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Fast Sol−Gel Synthetic Route to High-Surface-Area Alumina Aerogels

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Alumina aerogels produced by the sol−gel synthesis and dried under supercritical conditions have found increasing interest as catalysts and catalyst supports.[1−4] The most common process for making alumina gels, developed by Yoldas,[5,6] was to hydrolyze aluminum isopropoxide (AIP) or *sec*-butoxide (ASB) in a large excess of water with an acid catalyst. However, as the gel prepared would dissolve if subjected to supercritical conditions when the pores contained water, an additional solvent-exchange step was necessary to obtain alumina aerogels. In the other method, the sol−gel synthesis was carried out using AIP or ASB dissolved in various organic solvents such as benzene and alcohols,[7,8] where the alumina sol took at least several days for gelation to occur even at elevated temperatures. Thus, to obtain a uniform bulk gel by this method, it was occasionally required to use some additives during the sol−gel process both for controlling the rate of alkoxide hydrolysis and for accelerating the gelation.[9] We have applied the latter method to the preparation of alumina aerogels.

During the course of our work, it was possible to speed up and simplify the sol−gel procedure by modifying the traditional method under appropriately controlled conditions. The procedure for the preparation of alumina aerogels is illustrated in Figure 1. Aluminum *sec*-butoxide, $Al(OC_4H_9^{sec})_3$ was first dissolved in ethanol at 80 °C. The ASB was then partially hydrolyzed with water diluted with ethanol containing nitric acid. Once a clear alumina sol was formed after stirring for 2 h, the solution was cooled to room temperature. A transparent bulk gel was prepared within a few minutes at room temperature only by adding an appropriate amount of water diluted with ethanol into the sol. As reported by Yoldas,[10] the amount of water used for the initial partial hydrolysis of ASB in ethanol was highly critical for clear sol formation. The gel quality was significantly affected by the amount of water added in the gelation step. With the low water content, there was shrinkage of the gel network resulting in expulsion of liquid from the pores during aging. On the other hand, with the high water content, the resulting gel was not homogeneous due to uncontrollably fast gelation rate. Table 1 summarizes the sol−gel parameters which are optimal for obtaining a uniform and rubberlike gel.

The above sol−gel behavior may be dependent on the nature of the solvent. Hence, we have kept all the parameters constant and varied the type of solvent only. Methanol, *n*-propanol, 2-propanol, *n*-butanol, and *sec*-butanol were selected as other solvents. Out of the five

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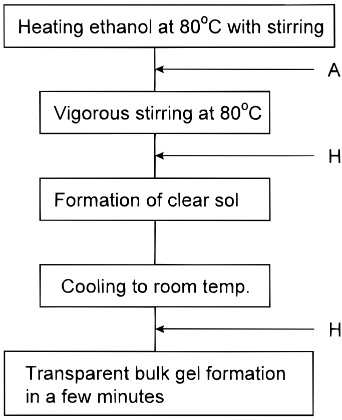

Figure 1. Fast sol–gel synthesis procedure for obtaining alumina aerogels.

Table 1. Sol–Gel Parameters Used To Prepare the Alumina Alcogels

step	ethanol (mL)	Al/ethanol (mmol/mL)	H_2O/Al (mol/mol)	HNO_3/Al (mol/mol)
hot ethanol	60			
add $Al(OC_4H_9^{sec})_3$		0.476		
add H_2O, HNO_3, and ethanol	40		0.5	1/23.7
add H_2O and ethanol	5		1.1	

alcohols, methanol and *sec*-butanol did not give rise to complete dissolution. Using 2-propanol or *n*-butanol, the solution did not form a bulk gel. In the case of *n*-propanol, the clear sol became a bulk but less transparent gel within a minute at room temperature. The gel was soft just after gelation, but its strength increased gradually with subsequent aging. The elastic behavior of the aged gel was comparable to that of the one obtained using ethanol. On the basis of these observations, the effect of solvent could be closely correlated with alcohol-exchange reactions which can significantly alter the hydrolysis behavior of aluminum alkoxides by forming mixed alkoxides. In general, the facility for alcohol exchange increases when the steric hindrance of the alkoxy group decreases: MeO > EtO > Pr^iO > Bu^tO.[11–13] It is also well-known that hydrolysis rates decrease with steric bulk of the alkoxy ligands.[13,14] When ASB was dissolved in alcohols with intermediate facility, mixed alkoxides modified by alcohol exchange had adjustable hydrolysis rates for obtaining transparent bulk gels. As a result, ethanol and *n*-propanol were found to be suitable solvents for our fast sol–gel synthetic route.

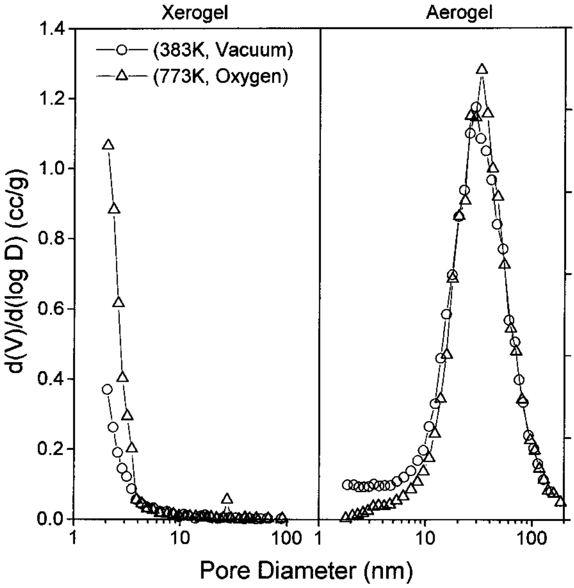

Figure 2. Pore size distributions of the alumina aerogel and xerogel samples before and after calcination at 773 K for 2 h.

Table 2. Textural Properties of the Alumina Aerogel and Xerogel Samples before and after Heat Treatment at Different Temperatures[a]

heat treatment (K)	xerogel			aerogel		
	S_{BET}	V_p	D_p	S_{BET}	V_p	D_p
383, vacuum	422	0.22	1.5	732	2.85	15.6
573, He	575	0.28	2.0	554	2.89	20.9
773, O_2	506	0.26	2.1	456	2.61	22.9
1073, O_2	95	0.07	2.9	356	2.27	25.5
1173, O_2	87	0.07	3.3	260	1.89	29.1
1273, O_2	35	0.12	13.7	175	1.35	30.9

[a] S_{BET}, BET surface area (m^2/g); V_p, total pore volume (cm^3/g); D_p, average pore diameter (nm).

The wet gel was aged for 3 h and then dried by flowing supercritical carbon dioxide in a supercritical extraction system at 333 K and 24 MPa. The gel prepared using *n*-propanol had to be aged overnight to obtain the structural rigidity required for supercritical drying. The product aerogel was heated in a tube furnace in flowing helium at 573 K for 2 h and then in flowing oxygen at 773 K for 2 h according to our standard calcination procedure.[15] An alumina xerogel, for comparison, was prepared by drying the wet gel prepared under the same sol–gel conditions in a vacuum oven at 383 K overnight.

The BET surface area, pore volume, and pore size distribution of the alumina samples were obtained from nitrogen adsorption–desorption at 77 K using adsorption porosimeter (Micromeritics, ASAP 2000). Figure 2 shows the pore size distribution of the alumina aerogel and xerogel samples prepared from the new sol–gel synthetic route. The alumina aerogel had pronounced mesoporosity in the range 10–100 nm with a relatively narrow pore-size distribution. Since the aerogels obtained from clear and firm gels had the rigid porous framework with better thermal stability, the pore-size distribution of the alumina aerogel did not change much as the sample was heated. It is also noted from Figure 2 that the alumina xerogel was exclusively microporous and had relatively poor thermal stability.

Table 2 shows textural properties of our alumina aerogel and xerogel samples. Although the preparation conditions have not been optimized for the highest surface area, the dried alumina aerogel has a surface area of above 700 m^2/g, which is greater than the traditional values less than 600 m^2/g.[2,8,9] Additional heat treatment up to 1000 °C did not radically change the textural characteristics of the calcined alumina aerogel. These results suggest that our alumina aerogel

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obtained from transparent bulk gels has the inherent rigid porous network structure of the polymeric gels. In the case of the xerogel, the increase of the surface area and pore volume, after calcination up to 500 °C, was a result of the removal of organic residues from micropores, rendering the surface accessible for the physical adsorption of nitrogen at 77 K. However, the surface area and pore volume of the calcined xerogel decreased dramatically after heat treatment at 800 °C. This is probably due to the exothermic phase transformation process evidenced by X-ray diffraction (XRD) and thermal analysis.

Thermal analysis was performed in flowing air at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the dried xerogel showed two appreciable exothermic peaks; one with sudden weight loss at 260 °C which is assigned to the decomposition of residual organics and another one with no weight loss at 800−900 °C indicating the phase transformation. On the other hand, the dried aerogel had only one exothermic peak at 260 °C. On the basis of XRD shown in Figure 3, the calcined alumina aerogel and xerogel samples remained amorphous up to 500 °C and contained a more ordered transition alumina phase, likely γ-alumina, after further heat treatment at 800 °C. However, the XRD peaks of the aerogel were much broader and weaker than those of the xerogel, indicating relatively retarded phase transformation for the aerogel.

The pronounced mesoporosity and high surface area of the alumina aerogel prepared by our fast sol−gel synthetic route and CO_2 supercritical drying, combined with its high thermal stability, renders it a promising catalyst or a catalyst support for use in various reactions. For further improvement of the textural and structural properties, the effect of the sol−gel parameters on the resulting textural and structural properties of alumina aerogels is currently being investigated in our laboratory.

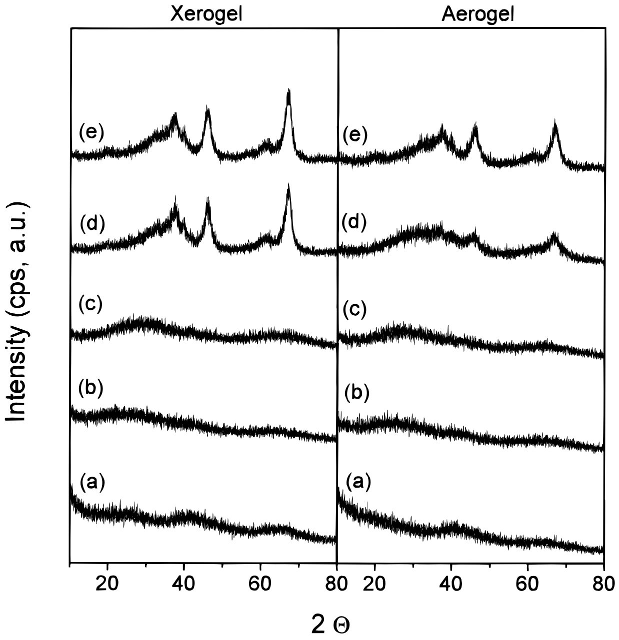

Figure 3. X-ray diffraction patterns of the alumina aerogel and xerogel samples before and after heat treatment at different temperatures: (a) as prepared; (b) 573 K; (c) 773 K; (d) 1073 K; (e) 1173 K.

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