

Preparation of thermally stable aluminas by hydrothermal treatment of an alkoxide-derived gel

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Catalytic combustion is expected to inhibit generation of thermal NO_x (nitrogen oxides) and increase combustion efficiency [1]. To control catalytic combustion, development of a catalyst support which can be used at temperatures above 1000 °C is necessary. Transition aluminas have been widely used as catalyst supports because of their high surface area and thermal stability. However, these aluminas could not be used as a support of catalytic combustion, since they rapidly decrease their specific surface area with transformation to the α form of alumina at temperatures above 1000 °C. Machida *et al.* [2] and Yamashita *et al.* [3] reported that the addition of alkaline earth and/or rare earth elements was attractive for stabilizing aluminas at high temperatures. In particular, alumina containing Ba, prepared by the sol-gel method, maintains $> 10 \text{ m}^2 \text{ g}^{-1}$ of specific surface area at high temperatures, i.e. $\geq 1400 \text{ }^\circ\text{C}$, because of the formation of low-sinterable barium hexa-aluminate ($\text{BaO}-6\text{Al}_2\text{O}_3$) [2]. Production of thermally stable aluminas with no additives by microstructural control was attempted; i.e. alumina aerogels dried under supercritical conditions [4], and alumina powders by complexing assisted sol-gel method using polyglycol [5] or by spray pyrolysis of a boehmite sol [6]. However, the thermal stability at $\geq 1400 \text{ }^\circ\text{C}$ was not achieved by the above methods. In our study, processing of an alumina which would operate stably at $\geq 1400 \text{ }^\circ\text{C}$, was researched. Alumina precursors were prepared by hydrothermal treatments of an alkoxide-derived gel. The resultant alumina was discovered to have a thermal stability over a range of higher temperatures, especially $\geq 1400 \text{ }^\circ\text{C}$.

Aluminas were prepared using reagent grade raw materials. Ethyl acetate aluminum di-iso-propylate (etac Al), 27.43 g, in ethanol, 25 ml, was hydrolysed with 1 M aqueous ammonia-ethanol (7.2 ml-50 ml; $\text{H}_2\text{O}/\text{etacAl} = 4$). The resultant transparent solution was aged at 60 °C for 4 days, after which a transparent alcogel was obtained. The alcogel was hydrothermally treated at a temperature between 170 and 270 °C for 6 h, and was dried in air at 100 °C. The alumina precursors obtained are called HT-170, HT-200, HT-240 and HT-270, the numbers indicating the temperature of the hydrothermal treatment. For comparison, an alumina aerogel was prepared. The above alcogel was treated for 6 h under the supercritical condition of ethanol (270 °C, 26.5 MPa), and then an alumina aerogel was

obtained by removing solvents with decreasing pressure.

The HTs were fired in air at a heating rate of $100 \text{ }^\circ\text{C min}^{-1}$ to various temperatures for 5 h, and the Brunauer-Emmett-Teller (BET) surface area was measured by the nitrogen adsorption method (monosorb, Quanta Chrome). Crystalline phases were identified by a powder X-ray diffraction method (XRD; RAD-RB, Rigaku Co.) using $\text{Cu K}\alpha$ radiation with a graphite monochromator. The aerogel obtained, a commercial γ -alumina (Puralox SBA-130, Condea Chemie) and a boehmite (Dispal 11N7-80, Vista Chemical) were used as comparative samples.

As for using alumina as a catalytic combustion support, one of most necessary factors is to keep a high specific surface area (SSA) after heating to $\geq 1000 \text{ }^\circ\text{C}$. Thus, the thermal stability of the HTs was estimated by changes on the SSAs of aluminas after heating. The HT-270 heated to $\geq 1200 \text{ }^\circ\text{C}$ maintained the highest SSA; 10.2 and $5.4 \text{ m}^2 \text{ g}^{-1}$ at 1400 and 1500 °C, respectively, while the HT-270 heated to $\leq 1100 \text{ }^\circ\text{C}$ had an SSA of about $100 \text{ m}^2 \text{ g}^{-1}$, which was the same value as that of γ -alumina and boehmite (Fig. 1). The aerogel at 1200 °C, which was reported to be one of the most thermally stable [4], had a high SSA of about $70 \text{ m}^2 \text{ g}^{-1}$ compared to that of HT-270, but its SSA at $\geq 1400 \text{ }^\circ\text{C}$ was

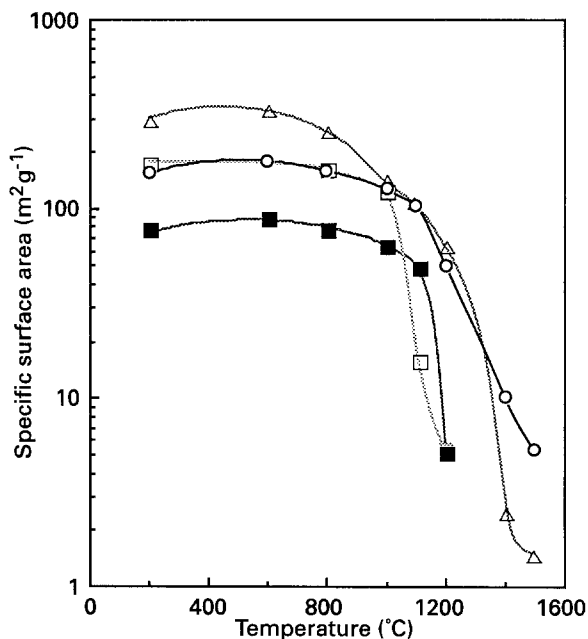


Figure 1 Change in the specific surface area of different aluminas after heating at various temperatures: (○), HT-270; (△), aerogel; (□), γ -alumina; (■), boehmite.

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$\leq 3 \text{ m}^2 \text{ g}^{-1}$. The alumina with no additive prepared by hydrothermal treatment of the alcogel could maintain a high SSA of $\geq 10 \text{ m}^2 \text{ g}^{-1}$ at high temperatures, $\geq 1400 \text{ }^\circ\text{C}$. The XRD results are shown in Fig. 2 and Table I. The HT-270 possessed a typical boehmite-type XRD pattern [7], and crystallized to α phase via γ , δ and θ phases at $1200 \text{ }^\circ\text{C}$. The α transformation temperature was elevated compared to that of the commercial γ -alumina and the boehmite (Table I). The aerogel with high thermal stability at $1200 \text{ }^\circ\text{C}$ also possessed a high α transformation temperature. Addition of La_2O_3 and SiO_2 is known to be attractive for thermal stability because of inhibition of α transformation [3, 8–10]. Similarly, the thermal stability at $\leq 1200 \text{ }^\circ\text{C}$ of the HT-270 is thought to be achieved by inhibiting α transformation; however, that at $\geq 1400 \text{ }^\circ\text{C}$ cannot be explained.

The effect of hydrothermal treating temperatures on the thermal stability are described. As-prepared HTs and the HTs after heating at $1000 \text{ }^\circ\text{C}$ showed slightly increasing SSAs with elevating hydrothermal treatment temperatures (Fig. 3). On the other hand, when heating at $1200 \text{ }^\circ\text{C}$, the SSA of HT-270 was $35.0 \text{ m}^2 \text{ g}^{-1}$, but $4.1 \text{ m}^2 \text{ g}^{-1}$ for the HT-170. The thermal stability of the HTs reversed at the temperature which is the α transformation temperature of usual transition aluminas. Even if heating at $1100 \text{ }^\circ\text{C}$ (Fig. 4), the effect of high temperature hydrothermal treatment was observed after long holds at temperature. After heating for 100 h the SSA of the HT-270 had hardly changed, i.e. about $70 \text{ m}^2 \text{ g}^{-1}$, while those of the HT-200 and HT-240 apparently decreased with time. Differences in these thermal

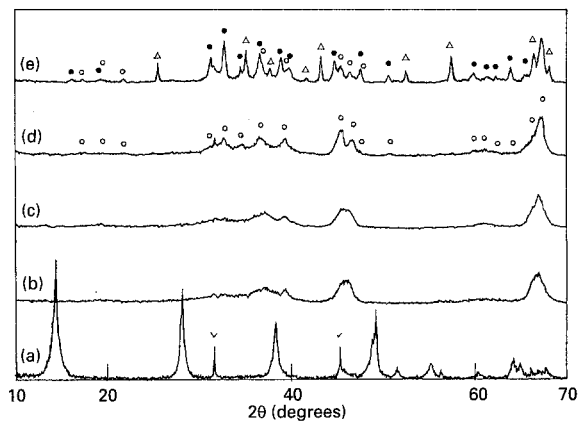


Figure 2 XRD patterns of the HT-270 after heating at various temperatures for 5 h. (a) As-prepared, (b) $600 \text{ }^\circ\text{C}$, (c) $800 \text{ }^\circ\text{C}$, (d) $1000 \text{ }^\circ\text{C}$ and (e) $1200 \text{ }^\circ\text{C}$: \circ , δ -alumina; \bullet , θ -alumina; Δ , α -alumina; ∇ , NaCl used as a support.

TABLE I Crystalline phases of different aluminas heated at various temperatures^a

Temperature ($^\circ\text{C}$)	HT-gel	Aerogel	γ -alumina	Boehmite
As-prepared	B	B	–	–
800	γ	γ	γ	γ
1000	δ	$\theta > \delta$	$\theta > \delta$	δ
1100	$\delta \gg \theta$	θ	$\alpha \gg \text{un}$	θ
1200	$\delta \gg \theta > \alpha$	$\theta \gg \alpha$	α	α

^aB, boehmite; γ , γ -alumina; δ , δ -alumina; θ , θ -alumina; α , α -alumina; un, unknown peak.

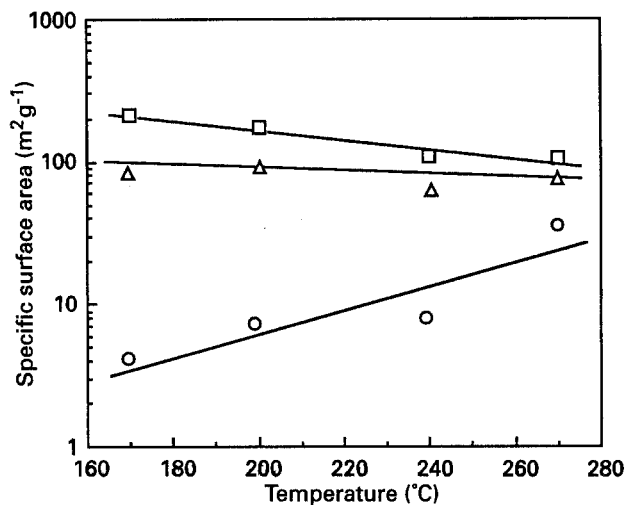


Figure 3 Hydrothermal treatment temperature versus specific surface area of the HTs after heating at various temperatures for 5 h: (\square), as-prepared; (Δ), $1000 \text{ }^\circ\text{C}$; (\circ), $1200 \text{ }^\circ\text{C}$.

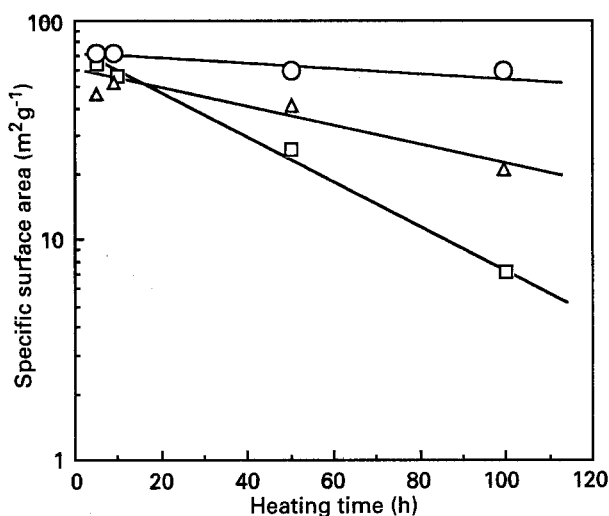


Figure 4 Heating time versus specific surface area of the HTs after heating at $1100 \text{ }^\circ\text{C}$: HT prepared by hydrothermal treatment at (\square), $200 \text{ }^\circ\text{C}$; (Δ), $240 \text{ }^\circ\text{C}$; (\circ), $270 \text{ }^\circ\text{C}$.

stabilities depends on thermal treatment temperatures. Adschiri *et al.* reported that hydrothermal conditions, i.e. pressure and temperature, strongly affect the particle size, morphology and crystal structure of boehmite from a metal salt aqueous solution [11]. Similarly, differences in morphology and crystal structure of the HTs would give their different thermal stability.

In conclusion, the alumina precursors were prepared by hydrothermal treatment of an alkoxide derived alcogel. The alumina treated at $270 \text{ }^\circ\text{C}$ (HT-270) showed the excellent thermal stability; with SSAs of 10.2 and $5.4 \text{ m}^2 \text{ g}^{-1}$ after heating at 1400 and $1500 \text{ }^\circ\text{C}$, respectively. As for heating at $1100 \text{ }^\circ\text{C}$, the SSA, about $70 \text{ m}^2 \text{ g}^{-1}$, of the HT-270 was constant for 100 h. These thermal stabilities depend on the hydrothermal conditions.

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