Preparation of heat-resistant alumina using a coprecipitation method

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Introduction

Forms of alumina with a large specific surface area, such as γ-alumina, are useful as supports for automotive or steam reforming catalysts. However, conventional porous alumina having a large specific surface area readily undergoes transition to the α-phase at temperatures of 1000°C or higher [1]. Transition to the α-phase tends to be more pronounced in the presence of water vapor [2] and under high pressure. In particular, reduction in the specific surface area of alumina used as catalyst supports decreases catalytic activity. Therefore, the material must possess heat resistance to maintain a large specific surface area, even at high temperatures. The present study describes a process for preparation of heat-resistant alumina using a coprecipitation method.

Materials and Methods

An ethanol solution of tetraethylorthosilicate was added to an aq. aluminum nitrate nonahydrate solution. The solution was heated, and aq. ammonia was added dropwise with stirring to adjust the pH to 8. Aluminum hydroxide and a silicon compound coprecipitated as the aqueous ammonia were then added. The dried precipitate was calcined at 1000°C in air to yield a heat-resistant alumina containing 0.5–10 mass% SiO_2 with respect to the total mass of SiO_2 plus Al_2O_3. Aging of the alumina was performed at 1200°C in air, 700°C under high pressure in the presence of water vapor in an autoclave, and at 1000°C in a 10% steam atmosphere.

Results and Discussion

Table 1 shows the specific surface area and crystalline phase of alumina after aging under various conditions. The control sample containing no added $Si0_2$ underwent complete phase transition to α-alumina by calcining for 30 hours at 1200°C. Standard γ-alumina (Kanto kagaku) that did not contain SiO_2 phase transitioned to α-alumina completely in 24 hours at 700°C in an atmosphere containing water vapor at 18 MPa. The industrial heat-resistant γ-Al_2O_3 (4 mass% SiO_2) phase transitioned to α-alumina completely in 30 hours at 1200°C. In contrast, the new heat-resistant alumina (5 mass% SiO_2) produced virtually no peaks derived from the α-phase under any of the calcining conditions, confirming that the θ-phase was retained. In addition, the prepared alumina possessed a greater specific surface area compared to the other samples.

Table 1. Spciefic surface area and crystalline phases of alumina after aging various conditions

Sample	SiO_2 /mass%	Fresh		700°C 18 MPa steam 24 h		1200°C 30 h air	
		S.A. /m^2g^{-1}	Crystalline phase	S.A. /m^2g^{-1}	Crystalline phase	S.A. /m^2g^{-1}	Crystalline phase
Standard Al_2O_3	0	168	γ	3	α	6	α
Industrial heat-resistant Al_2O_3	4	167	γ	45	α+θ	13	α
Novel heat-resistant Al_2O_3	3	226	γ	139	θ	55	α+θ
	5	244	γ	146	θ	74	θ

The samples were subjected to an aging test for a prolonged period at 1200°C. **Figure 1** shows the relationship between specific surface area of the heat-resistant alumina and calcining time at 1200°C. For the comparison sample containing no added $Si0_2$, the specific surface area decreased significantly very early in the test. For samples with added $Si0_2$, the specific surface area initially decreased, but no large reductions in specific surface area over long periods were observed after 96 hours. For example, the sample with 5 mass% SiO_2 exhibited superior heat resistance; it possessed a high specific surface area of approximately 40 m^2/g, which was retained even after more than 500 hours of calcining, and α-alumina was not observed.

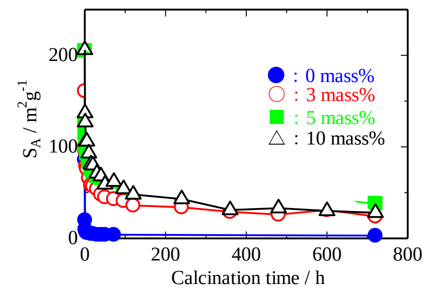

Figure 1. Relationship between specific surface area of heat-resistant alumina and calcination time at 1200°C

Figure 2 shows the relationship between silica concentration and specific surface area of the alumina material aged at 1000°C for 24 hours in an atmosphere containing 10% steam. The specific surface area of the heat-resistant alumina tended to increase upon addition of SiO_2 under all calcining conditions.

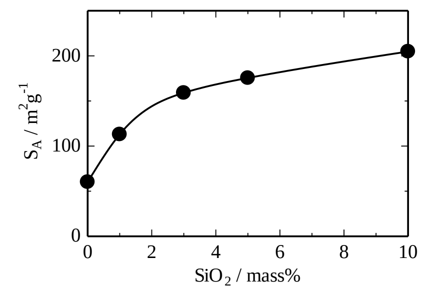

Figure 2. Relationship between SiO_2 concentration and specific surface area of alumina aged at 1000°C for 24 h in 10%

Significance

Heat-resistant alumina was prepared successfully using a coprecipitation method. The novel heat-resistant alumina prepared maintained a high specific surface area for a prolonged period at 1200°C. The high heat resistance of the alumina was due to dispersion of the silica in the alumina resulting from the preparation method.

References

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