

A novel alumina catalyst support with high thermal stability derived from silica-modified alumina aerogel

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A new alumina catalyst support with high thermal stability was synthesized. The high thermal stability was achieved through the synergetic effect of silica addition and the ultra-low bulk density (aerogel). The amount of silica was varied from 2.5 to 10 wt% and 5 wt% was found to be most effective for suppressing phase transformation; the θ phase remained even after heating at 1400 °C for 1 h. The surface areas of the present alumina with 5 wt% silica were 86 and 36 m²/g after heating at 1300 and at 1400 °C, respectively.

Keywords: alumina, aerogel, silica addition, thermal stability

1. Introduction

High thermal stability has recently been required for catalyst systems, such as automobile catalysts, high-temperature catalytic combustion, etc. One of the causes for the thermal degradation of catalysts or catalyst supports is the decrease in surface area. Alumina is most widely used as a catalyst support because of its large surface area. However, its surface area is decreased from 100–200 to 1–5 m²/g after heating at 1150 °C, at which the phase transformation concomitantly occurs from θ - to α -alumina. In order to maintain a large surface area even at high temperatures, suppression of the phase transformation is required. It is reported that the addition of other elements, such as Si, Zr, La, and so on, is effective for the suppression of the phase transformation [1–3]. It is also reported that decreasing the bulk density of alumina powders (aerogel) is an effective way for increasing the thermal stability of the resultant alumina [4]. Therefore, from the combination of these two methods we may expect a synergetic effect for the production of thermally stable alumina. This paper describes such possibility.

2. Experimental

The synthesis procedure was as follows. First, boehmite (AlO(OH)) sol was obtained according to the method given by Yoldas [5]. 0.1 mol (20.4 g) of Al(*i*-OC₃H₇)₃ was hydrolyzed with 80 ml hot water (80 °C) under vigorous stirring to obtain the precipitate of boehmite. Then, 10 ml HNO₃ (1 N) was added and refluxed at 90 °C in a flask for 1 h to obtain a transparent boehmite sol. Various amounts of Si(OC₂H₅)₄ (TEOS, 2.5–10 wt%) were also hydrolyzed with 10 ml HNO₃ (1 N) at room temperature followed by

the addition of the resultant TEOS sol to the boehmite sol. Then, 1–3 g urea was added and the mixture was refluxed at 90 °C in an oil bath. The viscosity of the sol increased and finally the sol changed into gel. The gel was immersed in ethanol for 3 days in order to replace the water and isopropanol in the pores with ethanol. Ethanol was changed once a day. In order to dry the gel without shrinkage, the gel was dried under the supercritical condition of ethanol (6.4 MPa, 516 K) in an autoclave. The dried gel was fired at the temperature between 1100 and 1400 °C for 1 h in the atmosphere. The crystalline phase was identified on a powder diffractometer (MXP3, MAC Science Inc.) operated at 40 kV and 20 mA with a Cu tube. BET surface area and pore size distribution were measured on a volumetric gas adsorption measurement instrument (Belsorp36, Nippon Bel Inc.) at liquid-nitrogen temperature. Larger pores were measured on a mercury porosimeter (Porosimeter 2000, Carlo Erba Strumentazione Inc.).

3. Results

Figure 1 shows the variation of BET surface area with the heating temperature. Alumina obtained by the thermal decomposition of boehmite was also indicated for comparison with the new alumina. The surface area of ordinary alumina was 20 m²/g at 1100 °C and 1 m²/g at 1400 °C. In contrast, the surface area of the new alumina kept high values, i.e., larger than 100 m²/g below 1200 °C and about 80 m²/g even at 1300 °C. Below 1300 °C, the three samples exhibited about the same surface area. At 1400 °C, a marked difference in the surface area was observed among the three samples. The alumina with 10 wt% silica exhibited the lowest surface area and that with 2.5 wt% silica had the surface area of 23 m²/g. The alumina with 5 wt% silica

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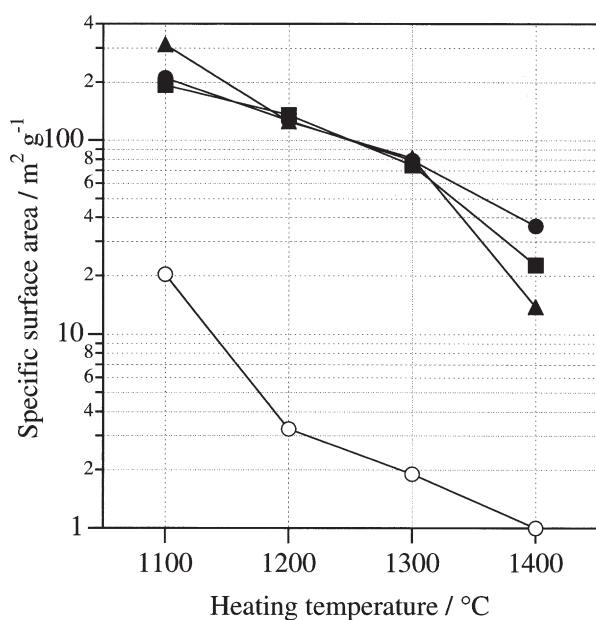


Figure 1. Change in surface area of alumina with heating temperature. (○) Alumina obtained by decomposition of boehmite, (■) silica 2.5 wt%, (●) silica 5 wt%, (▲) silica 10 wt%.

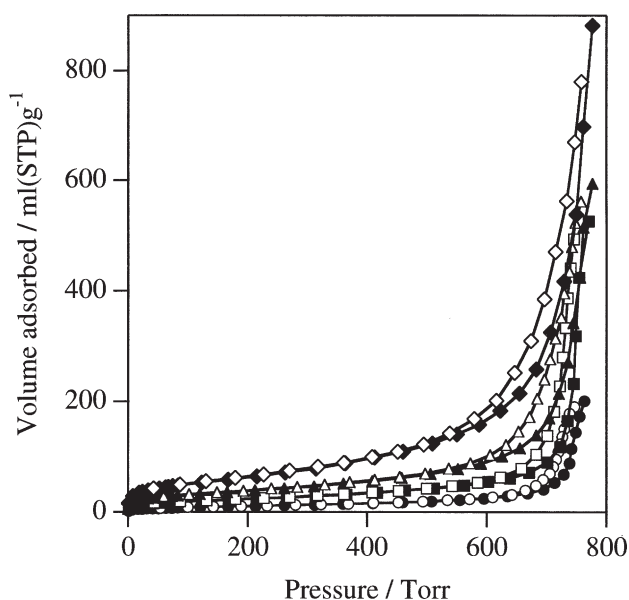


Figure 2. N₂-adsorption isotherms of alumina with 5 wt% silica at -196 °C. (●, ○) Heated at 1400 °C, (■, □) 1300 °C, (▲, △) 1200 °C, (◆, ◇) 1100 °C. Solid symbols are adsorption branch and open symbols are desorption branch.

showed the highest surface area (36 m²/g). This value is quite high compared with a conventional alumina.

Another feature of this alumina is its large pore size and large pore volume. Figure 2 shows the N₂-adsorption isotherms at liquid-nitrogen temperature and table 1 summarizes the pore diameter and the pore volume of the alumina with 5 wt% silica. The offsets of the adsorption isotherm were in the higher pressure and the isotherms of the samples were shifted to the higher pressure with the increase of the heating temperature. Pore size and pore vol-

Table 1
Pore diameter and pore volume of the alumina with 5 wt% silica.

Heating temperature (°C)	Pore diameter (nm)	Pore volume (cm ³ /g)
1100	10.8	1.28
1200	18.6	0.91
1300	36.6	0.82
1400	29.2	0.31

ume were calculated from the desorption branch by the DH method [6]. The pore diameter of a conventional γ -alumina is usually smaller than 10 nm. On the other hand, the pore diameters of our alumina were larger than 10 nm. The pore volume of a conventional alumina is usually around 0.5 cm³/g. In this alumina, pore volumes were around 0.8–1.0 cm³/g except for the sample heated at 1400 °C.

Large pore size and pore volume depends on the microstructure of the aerogel. Aerogel has quite a low bulk density and has quite large pores. The pore size distribution of the aerogel before high-temperature treatment exhibited a wide pore size distribution (2 nm–1 μ m). Pore volume was largest at the largest pore size (1 μ m) and decreased monotonically with the decrease of the pore size. After high-temperature heat treatment, macropores collapsed and mesopores remained. A conventional alumina had mesopores around 10 nm before heat treatment and mesopores had diminished and a small amount of macropores of about 150 nm remained after heat treatment. The feature of the microstructure of alumina aerogel is a small number of contacting points between the alumina crystallites compared with ordinary alumina. The crystallites of a conventional alumina adhered stiffly and a large number of contacting points exist. Necks are created at the contacting points at high temperatures and aluminum and oxygen atoms diffuse through the neck. Therefore, a small number of necks is preferable for preventing mass transfer, i.e., sintering.

The transformation of alumina from γ to α phase induces a marked reduction of surface area. In order to reveal the relationship between the alumina phase and the surface area, XRD patterns were taken. Figure 3 shows the XRD patterns of the aluminas heated at 1400 °C. As for the ordinary alumina shown in figure 1, it had already transformed to the α phase at 1100 °C and the surface area decreased to as low as 1 m²/g. Silica-modified alumina kept the θ phase below 1300 °C. The phase transformation was observed by heating at 1400 °C. The alumina with 2.5 wt% silica transformed to the α phase completely at this temperature. The alumina with 5 wt% silica still kept the θ phase along with a small amount of the α phase. The alumina with 10 wt% silica transformed to the α phase and mullite was also observed. The surface area of the alumina with 5 wt% silica was highest (36 m²/g) and the alumina with 10 wt% silica shows rather high surface area (24 m²/g) in spite of the complete transformation to the α phase. Formation of the mullite phase in the alumina with 10 wt% silica decreased the surface area considerably (13 m²/g). It is considered that an appropriate silica content exists to

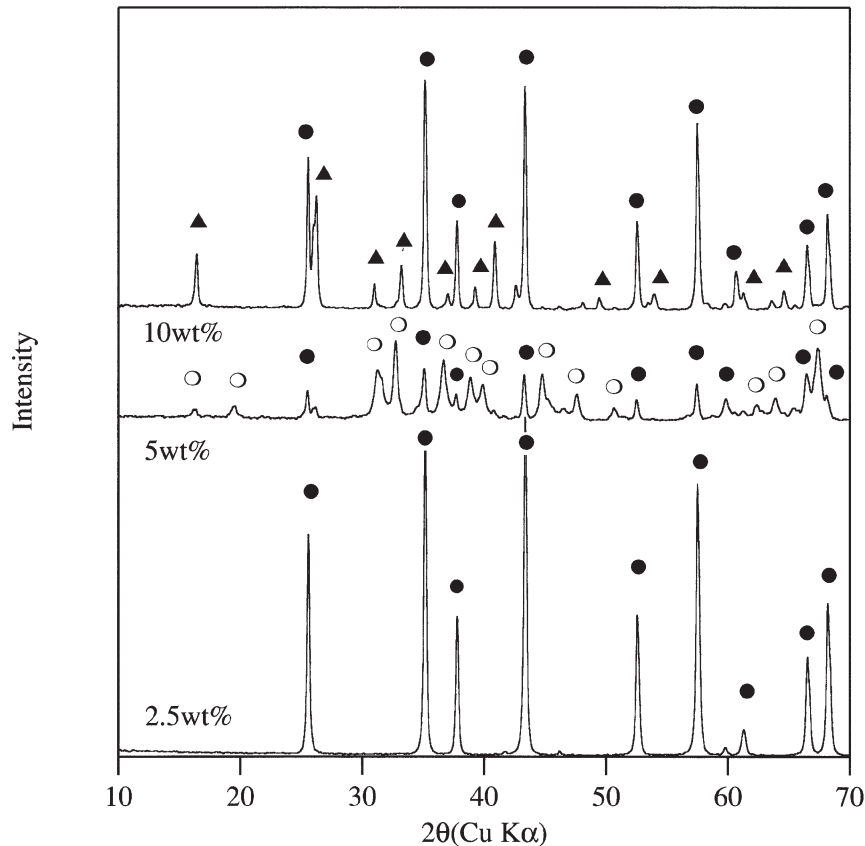


Figure 3. XRD patterns of aluminas with silica heated at 1400 °C. (○) θ -phase alumina, (●) α -phase alumina, (▲) mullite.

keep the θ phase. Too much silica does not result in the suppression of phase transformation.

4. Discussion

Here, the suppression mechanism of phase transformation is discussed. There seem to be at least two main causes for the suppression of phase transformation. One is the stabilization of the crystal structure of alumina by the addition of the other elements. Si, the ionic radius of which is similar to that of Al, may be incorporated into γ -phase alumina, when boehmite decomposes to form γ -phase alumina at about 500 °C. γ -alumina has a spinel structure and has many vacancies in the octahedral sites. Si can be incorporated into tetrahedral sites, and, as a result, extra Al atoms may be moved from tetrahedral to octahedral sites, thereby decreasing the total number of vacancies. A unit cell of spinel has 8 tetrahedral cation sites, 16 octahedral cation sites and 32 anion sites. In order to satisfy the stoichiometry, there have to be 2.7 vacancies in the octahedral sites. The percentage of vacancy sites to the total cation sites is about 10%. If Si atoms fill the tetrahedral sites and Al atoms fill the octahedral sites completely, silica content will be about 13 wt%. In this study, silica contents were less than 10 wt% and no silica containing crystalline phase was observed below 1300 °C. At higher temperature, the γ phase transforms to the monoclinic θ phase,

which also has tetrahedral and octahedral cation sites, and, therefore, Si atoms can still exist in the θ -alumina structure. By the incorporation of Si into the alumina structure, lattice vibration of alumina at high temperatures will be suppressed to suppress the rearrangement of atoms which leads to the nucleation of the α phase. Such an effect is also supported by the results of molecular dynamics simulation studies [7]. After phase transformation, mullite was observed in the alumina with 10 wt% silica. In the α phase, Al atoms are in octahedral sites. An excess amount of silica will be eliminated from the corundum structure to form the mullite.

Another cause of the suppression of phase transformation is the low bulk density. The low bulk density means the small number of contacting points between the alumina crystallites in a unit volume of alumina powder. At the contacting points, necks are developed at high temperature. At the neck, the surface curvature is negative, i.e., lower surface chemical potential than the flat surface and/or the surface with the positive curvature. Atoms migrate to the neck from the high chemical potential surface to enhance mass transportation. At the same time, at the surface with negative curvature, equilibrium vacancy concentration is higher than that at the surface with positive curvature and/or flat surface. High concentration of vacancies may result in the enhancement of lattice vibration and the rearrangement of surface atoms. Hence, the alumina with low bulk density is hard to transform to the α phase.

It is also reported another alumina with high surface area, derived from boehmite sol. The alumina is synthesized with a micelle structure by using bilayer-forming ammonium amphiphile [8]. Our alumina does not need such a special surfactant and can be synthesized from commercial boehmite sol. Our method is an industrially practical production process. The high surface area and large pore size of our new alumina should be favorable for the reaction process under high temperature and high space velocity conditions.

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