Synthesis of Thermally Stable Cs-Doped Alumina Nanoparticles by Microemulsion Method

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Cs-doped alumina nanoparticles were synthesized by microemulsion method and then characterized. Cs-doping greatly improved aluminas thermal stability. For an optimum molar ratio of Cs/Al = 1/11 the structure of γ-alumina can be preserved even at temperatures as high as 1330 °C.

Active alumina, especially γ-alumina, has been widely used as adsorbents, supports, and catalysts.[1,2] However, it transforms to α-alumina when it is used in high temperature processes such as partial oxidation, three-way catalysts, methane combustion, or steam reforming.[3] This transformation leads to drastic reduction in specific surface area and the collapse of pore structure which are essential elements in catalytic reactions. Two strategies can be adopted to overcome this sintering problem. One is to incorporate large cations, e.g. Ba^{2+},[4] La^{3+},[5] etc., into the matrix of active alumina to prevent the phase transition to α-alumina. The other way is to convert alumina into barium hexaaluminate (BHA) at the lowest temperature possible. BHA particles have been reported to grow anisotropically and thus they show better thermal stability than alumina.[4] If BHA is formed at low temperature, the growth of BHA particles can be suppressed.

Reverse microemulsion technique is now extensively used for the synthesis of nanoparticles. The uniformly nanosized water droplets of the microemulsions can be used as "constrained reactors" for tailoring the size of nanoparticles.[6–8]

The large ionic radius of Ba^{2+} or La^{3+}, Cs^{+} is expected to effectively retard the phase transition of γ to α-alumina. In this letter we report the synthesis of the nanostructured alumina doped with different amounts of Cs, i.e. Cs/Al molar ratio = 0, 1/24, 1/11, 1/9, and 1/6, by reverse microemulsion method. The Cs-doping effect on the γ to α-alumina phase transition was studied by nitrogen adsorption, powder X-ray diffraction (XRD), and thermogravimetry (TG)/differential thermal analysis (DTA) techniques.

We have already presented elsewhere the typical procedure for synthesis of barium-doped alumina nanocomposites.[9] Therefore, the synthesis procedure for Cs-doped alumina nanoparticles will be only briefly described. Appropriate amount of $CsNO_3$ (Wako) was dissolved in 50 ml distilled water, and then this $CsNO_3$ aqueous solution was emulsified in 140 ml isooctane (2,2,4-trimethylpentane, Aldrich) with the help of surfactant (20 ml polyethylene glycol 200, Wako) and cosurfactant (ca. 260 ml n-propanol, Wako) to obtain a stable W/O microemulsion. 1.836 g aluminum isopropoxide (Aldrich) was dissolved in 20 ml isopropanol (Wako) and 20 ml isooctane by vigorous stirring. This mixture was heated to 80 °C in order to increase the rate of alkoxide dissolution. After that, the solution of aluminum precursor was added to the microemulsion and hydrolyzed for about 20 h. Subsequently, the mixture was transferred to an autoclave and hydrothermally treated at 150 °C for 24 h. The Cs-doped alumina nanoparticles were then recovered by removing the solvents by rotoevaporation and then by decomposing the surfactant at 500 °C ("as-prepared" samples). After characterization, these "as-prepared" samples were calcined at 1100 °C for 24 h.

Nitrogen adsorption measurements were performed at −196 °C (BELSORP 28SA). The results are listed in Table 1. The specific surface area of the as-prepared samples decreased monotonically with increasing the Cs amount. The surface area of the high temperature calcined samples (1100 °C for 24 h) was also related to the Cs content but the highest surface area (102 m^2/g) was observed for the material with Cs to Al molar ratio of 1/11. Lower or higher Cs/Al molar ratios led to a decrease in the final surface area. The structure of Cs free sample collapsed after high temperature calcination (Sa ≈ 14 m^2/g). The experimental results are clearly proving that Cs-doping significantly improved the thermal stability of alumina.

Table 1. Morphology of Cs-doped aluminas

Cs/Al molar ratio	T_c[a] °C	Sa[b] m^2/g	D_p[c] nm	V_p[d] $\mu l/g^{-1}$	D[e] nm
0	500	263	5.5	861	5.0
	1100	14	mic.[f]	13	22
1/24	500	208	9.6	929	5.1
	1100	89	15	706	6.8
1/11	500	164	9.6	807	5.0
	1100	102	12	710	7.0
1/9	500	122	9.6	699	5.4
	1100	80	9.6	573	7.8
1/6	500	109	9.6	573	4.9
	1100	55	12	475	7.3

[a] T_c: Calcination temperature; [b] Sa: BET specific surface area; [c] D_P: Average pore size; [d] V_p: Pore volume; [e] D: XRD crystallite size; [f] mic.: micropores.

The pore size distribution (not shown here) of the analyzed samples, determined by D-H method on desorption branch, was approximately of Gaussian type. The average values of the pore size were located in the mesopore region (2–50 nm). After high temperature calcination (1100 °C for 24 h) the Cs-free alumina contained only micropores indicating that an extensive sintering took place. In contrast, the Cs-doped aluminas preserved their mesoporous structure (average pore size ≈12 nm) even after high temperature calcination. This thermally stable mesoporosity may have in future interesting applications in catalytic as well as in other fields.

The crystalline structure of the materials was investigated with a Rigaku Multiflex diffractometer using Cu K_α radiation. Figure 1 shows the XRD patterns of the samples calcined at 500, 1100, and 1330 °C. The crystalline phase of the as-prepared

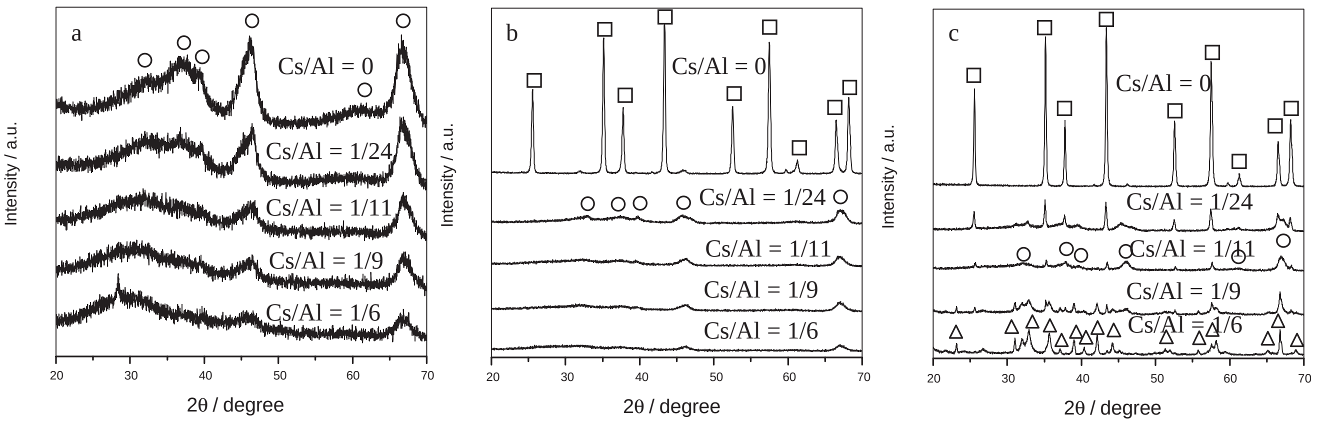

Figure 1. XRD patterns of Cs-doped aluminas calcined at (a) 500 °C, (b) 1100 °C, and (c) 1330 °C. (○) γ-Al_2O_3, (□) α-Al_2O_3, and (△) $Cs_2O{\cdot}11Al_2O_3$.

samples was γ-alumina (Figure 1a). The average crystallite size, calculated with Scherrer equation from the peak located at $2\theta \approx 68$ degrees, was ca. 5 nm (Table 1). The significant differences observed between the samples calcined at 1100 °C were related to the amount Cs contained by alumina matrix (Figure 1b). The main crystalline phase of Cs-free sample was α-alumina with an average crystallite size of ≈22 nm. On the other hand, the high temperature calcined Cs-doped aluminas, having the average crystallite size of ≈7 nm, preserved their initial γ-alumina structure. In addition to surface area and porosity data, the XRD results are proving that Cs-doping is very effective in promoting the thermal stability of alumina.

The effect of Cs-doping on the γ to α-alumina phase transition of the as-prepared samples was investigated (in the air flow, ≈200 ml/min) by TG/DTA (Seiko 320U). The temperature was increased from 400 to 1330 °C with 10 °C/min and then kept at this temperature for 15 min. After that, the crystalline phases of these samples were analyzed by XRD (Figure 1c). In the cases of aluminas with Cs/Al = 1/24 and 1/11, only one exothermic peak was observed at 1216 and 1250 °C, respectively. As shown in Figure 1c, the presence of these exothermic peaks can be explained by the formation of small amounts of α-alumina. When Cs/Al ratio was increased to 1/9 and 1/6, two DTA peaks were detected. The broad endothermic peak located at ≈1076 and ≈1098 °C, respectively, are likely to be generated by the formation of $Cs_2O{\cdot}11Al_2O_3$ phase (Figure 1c). The exothermic peak, located at 1252 and 1295 °C, respectively, can be assigned to the nucleation and growth of α-alumina phase.[10]

Table 2 presents the evolution of the sample weight during the calcination in the temperature range 400–1300 °C. The molar ratio between the eliminated water and Al_2O_3 (N) was calculated by supposing that the decrease in sample weight was caused only by water elimination. It can be observed that, the higher was the Cs content in the sample the larger was the amount of water lost per mole of Al_2O_3. This means that the Cs-doping increased the amount of hydroxyl groups retained by the as-prepared samples. The water elimination for the Cs-doped samples took place in two distinct domains: low-temperature (400–1000 °C) and high temperature (1000–1300 °C) regions. The most significant weight decrease was observed in the high temperature domain. In contrast, most of the water of the Cs-free samples was eliminated below 850 °C. This also proves that the Cs-doping suppresses the γ to α-alumina phase transition as well as the sintering (growth) of nanoparticles for temperatures lower than 1200 °C. It is well known that the sintering process is accompanied by condensation and elimination of alumina hydroxyl groups as water.[11]

Table 2. Amount of water lost for each mole of Al_2O_3 during the TG/DT analysis in the temperature range of 400–1330 °C

Formula	$W_{400}{}^{a}$/mg	$W_{1300}{}^{b}$/mg	n^{c}	N^{d}
$Al_2O_3{\cdot}nH_2O$	16.316	15.997	0.11	0.11
$Cs_2O{\cdot}24Al_2O_3{\cdot}nH_2O$	32.121	30.727	6.58	0.27
$Cs_2O{\cdot}11Al_2O_3{\cdot}nH_2O$	33.662	31.913	4.05	0.37
$Cs_2O{\cdot}9Al_2O_3{\cdot}nH_2O$	44.670	41.912	4.12	0.46
$Cs_2O{\cdot}6Al_2O_3{\cdot}nH_2O$	51.524	47.723	3.66	0.61

[a] W_{400}: Weight of sample at 400 °C;
[b] W_{1300}: *Weightofsampleat*1300 °C;
[c] n: Mole number of water in the formula shown in the first column;
[d] N: Mole number of lost water for each mole of Al_2O_3.

References

1 M. F. L. Johnson, *J. Catal.*, **123**, 245 (1990).
2 F. Vaudry, S. Khodabandeh, and M. E. Davis, *Chem. Mater.*, **8**, 1451 (1996).
3 A. J. Zarur and J. Y. Ying, *Nature*, **403**, 65 (2000).
4 M. Machida, K. Eguchi, and H. Arai, *J. Catal.*, **103**, 385 (1987).
5 H. Sharper, E. B. Doesburg, and L. L. Reijen, *Appl. Catal., A*, **7**, 211 (1983).
6 M. J. Schwuger, K. Stickdorn, and R. Schomäcker, *Chem. Rev.*, **95**, 849 (1995).
7 J. H. Adair, T. Li, T. Kido, K. Havey, J. Moon, J. Mecholsky, A. Morrone, D. R. Talham, M. H. Ludwig, and L. Wang, *Mater. Sci. Eng., R*, **23**, 139 (1998).
8 A. J. Zarur, H. H. Hwu, and J. Y. Ying, *Langmuir*, **16**, 3042 (2000).
9 I. Balint, Z. You, and K. Aika, *Phys. Chem. Chem. Phys.*, **4**, 2501 (2002).
10 H. L. Wen and F. S. Yen, *J. Cryst. Growth*, **208**, 696 (2000).
11 M. Machida, A. Sato, T. Kijima, H. Inoue, K. Eguchi, and H. Arai, *Catal. Today*, **26**, 239 (1995).