed with 40 cm^3 of acetone and dried in a vacuum dryer at room temperature. The dried cake was taken into a platinum cricible and calcined at 750 °C for 1.5 h.

Measurement of Particle Size Distribution of Y_2O_3 Powder: The particle size distribution of Y_2O_3 powder was measured by a Micron Photo Sizer (Seishin Kigyo, model SK). About 2 mg of the Y_2O_3 powder was well dispersed in 10—20 cm^3 of methanol using a supersonic disperser. Particles having a diameter greater than 4 μmϕ were measured by natural sedimentation, and those under 4 μmϕ were measured by centrifugal sedimentation at 25±1 °C.

Results and Discussion

Preparative Conditions to Obtain Y_2O_3 Fine Powder. The relationship between the addition time of an aqueous ammonia solution (NH_3 aq.) to a strongly acidic yttrium oxalate solution, and the particle-size distribution of Y_2O_3 powder is shown in Table 1. The particle-size distribution weakly

Table 1. Effect of Addition Time of NH_3 aq. Solution into Strongly Acidic Yttrium Oxalate Solution against Particle Size Distribution of Y_2O_3 Powder

Addition time of NH_3 aq.	Particle size distribution of Y_2O_3 powder/%					
s	0—1	1—2	2—3	3—4	4—5	5—8(μm)
2[a]	79	12	3	4	0.5	1.5
5.2	73	15	5.5	5	1.0	0.4
9.6	66	19	7	5	1.5	1.5

a) Standard addition time of NH_3 aq. solution. Conditions: Agitation speed; 200 rpm Agitation time; 5 min.

Table 2. Effect of Agitation Speed in Strongly Acidic Yttrium Oxalate Solution under Addition of NH_3 aq. Solution against Particle Size Distribution of Y_2O_3 Powder

Agitation speed	Particle size distribution of Y_2O_3 powder/%					
rpm	0—1	1—2	2—3	3—4	4—5	5—8 (μm)
120	76.5	14.5	3.5	4.5	0.5	0.5
200	79	11.8	4.0	4.5	0.5	0.5
310	85	8	2.5	3	0.5	0.5

Conditions: Addition of NH_3 aq. soln; within 2 s. Agitation time; 5 min.

Table 3. Effect of Standing Time of the Neutralized Slurry by Addition of NH_3 aq. Soln. against Particle Size Distribution of Y_2O_3 Powder

Standing time of slurry	Particle size distribution of Y_2O_3 powder/%					
h	0—1	1—2	2—3	3—4	4—5	5—8 (μm)
0	76.5	13.0	4.5	3.5	0.5	2.0
1[a)]	76.0	12.5	3.5	4.0	2.0	2.0
16	74.5	12.5	4.5	5.0	1.0	2.5

a) Standard standing time of the slurry.
Conditions: Addition of NH_3 aq. soln; within 2 s. Agitation speed; 245 rpm. Agitation time; 5 min.

depends on the addition time, up to 10 seconds. In order to obtain Y_2O_3 fine powder with a D_{50} less than 1 μmϕ, it is preferable to add NH_3 aq. within two seconds. The effect of the agitation speed during the mixing of the two solutions is shown in Table 2. The agitation speed does not strongly affect the particle-size distribution. Agitation over 200 rpm was sufficient to obtain Y_2O_3 fine powder with a D_{50} less than 1 μmϕ. The relationship between the standing time of the slurry and the particle-size distribution is also shown in Table 3. The standing time had no significant effect on the particle-size distribution within 16 h. This fact is very important from an industrial viewpoint, since there is no crystal growth within 16 h; control of the process is therefore very easy. The relationship between the washing times of the precipitate with pure water and the particle-size distribution is given in Fig. 1, which shows that a minimum particle size is obtained by washing twice with water. Without washing, particles of Y_2O_3 become large since particles easily grow during calcination due to inorganic salts contamination in the precipitate. On the other hand, when the cake is washed more than four times, the particle size becomes large due to the dissolution and recrystallization of $NH_4Y(C_2O_4)_2 \cdot H_2O$ in the water.

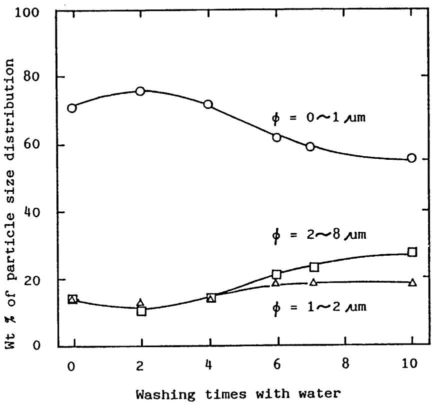

Fig. 1. Effect of water washing of precipitate obtained under standard conditions against particle size distribution of Y_2O_3 powder. ○; ϕ=0—1 μm △; ϕ=1—2 μm □; ϕ=2—8 μm.

The dried precipitate obtained by the proposed method was analyzed by X-ray diffraction. Almost all diffraction peaks were assigned as $NH_4Y(C_2O_4)_2 \cdot H_2O$, except for the three small unknown peaks shown in Table 4.

The thermal decomposition curve of the precipitate is shown in Fig. 2. Barrett et al.[2)] also reported a thermal decomposition curve of pure NH_4Y-

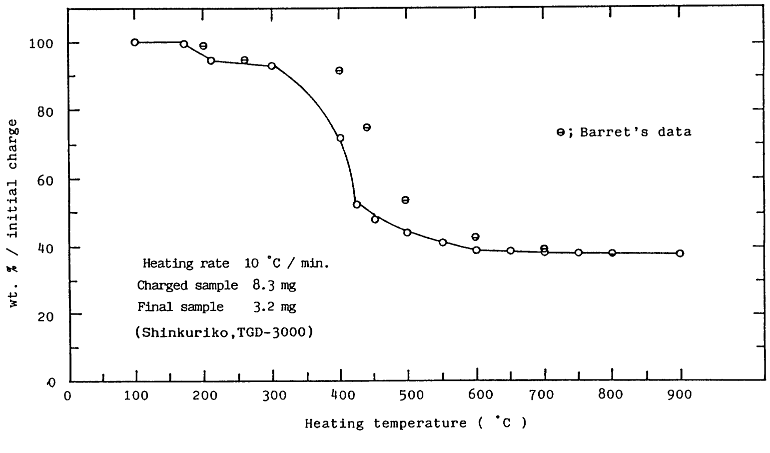

Fig. 2. Thermal decomposition curve of dried precipitate obtained under standard conditions.

Table 4. X-Ray Diffraction Data of Dried Precipitate Obtained under Standard Conditions

dA	I/I_0	dA	I/I_0	dA	I/I_0
7.25$^{a)}$	6.8	3.00	23	2.24	10.8
6.10	100	2.89	4.5	2.16	7.9
5.98	88	2.85	6.8	2.14	14.2
5.10	11.3	2.69	4	2.08	5.7
4.84	13	2.68	4	2.03	5.4
4.62	2.8	2.65$^{a)}$	2.8	2.00	10.8
4.27	34	2.59	6.8	1.89	7.9
3.95	4	2.55	9.1	1.83	9.1
3.67$^{a)}$	4.5	2.53	8.0	1.81	11.9
3.32	18	2.42	17.6	1.79	8.5
3.13	20	2.33	20.4	1.77	7.4
3.01	22	2.30	4.5		

a) Unidentified peak by ASTM card (22-1047). Measurement conditions by Rigaku-Denki, RAD-3A: target/filter; Cu/Ni, tube voltage; 20 kV, time constant; 2 s, chart speed ; 2 cm min^{-1}, scanning speed; 2° min^{-1}.

Table 5. Effect of Calcining Temperature of Precipitate Obtained under Standard Conditions against Particle Size Distribution of Y_2O_3 Powder

Calcining temperature	Particle size distribution of Y_2O_3 powder/%					
°C	0—1	1—2	2—3	3—4	4—5	5—10 (μm)
900	49	19	9.5	6	6	10.5
750	76	12.5	3.5	4	2	2

Table 6. Particle Size Distribution Data of Y_2O_3 Powder Obtained by a Trial Production under the Standard Preparative Conditions

Lot number	Particle size distribution of Y_2O_3 powder/%					
	0—1	1—2	2—3	3—4	4—5	5—8 (μm)
1	79	11	4	4.5	1.5	1
2	77	12.5	4	4.5	1.5	0.5
3	75	14	3.5	4.5	1	2
4	76	11	2	6.5	2	2.5
5	76	13.5	5	3.5	1.5	0.5
6	79	13.5	4.5	1.5	1	0.5

Table 7. Particle Size Distribution of Y_2O_3 Powder via $Y_2(C_2O_4)_3$ Precipitate Obtained by a Reaction of 0.1 mol dm^{-3} Yttrium Nitrate Solution and 0.25 mol dm^{-3} Oxalate Solution with a Special Equipment$^{a)}$

Source of oxalate ion	Particle size distribution of Y_2O_3 powder/%					
	0—1	1—2	2—3	3—4	4—5	5—8 (μm)
$H_2C_2O_4$	43	25	12	13	3	4
$(NH_4)_2C_2O_4$	65	25	5	3	1	1

a) PaipuRainHomoMikusa (Pipeline Homomixer), Model SL (Tokushu-kikakogyo K.K.). Conditions: Flow rate of each solution was 200 cm^3 min^{-1} and filtration, washing, drying, and calcination conditions of precipitate were the same as those of the standard.

$(C_2O_4)_2\cdot H_2O$ obtained at pH 2 (plotted in Fig. 2 by closed circles). The sample weight does not change over 700 °C. The particle-size distribution is sensitive to the calcination temperature. If the precipitate is calcined at 900 °C, the particle size of Y_2O_3 becomes much larger than that done at 750 °C, as shown in Table 5. According to the above-mentioned results, the standard preparative conditions for Y_2O_3 fine powder with a D_{50} less than 1 μmϕ were selected to be:

Addition time of NH_3 aq.: within 2 s
Agitation speed: 245 rpm
Standing time of the slurry: 1 h
Washing times of the precipitate with water: 2 times
Calcination conditions: 750 °C for 1.5 h

The particle-size distribution data of Y_2O_3 powder obtained under the standard preparative conditions are shown in Table 6. From an industrial viewpoint, it can be said that this standard procedure constantly gives a fine Y_2O_3 powder having a constant quality regarding particle size distribution. The standard deviation for particles having less than 1 μmϕ was evaluated as being 1.5. Such fine-powder quality could not be industrially obtained by the usual method for $Y_2(C_2O_4)_3$ precipitation. Even by the use of special equipment (Pipeline Homomixer) which is said to be very useful for obtaining a fine precipitate from solution, the obtained particle-size distribution

Table 8. Relation between Charged Molar Ratio of $H_2C_2O_4$ to $Y(NO_3)_3$ and Molar Fraction of $Y(C_2O_4)_2^-$ Ion

Equil. concenr. of $C_2O_4^{2-}$	Molar fraction of Y-oxal. complexes			Charged molar ratio
mol dm^{-3}	$Y(C_2O_4)^+$	$Y(C_2O_4)_2^-$	$Y(C_2O_4)_3^{3-}$	$H_2C_2O_4/Y(NO_3)_3$
6×10^{-4}	0.40	0.60	0	1.60
8×10^{-4}	0.28	0.72	0	1.72
1×10^{-3}	0.20	0.80	0	1.80
5×10^{-3}	0.06	0.85	0.07	2.0
1×10^{-2}	0	0.80	0.20	2.30
4×10^{-2}	0	0.65	0.35	2.75

Initial conditions: Concentr. of charged $Y(NO_3)_3$ is 1×10^{-1} mol dm^{-3}, pH of the solution is over 6.

of Y_2O_3 powder shown in Table 7 indicates that our process, via, $NH_4Y(C_2O_4)_2\cdot H_2O$ precipitate is superior.

Precipitation Mechanism of $NH_4Y(C_2O_4)_2\cdot H_2O$. The formation conditions,[2] the crystal structure,[3] and solubility product[4] of $NH_4Y(C_2O_4)_2\cdot H_2O$ have been reported. The concentration of Y^{3+} ion in solution can easily be calculated from the solubility products of $NH_4Y(C_2O_4)_2\cdot H_2O$ and $Y_2(C_2O_4)_3$ by using the following equations:

$$NH_4Y(C_2O_4)_2\cdot H_2O \rightleftarrows NH_4^+ + Y^{3+} + 2C_2O_4^{2-} + H_2O, \quad (1)$$

$$K_{sp} = [NH_4^+][Y^{3+}][C_2O_4^{2-}]^2 = 1.74\times 10^{-11},^{4)} \quad (2)$$

$$Y_2(C_2O_4)_3 \rightleftarrows 2\,Y^{3+} + 3\,C_2O_4^{2-}, \quad (3)$$

and

$$K_{sp} = [Y^{3+}]^2[C_2O_4^{2-}]^3 = 1.22\times 10^{-29}.^{5)} \quad (4)$$

Calculated concentrations of Y^{3+} ion at neutral pH are 1.4×10^{-3} mol dm^{-3} and 1.3×10^{-6} mol dm^{-3} for $NH_4Y(C_2O_4)_2\cdot H_2O$ and $Y_2(C_2O_4)_3$, respectively. Therefore, in the equilibrium state, $Y_2(C_2O_4)_3$ should precipitate predominantly from a neutral solution. However, in our study in which the charged molar ratio of $H_2C_2O_4$ to $Y(NO_3)_3$ is 1.7 and the slurry pH is about 8, $NH_4Y(C_2O_4)_2\cdot H_2O$ precipitates as confirmed by X-ray diffraction (Table 5). As a matter of course, we obtained a pure $NH_4Y(C_2O_4)_2\cdot H_2O$ by X-ray diffraction for a charged molar ratio of $H_2C_2O_4$ to $Y(NO_3)_3$ of 2.0; however, these conditions were evaluated to be costly and so not charming for obtaining fine Y_2O_3 powder from an industrial viewpoint. Barrett et al.[2] obtained $NH_4Y(C_2O_4)_2\cdot H_2O$ precipitate only in weakly acidic solutions (pH 2) and reported that the precipitate changed into $Y_2(C_2O_4)_3$ upon washing with 0.1 mol dm^{-3} hydrochloric acid. These results indicate that $NH_4Y(C_2O_4)_2\cdot H_2O$ should be a quasi-stable species. Furthermore, in order to understand the formation mechanism of $NH_4Y(C_2O_4)_2\cdot H_2O$, the molar fraction of yttrium oxalate complexes in solution were estimated by using the formation constants reported by Feibush et al.[6] (shown in Appendix). From the result, it is supposed that $Y(C_2O_4)_2^-$ is a dominant complex ion in the wide range of oxalate ion concentrations. Therefore, $Y(C_2O_4)_2^-$ ion easily reacts with the NH_4^+ ion existing as a dominant species, to make the ion pair in solution, because both ions have counter charges. Thus, the formation of $NH_4Y(C_2O_4)_2\cdot H_2O$ must be attributed to a kinetic phenomenon in nature; that is, ion pair formation is so fast that the $NH_4Y(C_2O_4)_2\cdot H_2O$ mainly precipitates in spite of its higher solubility than that of $Y_2(C_2O_4)_3$.

Appendix

Why Is $Y(C_2O_4)_2^-$ Ion a Dominant Species in Our Conditions? Feibush et al.[6] reported the formation constants of yttrium oxalate complexes in solution as follows;

$$K_1 = [Y^{3+}][C_2O_4^{2-}][Y(C_2O_4)^+]^{-1} = 3\times10^{-7},$$

$$K_2 = [Y^{3+}][C_2O_4^{2-}]^2[Y(C_2O_4)_2^-]^{-1} = 8\times10^{-11},$$

$$K_3 = [Y^{3+}][C_2O_4^{2-}]^3[Y(C_2O_4)_3^{3-}]^{-1} = 3.4\times10^{-12}.$$

By the use of these constants, relation between molar fraction of yttrium oxalate complexes ions and free concentrations of $C_2O_4^{2-}$ ion are summarized in Fig. 3. From these results, relation between the charged molar ratio of $H_2C_2O_4$ to $Y(NO_3)_3$ and the molar fraction of $Y(C_2O_4)_2^-$ complex ion and that of other complexes ions, can be obtained by using material balance equation under the initial conditions that the charged concentration of $Y(NO_3)_3$ is 1.0×10^{-1} mol dm^{-3} and the pH is over 6, (shown in Table 8) which is also shown in Fig. 4. The molar ratio, about 1.7 being our condition, gives high molar fraction of $Y(C_2O_4)_2^-$ ion. This fact shows that the ion is a dominant species as mentioned in the text. Therefore, if the formation of the ion is established before precipitation, it is well understood why $NH_4Y(C_2O_4)_2\cdot H_2O$ precipitates predominantly from the solution as mentioned in the text.

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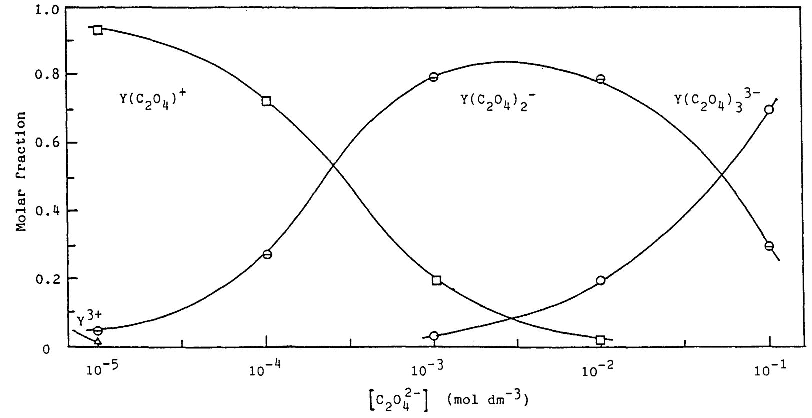

Fig. 3. Relation between the molar fraction of yttrium oxalate complexes and the free concentrations of $C_2O_4^{2-}$ ion in solution.

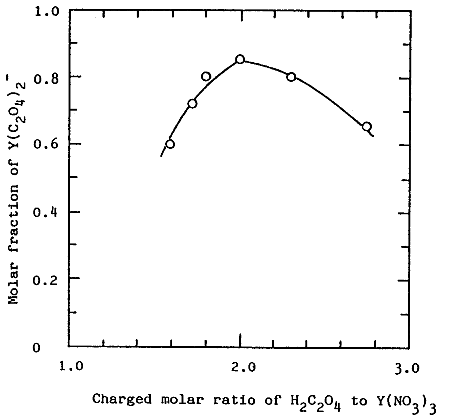

Fig. 4. Relation between the molar fraction of $Y(C_2O_4)_2^-$ complex ion and the charged molar ratio of $H_2C_2O_4$ to $Y(NO_3)_3$. Initial conditions: Charged concentration of $Y(NO_3)_3$ is 1.0×10^{-1} mol dm^{-3} and pH of the neutralized solution is over 6.

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References

1) Y. Minagawa and F. Yajima, *Chem. Lett.*, **1989**, 2129.

2) M. F. Barrett, T. R. R. McDonald, and N. E. Topp, *J. Inorg. Nucl. Chem.*, **26**, 931 (1964).

3) T. R. R. McDonald and J. M. Spink, *Acta Crystallogr.*, **23**, 944 (1967).

4) R. V. Bryzgalova and I. V. Chernitskaya, *Radiokhimiya*, **3**, 478 (1961); Gmelin Handbook, RE Main Vol. D5, (1984), p. 143.

5) T. R. Bhat and T. Venkateswara Rao, *Z. Anorg. Allgem. Chem.*, **332**, 204 (1964).

6) A. M. Feibush, Keith Rowley, and Louis Gordon, *Anal. Chem.*, **30**, 1610 (1958).