Synthesis of Mesoporous γ-Alumina through Pre- and Post-hydrolysis Methods

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Abstract–Two methods of pre- and post-hydrolysis are suggested for the preparation of mesoporous aluminas. These techniques were developed based on the control of the reaction rates of hydrolysis of aluminium precursors. The characteristics of the resulting materials, such as pore uniformities, porosity and crystalline shape, were investigated. Results show that these methods allow one to prepare tailor-made mesoporous aluminas at an ambient temperature.

Key words: γ-Alumina, Mesopore, Porosity

INTRODUCTION

Aluminas have been used in industrial catalysis, catalyst support, adsorbents and ion exchangers, because of their thermal, chemical, and mechanical stability and low cost [Park et al., 2000]. The performance, however, is limited due to the uncontrolled porosity, the deactivation by coke formation and plugging in the micropore that hinders the diffusion of reactants and products. Thus, alumina supports with a narrow pore size distribution, uniform pore structure and high pore volume are required for practical industrial applications.

The synthesis and characterization of mesoporous silicas or aluminosilicates of the M41S, HMS, and SBA types has been widely documented [Stein et al., 2000]. Mesoporous materials of this type are not restricted to silica, and have also been reported for transition metal oxides. However, in the case of mesoporous aluminium oxide, the strategies typically used in the synthesis of mesoporous silica have not always yielded satisfactory results. Moreover, relatively few studies on the synthesis of pure alumina have been reported to date. Davis and co-workers [1996] prepared mesoporous aluminas by the hydrolysis of aluminium alkoxides in the presence of a carboxylate surfactant. The resulting materials, however, had an approximately constant pore size (ca. 20 Å) that could not be tailored by changing the length of surfactant chains. Yada et al. [1996] reported the preparation of aluminium-based dodecyl sulfate mesophase using an electrostatic S^-I^+ assembly, and Pinnavaia et al. [1998] obtained mesoporous aluminas from electrically neutral assemblies of polyethylene oxide and aluminium alkoxides.

One limitation of the above synthetic strategies for mesoporous aluminas is that the rates of hydrolysis (and condensation) of aluminium alkoxides are much faster than that of the silicon alkoxides. Therefore, the hydrolysis reactions in aqueous media also lead to the formation of lamellar hydrated hydroxides, even in the presence of surfactant [Valenge et al., 2000]. Amoros and co-workers [1999] solved this problem by controlling the hydrolysis rate of the aluminium suspension by adding hydrolysis-retarding agents.

In this study, two synthetic methods of controlling the hydrolysis reaction of aluminium precursor are proposed, namely, pre-hydrolysis and post-hydrolysis methods. To our knowledge, this is the first time report that the pore properties of the mesoporous alumina including pore size and surface area were controlled via the fine tuning of the hydrolysis reaction condition using carboxylic acids as templates.

EXPERIMENTAL

A variety of surfactants were used to synthesize mesoporous aluminas. As anionic surfactants, alkyl chain carboxylic acids (Fluka), C_nH_{2n+1}-COONa (n is the carbon tail length) were used. Aluminium *sec*-butoxide (Fluka) was used as an aluminium precursor.

For the pre-hydrolysis method, the pH of the stabilized solution was controlled and at *ca.* 7. Hydrolysis of aluminium alkoxide dominates condensation and may result in homogeneous precipitation in acid [Brinker and Scherer, 1990]. Therefore, the initial pH of precursor solution was fixed to below 2. A typical synthetic procedure was as follows: appropriate amounts of the surfactant were pre-dissolved in a sodium hydroxide solution at a given pH of 8 to 12 (solution A). Aluminum sec-butoxide was then hydrolyzed in a nitric acid solution of pH 2 (solution B). Solution B was then added slowly, with vigorous stirring, to solution A, and this suspension was further stirred for 24 h. The product was then washed with de-ionized water and dried at 80 °C. The resulting materials were calcined for 3 h at 420 °C in air. The molar ratios of the reaction mixture were 1 Al(*sec*-BuO)$_3$: 0.2 carboxylic acids : 0.04-0.1 NaOH : 100 H$_2$O.

For the post-hydrolysis method, water and sec-butyl alcohol were used as a catalyst and as a solvent to dissolve surfactant, respectively. Aluminium source and surfactant were separately dissolved in *sec*-butyl alcohol, and the two solutions then mixed. Small amount of water was dropped into the mixture at a rate of 1 ml/min, and a white precipitate was formed. The rest of the experimental procedure is the same as that described above for the pre-hydrolysis method. The molar ratio of this reaction mixture was 1 Al(*sec*-BuO)$_3$: 0.2 carboxylic acids : 0.04 NaOH : 5 *sec*-BuOH : 4-50 H$_2$O. Aluminas prepared by using caproic, lauric, and stearic acids as templates are referred to as AlC, AlL and AlS, respectively.

Table 1. Pore properties of mesoporous aluminas prepared by pre- and post-hydrolysis reaction of aluminium butoxide with a variety of surfactants

Material	Surfactant formula	pH for the 1st/[H$_2$O]/ [Al(Bu^{s}O)$_3$] for the 2nd method	BJH pore size/nm	FWHM of PSD/nm	BET surface area/m^2 g^{-1}	Pore voulme/ cm^3 g^{-1}
AlC-1	C$_5$-COOH	10.8	3.66	0.60	553	0.44
AlC-2	C$_5$-COOH	7.3	4.37	1.87	575	0.78
AlC-3	C$_5$-COOH	5.0	5.58	7.64	250	0.33
AlL-1	C$_{11}$-COOH	7.1	4.75	2.03	355	0.55
AlS-1	C$_{17}$-COOH	7.2	5.14	3.50	392	0.64
AlS-2^a	C$_{17}$-COOH	48	7.75	2.88	386	1.00
AlS-3^a	C$_{17}$-COOH	32	7.72	2.98	377	1.01
AlS-4^a	C$_{17}$-COOH	16	7.14	2.92	369	0.90
AlS-5^a	C$_{17}$-COOH	4	3.52	1.38	420	0.60

^{a}Mesoporous aluminas prepared via post-hydrolysis method.

RESULTS AND DISCUSSION

The pore properties of the aluminas pre-hydrolysis were dependent on the pH of the stabilized reaction solution as listed in Table 1. Pore size increased with the decrease of the solution pH. However, the pore uniformity, based on the FWHM of the pore size distribution, was reduced due to the incomplete condensation of aluminium hydroxide and surfactant micelles. Oxolation reaction of aluminum alkoxide was minimized at IEP (ca. 8-9), and prepared aluminas at pH$_{IEP}$ showed poorly organized mesostructure [Valange et al., 2000], while prepared aluminas at pH 7 had a relatively well organized mesostructure and uniform pore size distribution. Therefore, the optimum synthetic pH was thought to be approximately 7. Mesoporous aluminas were synthesized at a pH of 7 by using a variety of surfactants with different carbon lengths as templates. Davis and co-workers [1996] also prepared many mesoporous aluminas by changing the surfactant length, and the aluminas produced had a constant pore size of ca. 20 Å, regardless of the surfactant chain lengths. In this study, we were able to prepare mesoporous aluminas with pore sizes that could be tailored by changing the surfactant carbon length under the pH-controlled solutions. With the increase in the length of the surfactant chain at the similar pH conditions at approximately 7, pore diameters in Table 1 increased linearly while the pore uniformity was reduced. Pore size increments obtained by increasing surfactant tail length were relatively smaller than those obtained by changing the reaction pH. These results suggested that the pore uniformity of mesoporous aluminas by the pre-hydrolysis method was primarily dependent upon the reaction pH.

The pore uniformity was also controlled by the post-hydrolysis method. With the exception of AlS-5, a larger quantity of water in the reaction increased the pore size, presumably the results of a swelling effect of solvent inner micelles. Nevertheless, pore uniformity of each was similar. When a very small amount of water was used a catalyst, as in the case of AlS-5, the pore size distribution was very narrow, and the surface area increased. In particular, its N$_2$ isotherm of the AlS-5 changed compared with the AlS-1. As shown in Fig. 1, AlS-5 showed both framework and textural porosity, and the N$_2$ isotherms of the AlC and AlL were similar to that of AlS-1. This is probably because the presence of small quantity of water
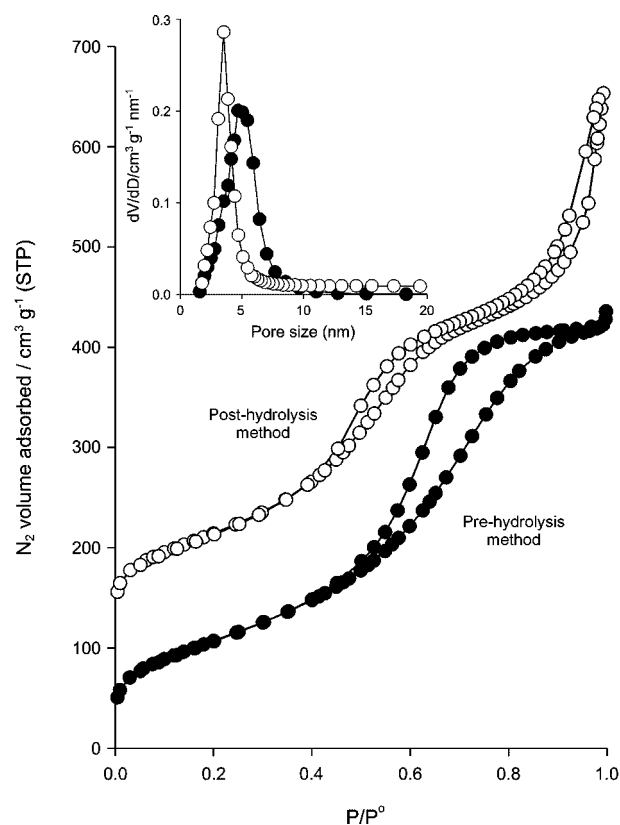

Fig. 1. N$_2$ adsorption-desorption isotherms of mesoporous aluminas, AlS-1 and AlS-5, prepared by pre-(◆) and post-(○) hydrolysis method. BJH pore sizes obtained from the desorption isotherms are included for comparison (insert figure).

resulted in the formation of small precipitated aggregates, and that upon further aggregation these gave rise to textural and framework porosity.

The TEM image of AlS-1 in Fig. 2 shows the surface morphology of mesoporous alumina prepared after calcinations at 420 °C. The pores were wormhole or sponge-like in appearance, which implies the advantage of having a highly inter-connected pore system. Similar pore morphology was found for disordered mesopo-

Fig. 2. TEM image of mesoporous alumina, AlS-1, calcined at 420 °C (1 bar: 20 nm).

rous silicas [Stein et al., 2000] and alumina [Zhang and Pinnavaia, 1998; Cabrera et al., 1999] when cationic or neutral surfactants were used.

FT-IR analysis (not shown here) illustrated the removal of the templates from the as-made materials, and the spectra of the resulting materials were dependent on the calcination time and temperature. As the calcination time increased from 1 to 5 h at 360 °C, the characteristic peaks of tail groups of surfactant (2,857 cm^{-1}) disappeared at relatively low temperature compared with those of head groups of surfactant (1,461 and 1,573 cm^{-1}), and templates were completely removed after 5 h at 360 °C. However, after the samples were calcined at up to 5 h at 360 °C, the pores shrank. Whereas the pores of alumina calcined at 3 h, 420 °C did not shrink, even after the template was completely removed.
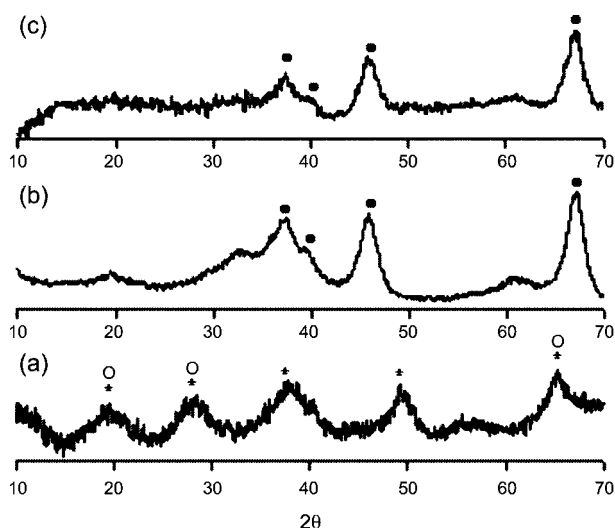

Fig. 3. XRD patterns of heat-treated alumina at (a) 25 (no heat treated), (b) 270, and (c) 420 [*, bayerite; ○, (pseudo) boehmite; •, γ-Al$_2$O$_3$].

The crystalline phase was confirmed by DSC, TGA and XRD analysis. The phase of as-made material shows boehmite and bayerite (Fig. 3). TGA result (not shown here) shows the occurrence of two groups of mass change, which are physically adsorbed water and stearic acid. This result is well agreed with DSC result. However, another peak approximately 220 °C appeared, which was the phase transformation aluminium hydroxide to γ-alumina. That was confirmed by XRD in Fig. 3. The phase of γ-alumina was retained up to 550 °C.

In conclusion, we report here the synthesis of mesoporous aluminas with pore sizes that can be tailored at ambient temperature. Precipitated hydroxides were formed in aluminium salt solutions by neutralization with bases at pH 7-12 by using a pre-hydrolysis method. The post-hydrolysis method was both simpler and more time-effective, and could be used to prepare aluminas with larger pore sizes than the pre-hydrolysis method. Pore properties of mesoporous aluminas in this article could also be controlled by using the carbon tail length of surfactants, the reaction pH by in the pre-hydrolysis method, and the water quantity used by the post-hydrolysis method.

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