Synthesis of Alumina from Alkoxide Modified by Organic Complexing Solvent

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Abstract

An alumina synthesized from aluminum isopropoxide reacted with 2-methyl-2,4-pentanediol (MPD) showed high specific surface area in a wide range of calcined temperatures. Several synthesis conditions of the alumina were investigated. Increased amount of MPD caused higher specific surface area of the formed alumina to a certain extent.

Introduction

Alumina is widely used as a support for various catalysts because of its high surface area and thermal stability.[1] Especially in automobile exhaust gas purification catalyst, alumina-based oxide support holding high surface area above 800°C are being used.[2] Further improvement on thermal stability of the catalyst, however, is demanded for exhaust gas of higher temperature. Therefore, we thought that it is extremely worthwhile to obtain thermostable high-surface-area alumina for catalyst support.

We have been studied syntheses of mixed oxide by sol-gel technique with aid of organic complexing agents to reveal that several high-boiling solvents miscible freely with water are effective for synthesis of homogeneous oxide with high surface area.[3] Recently, we found that aluminas synthesized from aluminum alkoxide using various organic solvents have different properties depending on the used solvents.[4-6] In this study our attention was focused on an alumina synthesized using 2-methyl-2,4-pentanediol (abbreviated as MPD) because a platinum catalyst using this alumina as a support showed higher catalytic activity for CO combustion reaction than conventional catalyst.[7]

Experimental

Synthesis of aluminas

The aluminas were synthesized from aluminum isopropoxide (abbreviated as AIP, Wako) and MPD (Tokyo Kasei) without further purification. A typical synthesis procedure of the alumina (alumina **1**) is shown as follows.

In a 300ml beaker 120 grams (0.59mol) of AIP and 108 grams (0.91mol, 1.56 molar equivalent to AIP) of MPD were reacted for 4 hours on an oil bath heated at 120°C. During the heating, vapor of 2-propanol was released out of the system. After lowering the bath temperature to 100°C, 90 grams of water was poured into the reacted viscous solution. The reaction mixture was vigorously stirred at this temperature for 2 hours and was aged for 12 hours at 80°C. The obtained slurry was dried at max. 150°C under vacuum, followed by stepwise calcination at 300°C (for 1 hour), 450, 600, 800, 1000°C and higher temperature (each step for 3 hours). The calcination was carried out under an air flow at 600°C or lower and under static air at the higher temperatures.

Several synthesis conditions of alumina 1 from MPD were examined in this study. The amount of MPD was varied from MPD/AIP= 0 to 1.56. In these experiments the initial solvent amount was adjusted to 108 grams by an addition of 1,4-dioxane causing no alcohol exchange. The hydrolysis temperature was changed from 50 to 100°C. Hydrolysis by acidic or basic water was also examined.

For comparison, three aluminas were prepared. One is prepared by the same procedure as described above except use of ethylene glycol (abbreviated as EG) instead of MPD (alumina 2). Second one is derived from gel by hydrolysis of AIP in 2-propanol at 70°C (alumina 3), and the other is from precipitate formed in aqueous aluminum sulfate and sodium aluminate in the presence of gluconic acid[8] (alumina 4). The latter preparation method is known as a typical one giving alumina of high surface area from inorganic salts.

Measurements

The thermal differential analysis (DTA) was carried out on a MAC Science TG-DTA 2100 instrument with a heating rate of 10 °C/min under a flow of 100 cm^3/min dry air. Transformation temperature to α-phase (abbreviated as Tα) presented hereafter was obtained from the exothermic peak above 1100°C on DTA. The specific surface area was determined by the BET method from N_2 adsorption data at 77 K using a Micromeritics AccuSorb 2100. The pore size distribution curve was obtained with a mercury porosimeter (Micromeritics AutoPore 9200). Pore size and volume presented hereafter indicate the most frequent pore diameter and summation of meso-pore volume smaller than 500Å, respectively.

Results and discussion
Thermal behavior of the aluminas

Figure 1 shows variation of the specific surface area on calcination temperature of alumina 1 to 4. Aluminas 1 and 3 show higher surface area than 2 and 4, especially in the range of 1000 to 1100°C. It should be emphasized that 1 keeps the highest surface area in the range of 600°C to 1100°C. Alumina 1 holds high specific surface area (136 m^2/g) even after calcination at 1000°C for 50 hours[5] (Fig. 2). In contrast the surface area of alumina 2 from EG, as well
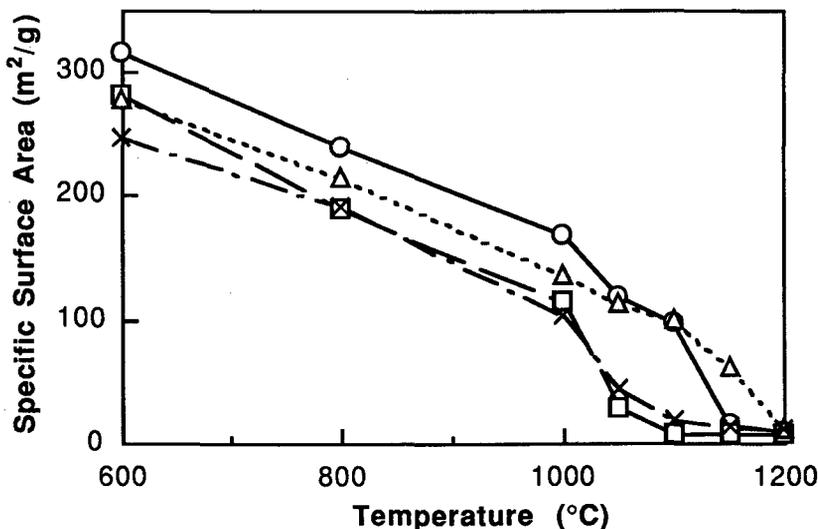
Fig. 1 Effect of the calcination temperature on the specific surface area of alumina **1** (O) , **2** (□), **3** (△), and **4** (✕) calcined for 3 hours at the temperature.

as **4** originated from non-alkoxide, remarkably deteriorates on calcination at the same temperature. We have clarified from TEM analysis that these differences among the used solvents are derived from deferences in particle size and shape.[6] A strong complexing solvent like EG so strongly covers and binds to the surface of an aluminum hydrate particle through the process from hydrolysis to initial stage of calcination to suppress growth of the particles. Therefore, small γ-alumina particles coarsen easily to cause rapid decrease of the surface area. In contrast, a weak complexing solvent like common alcohols forms well-grown needle-like particles giving relatively low surface area to withstand sintering at high temperature. MPD which is considered to have medium complexing ability forms short needle-like γ-alumina particles perhaps of an appropriate size and shape to hold high surface area in a wide temperature range.

Thus, alumina **1** synthesized using MPD is found to be very promising as catalyst support used in the wide temperature range up to 1100°C.
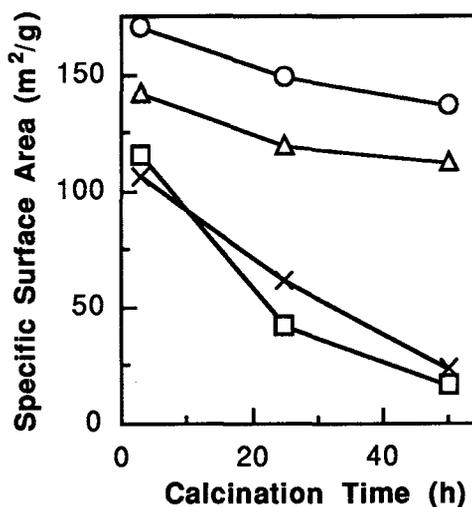

Fig. 2 Variation of the specific surface area of alumina **1** (O) , **2** (□), **3** (△), and **4** (✕) on calcination at 1000°C.
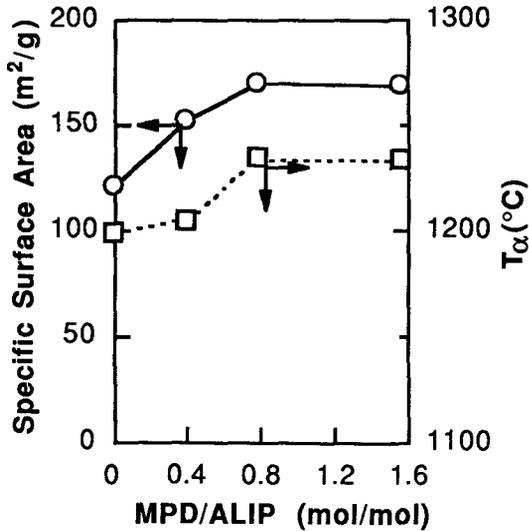
Fig. 3 Effect of amount of MPD on specific surface area (O) and Tα (transformation temperature to α-phase) (□) of the alumina calcined at 1000°C for 3 hours.

Effect of synthesis conditions on properties of the aluminas

Figure 3 shows variation of specific surface area and Tα of alumina 1 calcined at 1000°C for 3 hours depending on an amount of MPD. An increase of MPD up to MPD/ALIP=0.8 causes increase of both specific surface area and Tα. Pore distribution curve also grows sharper and the most frequent pore size becomes slightly larger as an amount of MPD increases (Fig. 4). These results clearly show a certain amount of MPD is effective for uniform growth of small particles. Excess amount of MPD would be effectless because a certain amount of MPD can fully cover the particle surface.
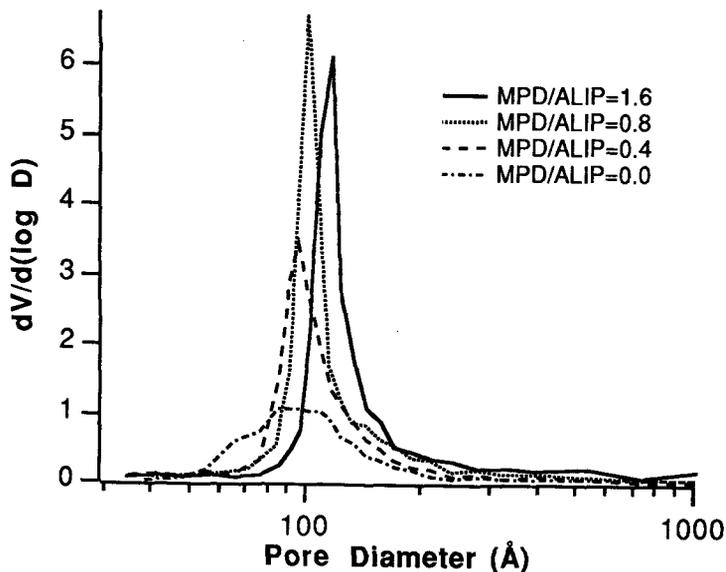

Fig. 4 Variation of pore distribution of the alumina calcined at 1000°C for 3 hours on amount of MPD.

Table 1 Effect of hydrolysis by acidic or basic water on properties of alumina from MPD.

Hydrolysis condition		Specific surface area(m²/g)		Pore size (Å)	Pore volume (cc/g)	Tα** (°C)
	Calc. Temp.*(°C)	800	1000	1000	1000	
H₂O		239	169	100	0.75	1233
1.5M AcOHaq		257	173	95	0.56	1209
1.5M NH₃aq		234	163	102	0.76	1238

*Calcination temperature, **Transformation temperature to α-phase

Table 2 Effect of hydrolysis temperature on properties of alumina from ALIP reacted with MPD at 120°C for 3 hours.

Hydrolysis temperature (°C)		Specific surface area(m²/g)		Pore size (Å)	Pore volume (cc/g)	Tα** (°C)
	Calc. Temp.*(°C)	800	1000	1000	1000	
50		257	188	92	0.92	1253
80		256	161	96	0.81	1229
100		254	164	100	0.83	1239

*Calcination temperature, **Transformation temperature to α-phase

Effect of temperature in alcohol exchange reaction was not so clear. Dissolution of ALIP in MPD, however, was insufficient under 100°C because alcohol exchange reaction did not fully proceed. On the while, decomposition of MPD often made the synthetic process not reproducible above 150°C.

Table 1 shows effect of addition of acid or base at hydrolysis. Hydrolysis by 1.5M acetic acid causes formation of slightly smaller particles than hydrolysis by water. Addition of 1.5M aqueous ammonia has no effect on the properties of the alumina. These results show that presence of MPD weaken the effect of pH in our experiments, though pH generally gives large effect on the size of the formed alumina particle.[9,10]

Table 2 shows effect of hydrolysis temperature. Although hydrolysis temperature gives a small effect on the specific surface areas of the alumina calcined at 800°C, hydrolysis at 50°C is assumed to favor thermostability above 1000°C. A reported result on an alumina directly

hydrolyzed in water revealed that hydrolysis at lower temperature apparently gave an alumina of large surface area after calcination at 550°C.[10] In comparison with this result, effect observed by us is considered to be relatively small. All these results led to the conclusion that presence of MPD governs particle growth rather than other factors in our synthetic procedure.

References

1. R.K. Oberlander, "Aluminas for Catalysts — Their Preparation and Properties"; pp. 63-112 in Applied Industrial Catalysts, Vol. 3. Edited by B.E. Leach. Academic Press, London, 1984.

2. W.S. Briggs, "Pelleted Catalyst Systems"; pp. 289-92 in Alumina Chemicals: Science and Technology Handbook. Edited by L.D. Hart. The American Ceramic Society, Westerville, Ohio, 1990.

3. S. Niwa, F. Mizukami, S. Isoyama, T. Tsuchiya, K. Shimizu, S. Imai, and J. Imamura, "Partial Hydrogenation of Benzene with Ruthenium Catalysts Prepared by a Chemical Mixing Procedure: Preparation and Properties of the Catalysts," *J. Chem. Technol. Biotechnol.*, **36**, 236-46 (1988).

4. K. Maeda, F. Mizukami, M Watanabe, S. Niwa, M. Toba, and K Shimizu, "Control of Pore Distribution of Alumina by Sol-Gel Method Using Polyether," *Chem. Ind.*, 807 (1989).

5. K. Maeda, F. Mizukami, M. Watanabe, N. Arai, S. Niwa, M. Toba, and K. Shimizu, "Synthesis of Thermostable High-Surface-Area Alumina for Catalyst Support," *J. Mater. Sci. Lett.*, **9**, 522-23 (1990).

6. K. Maeda, F. Mizukami, M Watanabe, S. Niwa, and M. Toba, "Thermal Behaviour of Alumina from Aluminium Alkoxide Reacted with Complexing Agent," *J. Chem. Soc., Faraday Trans.*, in press.

7. F. Mizukami, K. Maeda, M. Watanabe, K. Masuda, T. Sano, and K. Kuno, "Preparation of Thermostable High-Surface-Area Aluminas and Properties of the Alumina-Supported Pt Catalysts," in Catalysis and Automotive Pollution Control II. Elsevier, Amsterdam, in press.

8. Japanese Patent 1978-19000 (1978); A. Ozaki et al, Shokubai Chosei Kagaku; pp.207-208. Kodansha, Tokyo, 1980.

9. D.L. Trimm and A. Stanislaus, "The Control of Pore Size in Alumina Catalyst Supports: A Review," *Appl. Catal.*, **21**, 215-38 (1986).

10. T. Ono, Y. Ohguchi, and O. Togari, "Control of the Pore Structure of Porous Alumina"; pp. 631-41 in Preparation of Catalysts III. Edited by G. Poncelet, P. Grange, and P. Jacobs. Elsevier, Amsterdam, 1983.

11. M. Inoguchi, K. Tate, Y. Kaneko, Y. Satomi, K. Inaba, T. Mizutori, H. Kagaya, R. Nishiyama, S. Onishi, and T. Nagai, "Study on the Hydrodesulfurization Catalyst of Residual Fuel (Part 4) — Improvement of Catalyst Support," *Bull. Japan Petrol. Inst.*, **13**, 147-52 (1971).