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Preparation of fine particles of carnegieite by a mist decomposition method

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A mist of a hydrosol consisting of silica, alumina/$NaAlO_2$ and sodium hydroxide was produced by a supersonic atomization, and treated successively in three furnaces of different temperatures. The temperatures of the furnaces were adjusted for the evaporation of water, the dehydration and the crystallization of the mixed oxide, respectively. The spherical particles ($\approx 0.5\,\mu m$) of carnegieite were found to be formed in a narrow composition range of the raw materials at temperatures of 650 to 900° C. The factors affecting the properties of the particles were investigated.

1. Introduction

Fine particles of mixed oxide are obtained by the preparation of fine droplets of a solution of mixed metal salts, followed by drying and thermal decomposition. The properties of the oxide particles depend greatly on the method used in each of these processes.

A nozzle for one or two fluids, a rotator called "wheel" or "disc", or a supersonic vibrator is used for the preparation of fine droplets. Several methods have been reported for the drying and the thermal decomposition treatments of the droplets. A two-stage method was used by de Lau [1], where the dried particles of soluble metal salt were collected and treated for the thermal decomposition. Roy *et al.* [2] injected the droplets into a furnace of a high temperature where drying and thermal decomposition processes occurred simultaneously. The use of a combustible solvent and the combustion of the droplet jet were adopted by Yamazaki and Sato [3] for obtaining a high temperature. Tokunaga *et al.* [4] succeeded in expanding the temperature range of stable combustion by injecting the combustible droplets into a furnace at a controlled temperature. Imai and Orito [5] treated the droplets of a mixed nitrates solution successively in three furnaces at different temperatures to prepare fine spherical particles of a perovskite ($CoLaO_3$).

In the present study, a mist of a mixed hydrosol is produced by a supersonic vibrator, and treated successively in the three furnaces at different temperatures. Fine spherical particles of carnegieite are prepared and the factors influencing the properties of the particles are investigated.

2. Experimental techniques

Fig. 1 shows a schematic diagram of the apparatus. The mist of a mixed hydrosol of silica, alumina/$NaAlO_2$ and sodium hydroxide is generated by a supersonic vibrator, the diameter of the droplet being ca. $5\,\mu m$. The mist flowed successively into three furnaces, B_1, B_2, and B_3, at different temperatures. The fine particles of the oxide were collected by the glass filter which was maintained at a temperature of 120° C.

The temperatures of the furnaces, T_1, T_2, and T_3, were adjusted for the evaporation of water (140° C), dehydration (400° C) and the crystallization of the oxide (500 to 900° C), respectively. The characteristics of the fine particles were measured by changing the operating conditions, such as the temperature of the B_3 furnace and the composition of the raw materials. The concentration (C) of the aqueous solution, and the velocity of air (v) were kept constant at 0.8 wt% as the mixed oxide ($Na_2O + SiO_2 + Al_2O_3$), and 1 litre

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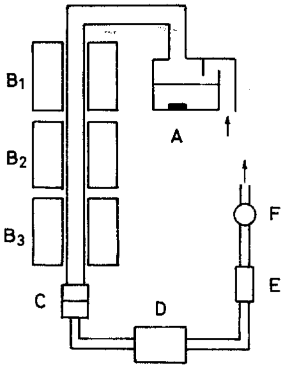

Figure 1 Schematic diagram of the apparatus. A, supersonic vibrator; $B_1 - B_3$, furnaces; C, filter; D, tail gas treatment; E, flow meter; F, pump.

min^{-1}, respectively. It should be noted that the retention time of the mist in the constant temperature portion (± 5° C) of the furnaces was ca. 10 sec.

The solution of the raw materials was prepared with silica sol, alumina sol, $NaAlO_2$ (Kantou Kagaku Co Ltd) and sodium hydroxide (Wako Junyaku Industry Co. Ltd). The silica sol was prepared by the ion exchange of sodium silicate (Kantou Kagaku Co. Ltd), whereas the alumina sol was prepared by the neutralization of aluminum nitrate (Wako Junyaku Industry Co. Ltd) with ammonium hydroxide (Wako Junyaku Industry Co. Ltd), followed by washing and peptization.

The characterization of the particles was made by means of following analytical instruments: a Rigaku Denki powder X-ray diffractometer, a Hitachi HSM2 scanning electron microscope (SEM) and a Hitachi 295 infrared (IR) spectrometer. The specific surface area was measured by the BET method from the adsorption of nitrogen at liquid nitrogen temperature.

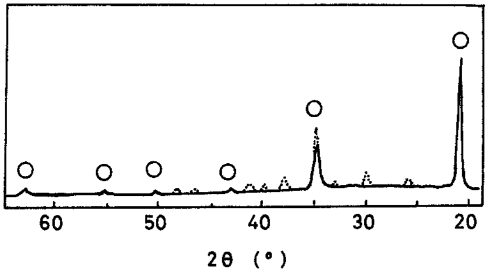

Figure 2 X-ray spectra of fine particles. $T_1 = 170$, $T_2 = 400$, $T_3 = 700°$ C, Si/Al = 1.25, NaOH concentration = 0.50 wt %; —— after washing, ····· before washing.

3. Results and discussion

Fig. 2 shows the X-ray spectra of the particles prepared in a representative condition ($T_1 = 170$, $T_2 = 400$, $T_3 = 700°$ C, Si/Al = 1.25, NaOH concentration = 0.50 wt %). Although the spectrum of the original sample contains several peaks assigned to those of sodium carbonate, the spectrum is in good agreement with that (indicated by ○ marks in the figure, ASTM Card No. 10-33) of Na_2O excess type carnegieite [6] after washing with dilute sodium nitrate solution. The phase change of the sample to nepherine was observed during heat treatment for 45 min at 1200° C, as reported in the literature [7]. These facts indicate that the fine particles of the carnegieite are produced.

Effects of various factors were investigated, and it was found that the composition of the reactant sol and the temperature of B_3 furnace were the most effective for the formation of the carnegieite. In Fig. 3, the X-ray diffraction intensity of the carnegieite (1 1 1) and the specific surface area are plotted as the function of the NaOH concentration, the Si/Al ratio in the sol being kept constant at 1.00 and 1.25. A maximum in the diffraction intensity was observed at a concentration of ≈ 0.5 wt % in either case. On the other hand, the specific surface area of the particles remained almost constant at 5 to 7 m^2 g^{-1}. The effects of the Si/Al ratio are shown in Fig. 4. In this case, the reactant sol contained $Na_{(1+x)}Al_{(1+x)}Si_{(1-x)}O_4 \cdot 0.84NaO_{0.5}$ as mixed oxide. The value of x was changed in order to study the effect of the Si/Al ratio. As the (0 1 1) peak of the unreacted sodium aluminate, overlapping to the (1 1 1) peak of the carnegieite, gave a considerable effect in the aluminium excess composition range, the data are presented with the samples after washing with a dilute sodium nitrate solution. The X-ray diffraction intensity showed a maximum at Si/(Si + Al) = 55 at %. The increase of the specific surface area, observed in the range below Si/(Si + Al) ≈ 50 at %, may be ascribed to the amorphous alumina formed from the unreacted sodium aluminate during the washing. In all of these experiments, other conditions were kept constant as follows: $T_1 = 170$, $T_2 = 400$, $T_3 = 700°$ C. These results indicate that the fine particles of the carnegieite structure are formed in a narrow composition range of the reactant sol.

The experimental results on the effects of T_3, shown in Fig. 5, indicated that the particles of the

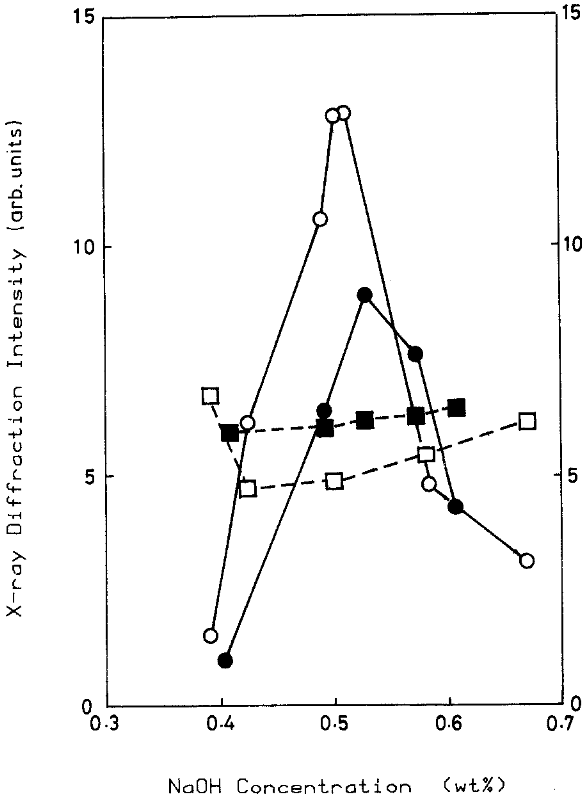

Figure 3 Effects of NaOH concentration. $T_1 = 170$, $T_2 = 400$, $T_3 = 700°$C, ○□, Si/Al = 1.25; ●■, Si/Al = 1.00; ○●, X-ray intensity; □■, specific surface area.

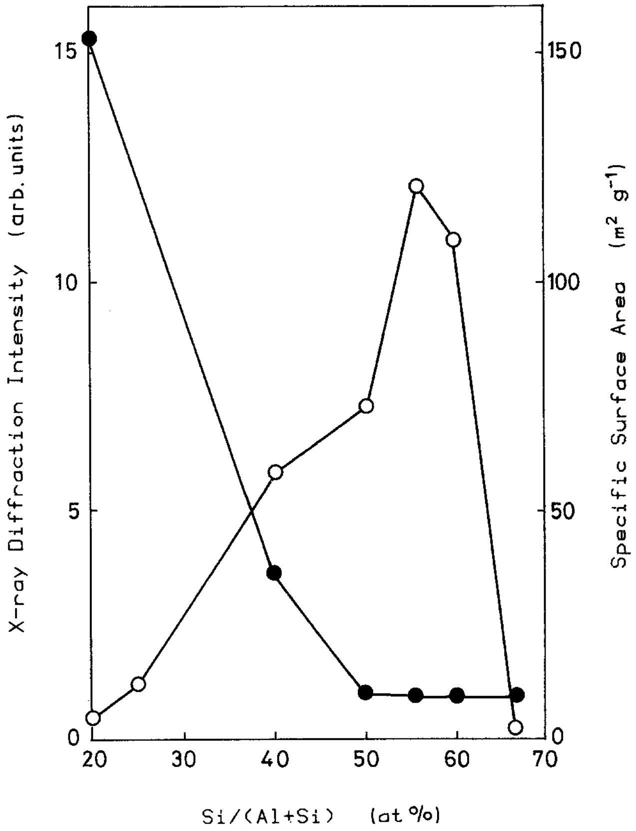

Figure 4 Effects of Si/Al ratio. ○, X-ray intensity; ●, specific surface area.

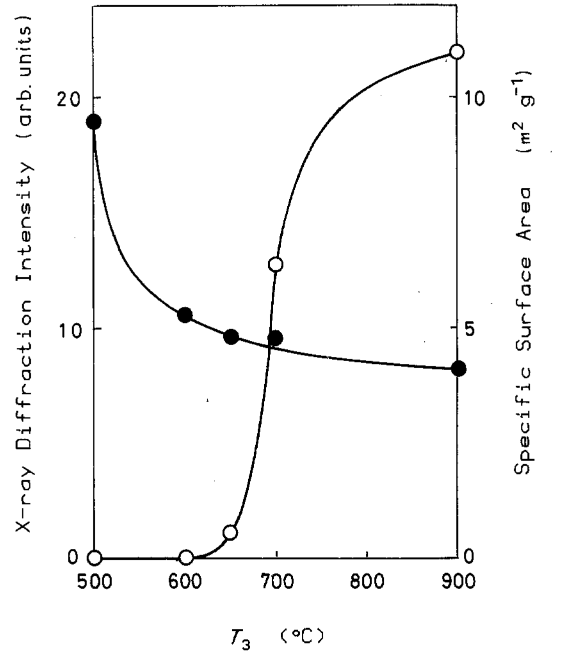

Figure 5 Effects of T_3. Si/Al = 1.25, NaOH concentration = 0.50 wt %. ○, X-ray intensity; ●, specific surface area.

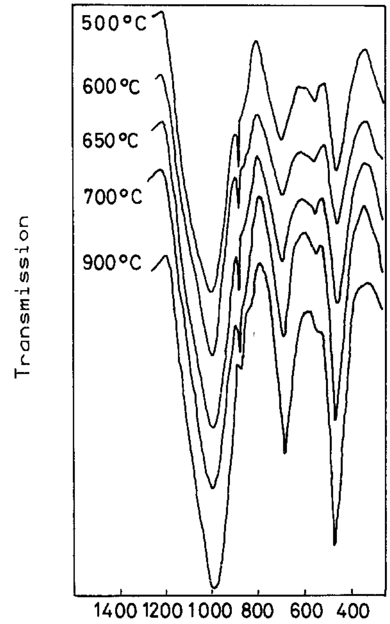

Figure 6 Infra-red spectra.

carnegieite were produced at temperatures higher than 650° C. The figure also indicates that the decrease of the specific surface area of the sample was small above 650° C. IR spectra of these samples are shown in Fig. 6. The temperature of the B_3 furnace is written in the figure. The absorption bands at 880 and 550 cm^{-1} are those assigned to sodium carbonate, and they disappeared after washing. The other three bands are those of aluminosilicate. The band at 990 cm^{-1} is observed in almost all the aluminosilicates, and is assigned to the asymmetrical stretching vibration of SiO_4 or AlO_4 [8]. The bands at 690 and 470 cm^{-1} are observed in nepherine which has the similar structure to that of carnegieite [8], and may be assigned to the common crystal structure of these compounds. These two absorption bands increased with increasing temperature. It should be noted that these two bands were observed below 600° C where no crystalline peak was observed in X-ray

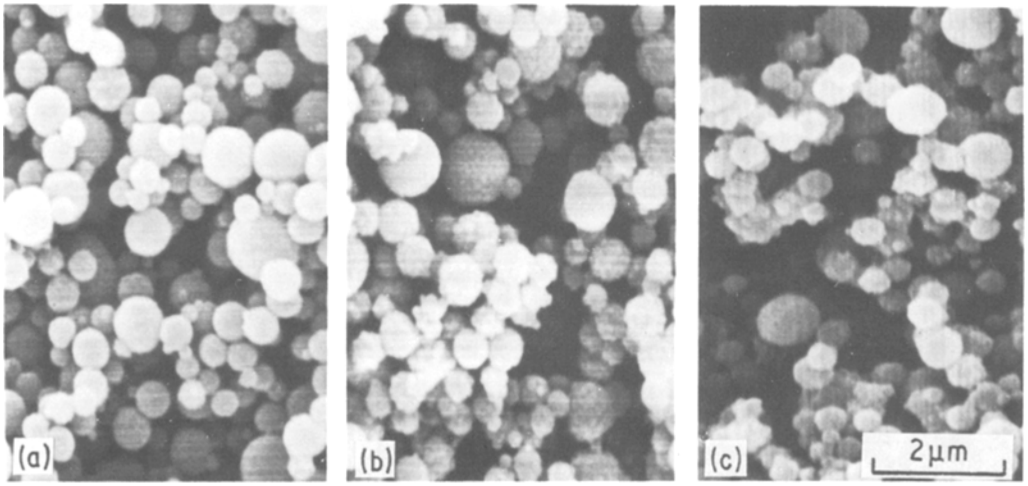

Figure 7 Scanning electron micrographs of carnegieite fine particles T_1 = 170, T_2 = 400, T_3 = 700° C, Si/Al = 1.00. NaOH concentration: (a) 0.40, (b) 0.52, (c) 0.61 wt %.

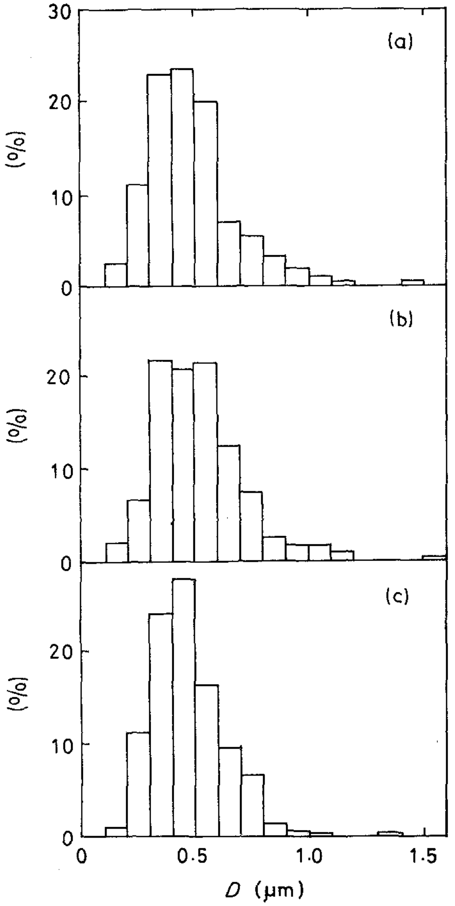

Figure 8 Particle size distribution.

diffraction. This may suggest that very small crystallites were formed at temperatures below 600° C.

Fig. 7 shows SEM photographs of the particles obtained with the solutions of different composition (Si/Al = 1.00 and NaOH concentration = 0.40 to 0.61 wt %). The particles are spherical and smaller than ca. 1 μm. The particle size distribution histograms of these samples (a, b and c) are shown in Fig. 8. They are almost the same, irrespective of NaOH concentration, or irrespective of the degree of formation of the carnegieite structure. The histograms of the samples shown in Fig. 5 were almost the same as those shown in Fig. 8. This is consistent with the results that the particle size is determined almost completely by the total concentration of reactant solution [5]. The number mean diameters of the samples (a, b and c) are 0.48, 0.52 and 0.61 μm, respectively, and are almost constant. The surface area calculated from the mean diameter, 5 $m^2 g^{-1}$, is almost the same as the observed BET surface area, suggesting that the particles are nonporous.

The Na_2O excess type carnegieite can be prepared by heat treatment (700° C) of the gel obtained by the coprecipitation of sodium silicate and aluminium nitrate. However, the specific surface areas of the samples prepared by this method were less than 1 $m^2 g^{-1}$. Therefore, the mist decomposition method can be an effective method to avoid the decrease of the specific surface area during crystal phase formation.

References

1. J. M. M. DE LAU, *Ceram. Bull.* 49 (1970) 572.
2. D. M. ROY, R. R. NEURGAONKAR, T. P. O'HOLLERAN and R. ROY, *ibid.* 56 (1977) 1023.
3. Y. YAMAZAKI and M. SATO, *Huntai oyobi Hunmatu-Yakin* 18 (1972) 280.
4. F. TOKUNAGA, Y. SUYAMA and A. KATO, *ibid.* 24 (1977) 43.
5. H. IMAI and F. ORITO, *Nippon Kagaku Kaishi* (1984) 851.
6. W. BORCHERT and J. KEIDEL, *Mineral u. Petrog.* 1 (1947) 2.
7. Y. KUBO, G. YAMAGUCHI and K. KASAHARA, *Mineralogical J.* 5 (1967) 213.
8. VON H. LEHMANN and H. DUTZ, *Tonind.-Ztg. Keram. Rundsch.* 83 (1959) 219.

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