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Control of micropore size distribution in alumina by the hydrothermal treatment of an alkoxide derived-alcogel

TOSHIMI FUKUI*, MAKOTO HORI
Technical Research Center, Krosaki Corporation, 1-1 Higashihama, Yahata-nishi, Kitakyushu 806, Japan

Alumina precursors were prepared by hydrothermal treatment of an alkoxide derived-alcogel. By selection of appropriate hydrothermal conditions aluminas with a variety of pore distributions were obtained, and the pore radius can be easily controlled from 5.0 to 23.5 nm. The hydrothermal conditions were found to strongly affect pore size distribution: (i) elevating the hydrothermal temperature and increasing the time increased the particle size of boehmite, resulting in the above average pore radius of the aluminas; (ii) the alumina obtained from HT-270-10 had an average pore radius of approximately 20 nm and $\geqslant 1$ ml g^{-1} pore volume, which were maintained until 1000 °C. After heating at 1200 °C for 5 h, their values were 17.9 nm and 0.45 ml g^{-1}, respectively; (iii) the hydrothermal treatment with ethanol gave boehmites with a large particle size and aluminas with a sharp pore distribution and small pore radius. These results were explained by differences in the three-dimensional structures formed by the hydrothermal treatments.

1. Introduction

Alumina is the most widely used material for supports and carriers of a variety of industrial catalysts, since it is inexpensive, chemically and thermally stable and it is possible to select a wide range of surface areas and porosities [1]. Porous alumina can be prepared by the dehydration of pseudo-boehmites, thus, the pore structure is affected by the size and shape of the pseudo-boehmite particle. Further, their aggregation and steric disposition during gelation, drying and calcining are important.

To control the pore distribution of an alumina, several methods have been applied; e.g. the addition of water soluble organic polymers to an aluminium nitrate derived-sol or water glass solution [2]; the pH swinging methods using sodium aluminate and aluminium nitrate [3]; the grain growth of pseudo-boehmite [4]; the glycothermal treatment of an aluminium alkoxide [5, 6].

The gels prepared by the hydrolysis of a metal alkoxide, i.e. the sol–gel method, have a large surface area and large pore volume, but their pore radii are usually very small, i.e. an average radius of several nanometres. Maeda *et al.* [7] indicated that the hydrolysis of an aluminium alkoxide with a polyglycol was attractive for the control of pore distribution. As the method does not involve an organic additive, drying of the alkoxide derived-alcogel under a supercritical condition of ethanol or CO_2 gave a large surface area of $\geqslant 400$ m^2 g^{-1} and large pore diameter of $\geqslant 10$ nm [8, 9].

In our earlier papers [10, 11], the thermally stable alumina was prepared by the hydrothermal treatment of an alkoxide derived-alcogel. Under particle fixed-condition, irregular grain growth of boehmite particles was observed, resulting in the appearance of a thermal stable alumina. In this paper, pore distribution of the boehmite prepared from an alcogel and the resultant aluminas were investigated. The influence of hydrothermal conditions on pore structure were discussed.

2. Experimental details

2.1. Preparation of alumina precursors

Aluminas were prepared using reagent-grade raw materials. Since Al alkoxides are sensitive to moisture, inhomogeneous precipitates are generated by the addition of water. In this study, in order to stabilize an Al alkoxide, ethyl acetoacetate, which easily decomposes on heating, was selected as a polydentate chelating reagent. Ethyl acetoacetate aluminium di-iso-propylate (etacAl) is synthesized as denoted by Equation 1.

EtacAl (27.43 g) in ethanol (25 ml) was hydrolysed with 1 M aqueous ammonia-ethanol (7.2–50 ml; H_2O/etacAl = 4). The resultant transparent solution was aged at 60 °C for 2 days, after which a transparent alcogel was obtained. The alcogel was hydrothermally

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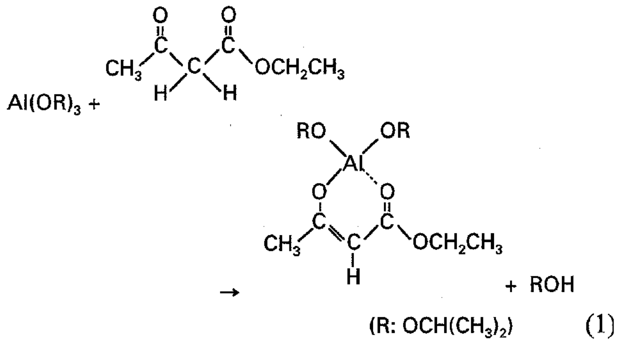
*To whom correspondence should be addressed.



(1)

treated under various conditions, e.g. temperature and solvent, and then dried in air at 100 °C. The alumina precursors obtained were labelled HT-170-6, HT-240-6, HT-270-6 and so on (the first and second number indicating the hydrothermal temperature treatment and holding time, respectively).

2.2. Characterization

Nitrogen isotherms of the HTs calcined were measured using an Autosorb (Quanta Chrome) at 77.4 K employing the conventional constant-volume method. Pore distributions in the range 1–100 nm were calculated from the nitrogen adsorption isotherms by the Barrett-Joyner-Halenda (BJH) method. Pore volumes were determined using the complete adsorption–desorption isotherm of nitrogen by the t curve method. Brunauer–Emmer–Teller (BET) surface areas were calculated from the nitrogen adsorption at 77.4 K. Crystalline phases were identified by powder X ray diffraction (XRD; RAD-RB, Rigaku Co.) using CuK$_\alpha$ radiation with a graphite monochromator. The crystallite size was determined by the X-ray line broadening technique from the Scherrer equation using the integral width of the diffraction peak.

3. Results and discussion

3.1. Influence of hydrothermal temperature and holding time

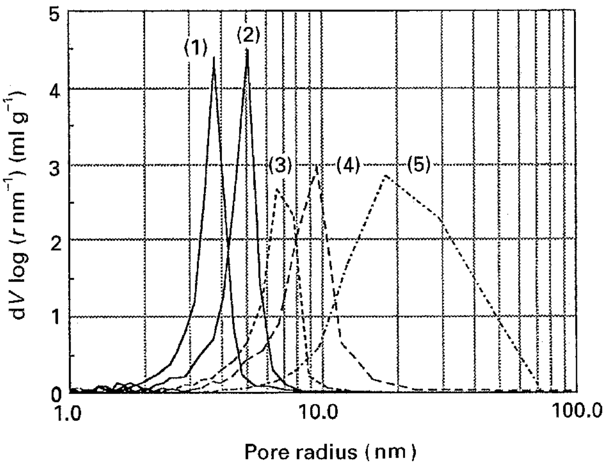


Figure 1 Pore distribution of the aluminas calcined at 600 °C for 5 h; (1) HT-170-6, (2) HT-200-6, (3) HT-240-6, (4) HT-270-6 and (5) HT-270-10.

The alkoxide derived-alcogel was hydrothermally treated under various conditions. Properties of the aluminas obtained are shown in Table I. Fig. 1 shows the pore distribution of the aluminas on calcining the HT-X-6 (X = 170, 200, 240 and 270) and HT-270-10 at 600 °C for 5 h. The average pore radius linearly increased from 5.0 to 10.6 nm on elevating the hydrothermal temperature from 170 to 270 °C, while the specific surface area decreased from 208 to 126 m^2 g^{-1} (Fig. 2 and Table I). The present alcogel crystallized to boehmite by the hydrothermal treatment [11]. Their crystalline sizes increased with increasing temperature which also corresponded to the decrease in the surface areas (Table I). Further, holding time also affected the pore radius (Fig. 1 and Table I). Thus, these changes in the pore distributions are caused by grain growth of the boehmite particles. In other words, pore distribution of the aluminas can be easily controlled by adjusting hydrothermal temperature and time.

3.2. Change of pore structure during calcining

Fig. 3 shows calcining temperature dependence on pore distribution of the HT-270-10. As-prepared,

TABLE I Properties of the resultant aluminas

Sample	Calcining temperature (°C)	Pore radius (nm)		Pore volume (ml g^{-1})	Specific surface area (m^2 g^{-1})	Crystalline size[a] (nm)
		Peak position	Average			
HT-170-6	600	3.7	5.0	0.52	208	–
HT-200-6		5.1	6.6	0.58	177	5.5
HT-240-6		6.7	8.1	0.52	129	14.5
HT-270-6		9.6	10.6	0.67	126	15.2
HT-270-10	as-prepared	12.5 and 28.4	18.1	1.06	113	13.5
	600	17.9	18.4	1.36	148	–
	800	17.6	15.8	1.05	133	–
	1000	17.7	20.6	1.11	107	–
	1100	17.7	23.5	0.89	76	–
	1200	12.7	17.9	0.45	51	–
HT-170-6WV	600	5.1	5.1	0.70	273	2.7
HT-170-6E		3.2	4.1	0.48	235	3.9
HT-170-6EV		3.2	4.0	0.48	243	3.8

[a] Crystalline size of boehmite on the (0 2 0) plane calculated by Scherrer's equation ($K = 1.1$).

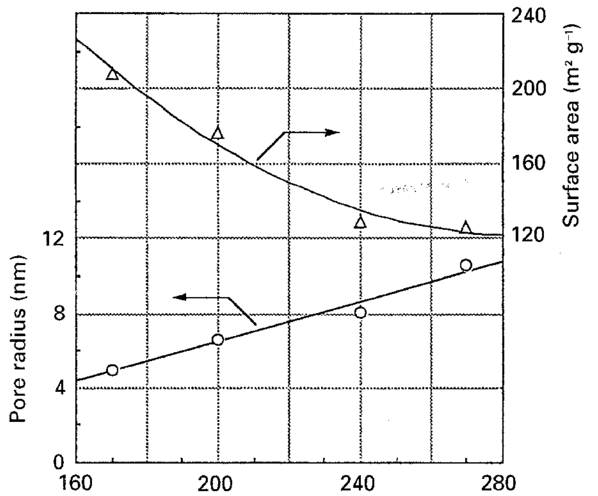


Figure 2 Hydrothermal temperature versus average pore radius and specific surface area of the aluminas.

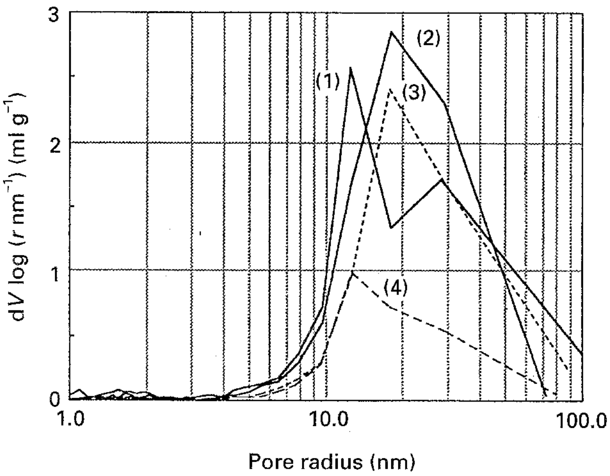


Figure 3 Pore distribution of HT-270-10 calcined at different temperatures for 5 h; (1) as-prepared, (2) 600 °C, (3) 1000 °C and (4) 1200 °C.

HT-270-10 had two peaks at 12.5 and 28.4 nm in the pore distribution. After crystallization to an alumina, the peaks in the pore distribution changed to a single peak. Its position was approximately 18 nm and remained almost unchanged on elevating the calcining temperature. The pore volume was $\geqslant 1.0\,\text{ml}\,\text{g}^{-1}$ at $\leqslant 1000\,°\text{C}$; further, a pore volume of $0.45\,\text{ml}\,\text{g}^{-1}$ was obtained at 1200 °C (Table I). On the other hand, surface area decreased with increasing temperature. During calcining, the HT-270-10 crystallized to transition aluminas such as γ, δ and θ, but α-alumina was only found as a trace at 1200 °C [11]. Accordingly, a rigid three-dimensional skeleton, which was almost unchanged by sintering and grain growth, was thought to be formed.

3.3. Influence of the solvents and setting condition of the alcogel

The alcogel was treated at 170 °C for 6 h (i) by dipping in water, HT-170-6, (ii) by water vapour, HT-170-6WV, (iii) by water vapour with dipping in ethanol, HT-170-6E, and (iv) by ethanol–water vapour (1 : 1 volume ratio), HT-170-6EV. Pore distributions of the resultant HTs calcined at 600 °C are shown in Fig. 4. The HT-170-6E and HT-170-6EV treated with ethanol had a sharp peak in the pore distribution and a small average pore radius. On the other hand, treatment with water vapour, the HT-170-6WV, produced a larger pore radius of 5.1 nm and a pore volume which increased from 0.48 to $0.70\,\text{ml}\,\text{g}^{-1}$. The pore distribution is thought to be determined by the grain size and the aggregation of the boehmite particles. HT-1706WV had a smaller crystalline size and larger surface area compared with HT-170-6E and HT-170-6EV; thus, its average pore radius and pore volume was expected to be smaller, but was in fact larger (Table I). Crystalline size of boehmite in individual plane directions and anisotropic ratio of grain growth to (0 2 0) plane (hereafter referred to as $R_{(***)}$, e.g. $R_{(200)}$ indicates the anisotropic ratio of the (2 0 0) plane) are shown in Table II. A commercial boehmite sample (Catapal D, Vista Chemical) was used for comparison. The HTs are found to have high grain-growth anisotropy when compared with Catapal D. In particular, $R_{(200)}$ and $R_{(002)}$ of HT-170-6WV had the values 3.7 and 5.8, respectively, which were large compared to those obtained for the other HTs. Packing of the plate particles tends to be a loose packing, and this loose packing texture would be maintained

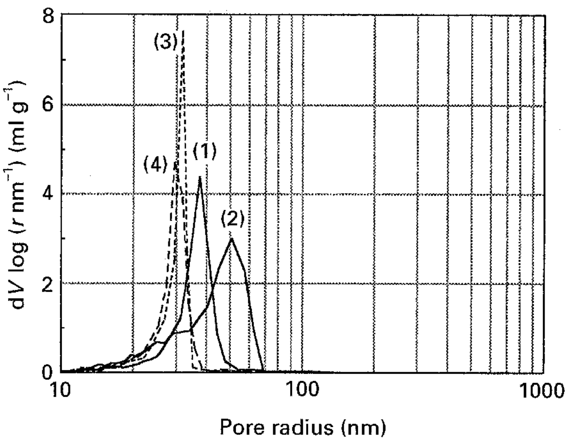


Figure 4 Pore distribution of the aluminas calcined at 600 °C for 5 h; (1) HT-170-6, (2) HT-170-6WV, (3) HT-170-6E and (4) HT-170 EV.

TABLE II Crystalline size and anisotropy of as-prepared boehmite

	(0 2 0)	(1 2 0)	(2 0 0)	(0 0 2)
HT-170-6WV	2.7	5.2	10.0	15.7
	–	1.9	3.7	5.8
HT-170-6E	3.9	6.9	11.9	14.5
	–	1.8	3.1	3.8
HT-170-6EV	3.8	6.8	11.5	14.6
	–	1.8	3.1	3.9
Catapal D	4.4	9.6	9.6	13.6
	–	1.6	1.9	2.2

Upper line: crystalline size, nm.
Lower line: anisotropy of crystalline size on individual plane to (0 2 0) plane.

after being crystallized to alumina. Thereby, these differences in the three-dimensional networks of the particles would produce the different pore distributions, but not for particle size.

The present alcogel, which is amorphous, was prepared by the hydrolysis of etacAl with ammonia water at ambient temperature, and crystallized to form boehmite by applying the hydrothermal treatment. Nucleation and grain growth of boehmite occur through dissolution to hot water and precipitation of Al components. Therefore, the particle size of the boehmite was determined by the relationship between the dissolution and precipitation rates. Low solubility means slow mobility of the Al components and a fast grain growth rate, thus, gel skeleton rearrangement in ethanol is expected to be inhibited. Actually, simultaneous use of ethanol increased particle size, but pore size remained small. In the case of water only, movement of Al components was accelerated due to repetition of the dissolution–precipitation process, resulting in large pores and a small particle size. Accordingly, differences in pore distribution are explained by the differences in the three-dimensional structures formed by the hydrothermal treatments.

4. Conclusions

Alumina precursors were prepared by hydrothermal treatment of an alkoxide derived-alcogel. Pore distribution of the resultant aluminas were examined, and the influence of the hydrothermal conditions on the pore structure was discussed.

1. Increasing hydrothermal temperature and time increased the particle size of boehmite, resulting in an average pore radius for the aluminas.

2. The alumina obtained from the HT-270-10 had an average pore radius of approximately 20 nm and a pore volume $\geqslant 1\,\mathrm{ml\,g^{-1}}$, which were maintained up to 1000 °C. Further, after heating at 1200 °C for 5 h, these values changed to 17.9 nm and $0.45\,\mathrm{ml\,g^{-1}}$, respectively.

3. The hydrothermal treatment with ethanol gave boehmites with large particle size and aluminas with a sharp pore distribution and small pore radius. These results were explained by differences in the three-dimensional structures formed by the hydrothermal treatments.

By selection of appropriate hydrothermal conditions, aluminas with various pore distributions were obtained, and their pore radii were easily produced to obtain values ranging from 5.0 to 23.5 nm.

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