

Synthesis of High-Surface-Area Zirconia Aerogels with a Well-Developed Mesoporous Texture Using CO₂ Supercritical Drying

Dong Jin Suh* and Tae-Jin Park

Clean Technology Research Center, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 136-791, Korea

Hyoung-Yong Han and Jong-Choo Lim

Department of Chemical Engineering, Dongguk University, 3-26 Phil-dong, Joong-ku, Seoul 100-715, Korea

Received January 22, 2002

Revised Manuscript Received February 26, 2002

Zirconia has attracted considerable interest for catalytic applications since it has redox properties as well as acidic and basic character.^{1,2} For use in catalysts or catalyst supports, it will be advantageous to prepare zirconia in a stable and high-surface-area form such as an aerogel. Aerogels are a class of extremely lightweight, porous materials composed of a three-dimensional network of nanoscale particles surrounded by a large volume of mesoporosity.³ As a consequence of this unique structure, aerogels retain very high specific surface areas. Zirconia aerogels can be prepared by an acid-catalyzed sol–gel method using zirconium alkoxides and subsequent supercritical drying to avoid collapse of the original gel structure due to surface tension.^{4–8} The resulting uncalcined zirconia aerogels have very high surface areas, sometimes up to 500 m²/g.^{7,8} However, the high surface area decreases markedly with increase of calcination temperature. From previous studies, surface areas of calcined zirconia aerogels were not much higher than those of conventional precipitated samples. In particular, when supercritical CO₂ was used for drying, surface areas of zirconia aerogels after calcination at 773 K were mostly below 100 m²/g.^{4,6,8–10} The reported results of calcined samples are not quite consistent. We describe here a reproducible preparation procedure for obtaining high-surface-area zirconia aerogels only by careful control of some sol–gel parameters.

The procedure for the preparation of zirconia aerogels is similar to that of transition metal oxide aerogels described previously.⁶ For typical zirconia alcogels, two beakers were prepared: one with zirconium(IV) *n*-propoxide, *n*-propanol, and nitric acid and the other with

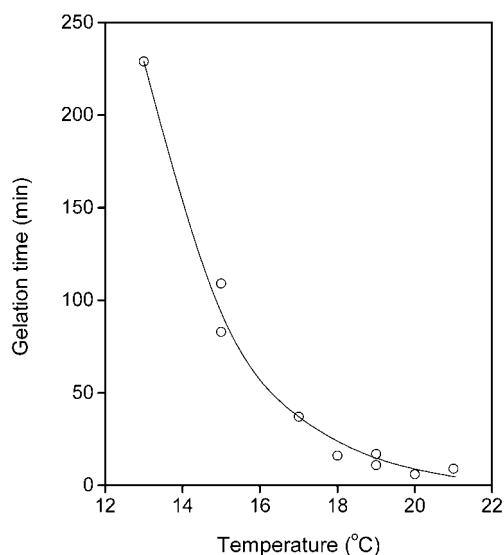


Figure 1. Effect of temperature on the gelation time.

water and *n*-propanol. The molar ratio of Zr(OPr^{*n*})₄:*n*-PrOH:H₂O:HNO₃ was kept constant at 1:13.38:4.09:1.09. The two solutions were combined and vigorously stirred until gelation caused the vortex created by the stirring to disappear. The alcogel was then sealed and allowed to age. The propanol solvent entrapped in the gel network was removed from the aged gel by flowing supercritical carbon dioxide in a supercritical extraction system at 333 K and 24 MPa. The product aerogel was ground to <100 mesh and 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, which was a standard calcination procedure. The BET surface areas, pore volumes, and pore size distributions of the dried and calcined samples were determined by nitrogen adsorption–desorption at 77 K using a Micromeritics ASAP 2000 instrument. The above sol–gel conditions were determined from previous studies to maximize specific surface areas of zirconia aerogels.

The hydrolysis and condensation behavior of zirconium alkoxides differs fundamentally from those of silicon, aluminum, and titanium alkoxides.^{11–13} The sol–gel process of zirconium alkoxides is complicated and difficult to control because of its high sensitivity to various sol–gel parameters. In particular, as shown in Figure 1, the gelation rate was quite dependent on temperature in contrast to other sol–gel systems. The gelation times and sol–gel product properties were not quite consistent unless the sol–gel temperature was controlled very carefully. Another factor to be considered is how to reduce the greater reactivity of zirconia alkoxides with respect to water. When a stoichiometric amount of water with acid and alcohol was directly added into the alkoxide solution, localized condensations often occurred, resulting in translucent or sometimes opaque gels. The alkoxide solution must be acidified before the hydrolysis step to prepare transparent ho-

* To whom correspondence should be addressed. E-mail: djsuh@kist.re.kr. Fax: 82-2-958-5199

(1) Tanabe, K. *Mater. Chem. Phys.* **1985**, *13*, 347.
 (2) Yamaguchi, T. *Catal. Today* **1994**, *20*, 199.
 (3) Gesser, H. D.; Goswami, P. C. *Chem. Rev.* **1989**, *89*, 765.
 (4) Ward, D. A.; Ko, E. I. *Chem. Mater.* **1993**, *5*, 956.
 (5) Stocker, C.; Schneider, M.; Baiker, A. *J. Porous Mater.* **1995**, *2*, 171.
 (6) Suh, D. J.; Park, T.-J. *Chem. Mater.* **1996**, *8*, 509.
 (7) Bedilo, A. F.; Klabunde, K. J. *NanoStruct. Mater.* **1997**, *8*, 119.
 (8) Mrowiec, J.; Pajak, L.; Jarzebski, A. B.; Lachowski, A. I.; Malinowski, J. J. *J. Non-Cryst. Solids* **1998**, *225*, 115.
 (9) Stocker, C.; Baiker, A. *J. Sol-Gel Sci. Technol.* **1997**, *10*, 269.
 (10) Stocker, C.; Baiker, A. *J. Non-Cryst. Solids* **1998**, *223*, 165.

(11) Bradley, D. C.; Carter, D. G. *Can. J. Chem.* **1961**, *39*, 1434.
 (12) Bradley, D. C.; Carter, D. G. *Can. J. Chem.* **1962**, *40*, 15.
 (13) Yoldas, B. E. *J. Am. Ceram. Soc.* **1982**, *65*, 387.

Table 1. Effect of Aging Conditions on the Textural Properties of Zirconia Aerogels after Calcination at 773 K for 2 h

chelating agent used (mol/mol of Zr)	aging temp (K)	aging time (days)	BET surface area ($\text{m}^2 \text{g}^{-1}$)	pore volume ($\text{cm}^3 \text{g}^{-1}$)	mean pore diameter ^a (nm)
none	room temp	2	114	0.44	15.4
		5	125	0.45	14.3
	7	132	0.41	12.3	
	18	133	0.42	12.5	
	47	136	0.43	12.6	
acetic acid (0.1)	room temp	2 h ^b	129	0.44	13.6
		1	145	0.49	13.4
acetic acid (0.08)	room temp	3	96	0.37	15.6
		5	118	0.32	11.0
acetylacetone (0.1)	room temp	3	110	0.40	14.5
		21	130	0.41	12.6
acetylacetone (0.1)	room temp	2	108	0.44	16.3
		24	141	0.39	11.2

^a Calculated from $4 \times (\text{pore volume})/(\text{BET surface area})$. ^b After aging at room temperature for 1 day.

homogeneous gels rather than precipitates. The formation of transparent polymeric alcogels was found to be critical for obtaining the high surface areas and narrow pore size distributions of the resulting aerogels.⁶

The greater reactivity of zirconium alkoxides required much higher acid content to prepare homogeneous gels rather than precipitates. Zirconia alcogels were synthesized in about 1 h under these highly acidic conditions and should be then aged for more than 1 day to obtain the structural rigidity for subsequent supercritical drying. Zirconia aerogels prepared in this way, however, had much lower surface areas of about $100 \text{ m}^2/\text{g}$ after calcination at 773 K compared with other transition metal oxide aerogels.⁶ The pore size distribution was also relatively broader even after aging for a few days. It is here noteworthy that the aging process may change the structure of the initial alcogel and, in turn, the properties of the resulting aerogel.

The effect of aging conditions on the textural properties of calcined zirconia aerogels are summarized in Table 1. As shown in Figure 2a, the pore size distribution became narrower with aging at the expense of larger pore portions. A narrow and much sharper pore size distribution of calcined zirconia aerogels was finally obtained after aging for at least 10 days. The corresponding surface area increased with no noticeable change in pore volume, but remained almost constant with more extended aging. As shown in Figure 3, the additional use of acetic acid or acetylacetone as a chelating agent to suppress rapid hydrolysis and control reaction kinetics, resulting in increased gelation time and precipitation prevention, did not affect the aging behavior. The rate of aging could be greatly accelerated by raising the temperature. As shown in Figure 2b, further aging at 308 K for 1 day led to the narrow pore size distribution comparable to that obtained by aging at room temperature for the periods of up to 47 days. The resulting pore size distribution remained almost unchanged with very little shift to larger pores. Consequently, the highest surface area was obtained in a short period by aging at slightly elevated temperatures. In fact, compared to CO_2 supercritical drying, alcohol supercritical drying is believed to be effective in the production of high-surface-area zirconia aerogels with

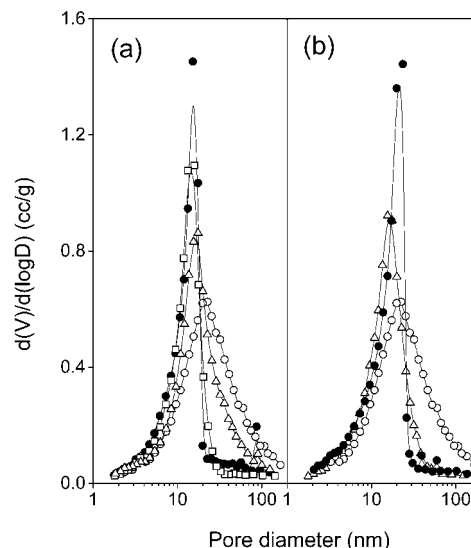


Figure 2. Effect of aging conditions on the pore size distributions of calcined zirconia aerogels: (a) aged at room temperature for 2 days (○), 5 days (△), 7 days (□), and 47 days (●); (b) aged at room temperature for 2 days (○), aged at room temperature for 1 day and 308 K for 2 h (△), and aged at room temperature for 1 day and 308 K for 1 day (●). All samples were calcined at 773 K in oxygen for 2 h.

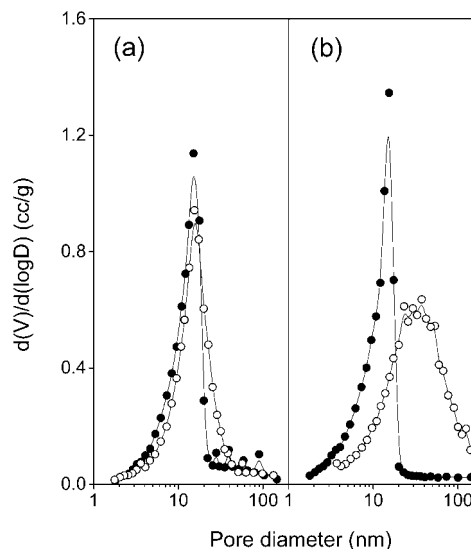


Figure 3. Effect of aging time on the pore size distributions of zirconia aerogels prepared by the sol-gel process with a chelating agent: (a) acetic acid (0.08 mol/mol of Zr), aged at room temperature for 3 days (○) and 21 days (●); (b) acetylacetone (0.1 mol/mol of Zr), aged at room temperature for 2 days (○) and 24 days (●). All samples were calcined at 773 K in oxygen for 2 h.

narrow pore size distributions due to accelerated aging at the high drying temperature.^{4,10} The pore size distributions of such high-surface-area aerogels did not vary much upon calcination up to 773 K. However, sintering at higher temperatures may cause the rearrangement of pore volume toward large pores, possibly by pore coalescence.¹⁴

Different aging behavior was reported for titania aerogels.¹⁵ For titania aerogels prepared under weakly

(14) Lorenzano-Porras, C. F.; Reeder, D. H.; Annen, M. J.; Carr, P. W.; McCormick, A. V. *Ind. Eng. Chem. Res.* **1995**, *34*, 2719.

(15) Suh, D. J.; Park, T.-J. *J. Mater. Sci. Lett.* **1997**, *16*, 490.

acidic conditions, the pore size distribution shifted to larger pores with extended aging, whereas the surface area remained virtually unaffected. The difference in this aging behavior is probably due to the use of a higher amount of nitric acid in the zirconia sol-gel processing. More acidic conditions strongly inhibit the condensation

process which is generally known to induce the textural modification during aging.^{16,17} Thus, the pore size distribution of zirconia aerogels did not shift toward larger pores with aging.

Acknowledgment. The author Jong-Choo Lim is thankful for the financial support from the Dongguk University research fund.

CM025516R

(16) Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979.

(17) Brinker, C. J.; Scherer, G. W. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*; Academic Press: New York, 1990.