Microporous Structure of Alumina Prepared by a Salt Catalytic Sol-Gel Process

Kazuhiko Tanaka, Tomohito Imai, Yasushi Murakami,* Taki Matsumoto, Wataru Sugimoto, and Yoshio Takasu
Department of Fine Materials Engineering, Faculty of Textile Science and Technology, Shinshu University,
3-15-1 Tokida, Ueda 386-8567

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A microporous structure of alumina with a narrow distribution of the pore size (~0.4 nm in diameter) was synthesized by a salt catalytic sol-gel process of dilute $Al(OCH(CH_3)_2)_3$ and H_2O solution without any template molecule. The specific surface area of alumina after the calcination at 300 °C was 960 m^2g^{-1} while it was 170 m^2g^{-1} even after the calcination at 900 °C.

Microporous materials have been utilized in various fields such as catalysis, molecular sieving and selective adsorption. In particular, microporous structures of metal oxides were popular for silica-based oxides. Alumina is a potential material employed as catalysts, adsorbents, thermally conductive materials. Many important applications in separation, such as hyperfiltration, reverse osmosis, and gas separation require membranes having pores smaller than 2 nm[1].

Zeng and his collaborators have prepared alumina by a sol-gel process using the precursor system of aluminum tri-*s*-butoxide – 2,4-pentanedion (acetylacetone) – 2-propanol –nitric acid. Acetylacetone in the mole ratios of 0.3–0.4 to aluminum tri-*s*-butoxide was used as a chelating agent. The microporous form with a pore size (< 1.6 nm) was obtained by the calcinations at 200–300 °C ($S_{BET} = 674\,m^2g^{-1}$). They have proposed that micropores are formed by the development of intraparticle porosity during calcination.[2]

Although the organic template such as acetylacetone was effective for introducing micropores, the alumina network was broken during the release of organic groups. Much simpler method such as ''aluminum alkoxide to microporous alumina'' is required for the general applications. We focused on the dilute condition of reactants for the new method to prepare the microporous structure. We have revealed that the microporous structure ($d_{pore} < 1$ nm) of titanium oxide was synthesized by the salt catalytic sol-gel process of the dilute titanium alkoxide and H_2O solution.[3]

If the alkoxide content was small to introduce the micropores and the water content was also small to control the mesopore formation, the reaction was too slow for the polycondensation of aluminum alkoxide species. We have found that a salt catalyst such as ammonium carbonate or ammonium acetate accelerates polycondensation more effectively than conventional catalysts such as acid or base catalysts.[4,5] The salt catalyst allows the sol-gel process under a dilute condition of reactants. In this study, a microporous structure of alumina is synthesized by a salt catalytic sol-gel process of dilute aluminum isopropoxide ($Al(OCH(CH_3)_2)_3$) and H_2O solution.

In nitrogen atmosphere, 15 ml of a butanol solution containing 10 mmol of $Al(OCH(CH_3)_2)_3$ and 10 ml of another butanol solution containing 20 mmol of H_2O and 0.1 mmol of ammonium acetate were prepared. A sol-gel reaction started when the two butanol solutions were mixed to be a total of 25 ml ($Al(OCH(CH_3)_2)_3$: 0.4 M, H_2O: 0.8 M and CH_3COONH_4: 0.004 M). Reaction temperature was kept to be at 25 °C. Separated gel was obtained after five days. The resulting gels were dried in vacuo at room temperature for 6 h. Dried alumina was calcined at temperatures 300–1000 °C for 2 h in air. A nitrogen adsorption-desorption isotherm was measured after calcined alumina was degassed at 200 °C for another 2 h.

The N_2 adsorption-desorption isotherm of the alumina calcined at 300 °C is of type I. The pore diameter of alumina was estimated to be about 0.4 nm with narrow distribution by the MP method (see Figure 1), while no mesopore was observed by the BJH method (see Figure 1 inset). The specific surface area of alumina calcined at 300 °C was ca. 960 m^2g^{-1} (see Table 1). The thermogravimetric data shows that ca. 70% of the organic residue was removed at 300 °C.

The isotherms of the alumina calcined at 400–900 °C are of type IV. The inset in Figure 1 shows the mesopore distibution for the calcined alumina by the BJH method. Pore diameters of the alumina calcined at 400–900 °C were distributed in 2–6 nm. The mesopore was formed by the calcination above 400 °C since the primary particles would be aggregated.

Figure 1 shows the micropore distribution for the calcined alumina by the MP method. After the calcination at 600 °C, the micropore of 0.6–0.8 nm was observed. The microporous structure was formed in the primary particles during the sol-gel reaction. The thermogravimetric data shows that all the organic

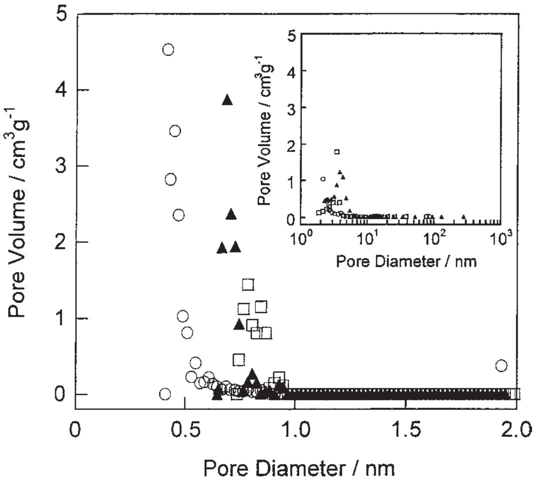

Figure 1. Micropore size distributions obtained by the MP method for nitrogen adsorption-desorption isotherms of alumina prepared by the salt catalytic sol-gel process at 25 °C. These samples were calcined at 300 °C (○), 600 °C (▲) and 900 °C (□) for two hours. In the inset, mesopore size distributions obtained by the BJH method.

residues were removed below 600 °C. The micropore in the alumina calcined at 300 °C was much smaller ($d_{pore} < 0.5$ nm) since the organic residue is on the micropore of alumina surface. The micropore still remains even after the calcination at 900 °C.

Table 1. Specific surface areas of alumina calcined at various temperatures

Calcined temp. /°C	Specified surface areas*1 /m^2g^{-1}
300	960
400	500
500	410
600	310
800	220
900	170
1000	2

*1 Specific surface area was estimated using the BET model for all samples except the sample calcined at 300 °C where it was based on the Langmuir model.

Table 1 lists the specific surface areas of the alumina calcined at various temperatures. The specific surface area of alumina decreased gradually with an increase in the calcination temperature and was still 170 m^2g^{-1} after the calcination at 900 °C.

Figure 2 shows the XRD patterns of the calcined alumina. No peak was observed for alumina heated at 300 or 600 °C. The peaks due to γ-alumina appeared after the calcination at 900 °C. Differential thermal analysis shows the crystallization at ca. 850 °C. This crystallization temperature of alumina is highr than that of the conventional alumina. The microporous structure would prevent the crystallization. The peaks due to α-alumina was observed after the calcination at 1000 °C. The surface area considerably decreased by the transformation of γ-alumina to α-alumina.

Alumina was prepared by the salt-catalytic sol-gel process under dilute conditions of reactants, which has a larger number of micropores ($d_{pore} \sim 0.4$ nm) but few mesopores. These micropores remain after the calcinations even at 900 °C. The alumina prepared by this method has a potential for applications of porous materials with thermal stability.

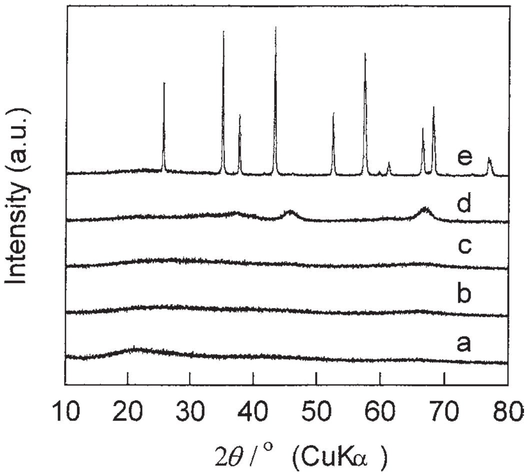

Figure 2. XRD patterns of alumina (a) as prepared, and calcined at (b) 300 °C, (c) 600 °C, (d) 900 °C, and (e) 1000 °C for 2 h.

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