Aging Behavior of Metal Oxide Aerogels

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Abstract−Aerogels of titania, zirconia, niobia, and silica were prepared by CO_2 supercritical drying of the corresponding alcogels. Their porous texture could be modified by further aging of the alcogels. This kind of textural modification was found to be different according to the nature of the metal precursor and sol-gel conditions.

Key words: Aerogel, Sol-gel, Supercritical Drying, Aging, Pore Structural Properties

INTRODUCTION

Aerogels are highly porous solids made by the sol-gel synthesis and subsequent removal of the liquid solvent from within the pores of the gel by employing supercritical drying. The most common sol-gel process involves the controlled hydrolysis of an alkoxide precursor followed by condensation to form a three-dimensional polymeric gel network [Hench and West, 1990]. Even though hydrolysis and condensation occur concurrently, it is possible to vary not only the absolute but also the relative rates by adjusting a host of so-called sol-gel parameters that include the type and concentration of alkoxide precursor, type of solvent, acid or base content, water content, and temperature [Brinker and Scherer, 1990]. These parameters affect the structure of the initial gel and, in turn, the properties of the resulting aerogel. Before supercritical drying, the structure and chemistry of a wet gel may be considerably altered by varying the aging conditions such as time, temperature, pH, and pore fluid. However, at present, an understanding of the cause and effect is at best qualitative. For this reason aging is often an overlooked step in the sol-gel synthesis of metal oxides. It is therefore scientifically and technologically important to determine how wet gels can undergo textural changes during aging. In this work, various metal oxide aerogels with mesoporosity have been prepared by the formation of a polymeric alcogel under appropriate sol-gel conditions followed by CO_2 supercritical drying. Here we present the effect of aging on the pore structural properties of the metal oxide aerogels thus obtained.

EXPERIMENTAL

The details of the preparation of metal oxide aerogels were described previously [Suh and Park, 1996]. Alcogels were prepared from metal alkoxide, alcohol solvent, H_2O, and acid or base catalyst. Table 1 lists the sol-gel parameters used in pre-

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Table 1. Sol-gel conditions used in preparing the alcogels

Metal	Solvent	Precursor (mol/*l* solvent)		Water (mol)[a]	Catalyst (mol)[a]	
Ti	methanol	$Ti(OC_4H_9^n)_4$	0.625	4.1	HNO_3	0.018
Zr	1-propanol	$Zr(OC_3H_7^n)_4$	0.625	4.1	HNO_3	1.09
Nb	methanol	$Nb(OC_2H_5)_5$	0.625	5.1	HNO_3	0.169
Si	methanol	$Si(OC_2H_5)_4$	2.076	8.67	NH_4OH	0.05
					NH_4F	0.003-0.32

[a]per mol of metal precursor.

paring the alcogels. The alcogel was covered with plastic film and aged under different conditions in order to study the aging effect. Unlike the most common aging process, which allows the alcogel to remain in its mother liquor, the aging fluid was not used in this work. The solvent entrapped in the gel network was removed from the aged gel by flowing supercritical CO_2 at 333 K and 24 MPa. The product aerogel was ground to <100 mesh and calcined in a tube furnace in flowing He at 573 K for 2 h and then in flowing O_2 at 773 K for 2 h, which was the standard calcination procedure in this study. After this calcination step, it was slowly cooled to room temperature and stored in a desiccator. 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 by using a Micromeritics ASAP 2000 instrument. Prior to the measurements, all samples were outgassed under vacuum at 383 K overnight.

RESULTS AND DISCUSSION

1. Titania Aerogel

Table 2 shows the effect of aging conditions on the textural properties of titania aerogels. Over the range studied, aging conditions had no significant effect on the surface area of the calcined product. On the contrary, the pore volume and pore size were shown to increase with the extent of aging. This kind of textural modification induced by aging is well known for silica gels soaked in solutions [Smith et al., 1990]. It has been reported that condensation in silica gels continues long after gelation [Brinker and Scherer, 1990; Vega and Scherer, 1989]. Similarly,

Table 2. Effect of aging conditions on the textural properties of titania aerogels after calcination at 773 K for 2 h

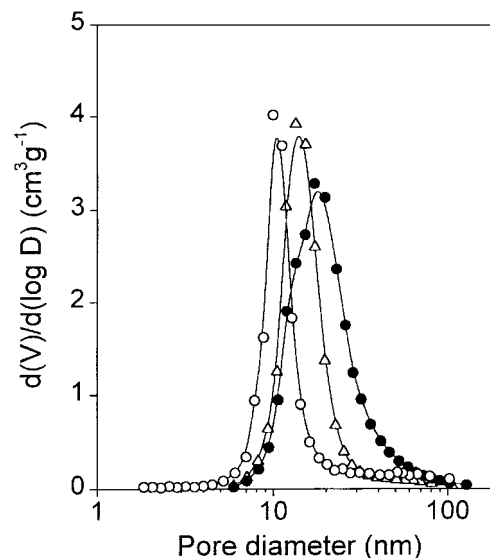| Aging temperature (K)	Aging time	BET surface area (m²/g)	Total pore volume (cc/g)	Average pore diameter[a] (nm)
Room temperature	3 hours	211	0.91	17.3
	15 days	206	0.90	17.5
	38 days	200	0.99	19.8
	80 days	204	1.04	20.4
323	1 hour	226	1.11	19.6
	2 hours	211	1.07	20.3
	12 hours	220	1.28	23.3

[a] calculated from 4×(pore volume)/(BET surface area).

Fig. 1. Effect of aging time on the pore size distributions of titania aerogels aged at room temperature for (○), 3 hours; (△) 38 hours; (●) 80 days. All samples were calcined at 773 K in O₂ for 2 hours.

Fig. 2. Effect of aging temperature on the pore size distribution of titania aerogels. Aged at: (○), room temperature for 3 hours; (△) 323 K for 2 hours; (●) 323 K for 12 hours. All samples were calcined at 773 K in O₂ for 2 hours.

aging of titania alcogels may modify their texture by continued condensation reactions leading to a more branched gel network. The more branched the gel network is, the larger interconnected particle may be formed and the resulting pore size will become larger.

The changes in the pore size distribution during aging at room temperature and 373 K are clearly shown in Figs. 1 and 2. With prolonged aging at room temperature, larger pores were newly produced without changing the original peak maximum in the pore size distribution curve, and thus even bimodal distributions could be observed. Presumably, at room temperature, there is a lower driving force for the entire pore structural changes by further condensation. Thus, the overall pore structure was better preserved and these textural changes occurred only in limited regions of the gel. Since the aging behavior can be thermally activated, it is possible to change the overall pore size distribution of the final aerogel by raising the aging temperature. As shown in Fig. 2, at the higher temperature, the pore size distribution became broader and progressively shifted to larger pore sizes during aging.

2. Zirconia Aerogel

The greater reactivity of zirconium alkoxides required much higher acid content in order to prepare homogeneous gels rather than precipitates. Zirconia alcogels were prepared in about one hour under these highly acidic conditions. To obtain structural rigidity for subsequent supercritical drying, they should be aged for more than one day. However, as shown in Fig. 3, their porous structure was not fully developed even after aging at room temperature for a few days. 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.
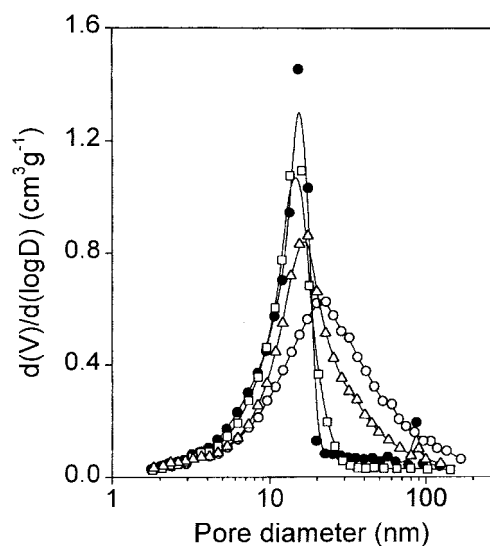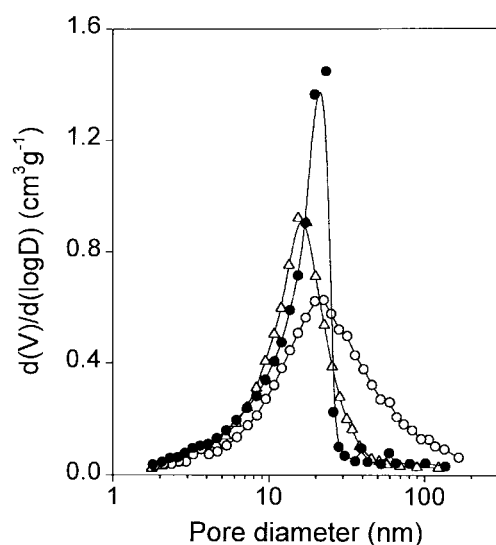

Fig. 3. Effect of aging time on the pore size distributions of zirconia aerogels aged at room temperature for (○), 2 days; (△) 5 days; (□) 7 days; (●) 47 days. All samples were calcined at 773 K in O₂ for 2 hours.

Table 3. Effect of aging conditions on the textural properties of zirconia aerogels after calcination at 773 K for 2 h

Aging temperature (K)	Aging time	BET surface area (m^2/g)	Total pore volume (cc/g)	Average pore diameter (nm)
Room temperature	2 days	114	0.44	15.4
	5 days	125	0.45	14.3
	7 days	132	0.41	12.3
	18 days	133	0.42	12.5
	47 days	136	0.43	12.6
308[a]	2 hours	129	0.44	13.6
	1 day	145	0.49	13.4

[a] after aging at room temperature for one day.

Table 4. Effect of aging time on the textural properties of niobia and silica aerogels after calcination at 773 K for 2 h

Aerogel	Aging time	BET surface area (m^2/g)	Total pore volume (cc/g)	Average pore diameter (nm)
Niobia	3 hours	246	0.76	12.2
	2 days	269	0.78	11.6
	15 days	256	0.86	13.4
	66 days	266	0.92	13.8
Silica[a]	1 day	1143	2.06	7.0
	5 days	976	2.13	8.7
	11 days	1035	4.52	17.4

[a] prepared by using an $NH_4F/TEOS$ molar ratio 0.04.

Fig. 4. Effect of aging temperature on the pore size distribution of zirconia aerogels. Aged at: (○), room temperature for 2 days; (△) room temperature for 1 day and 308 K for 2 hours; (●) room temperature for 1 day and 308 K for 1 day. All samples were calcined at 773 K in O_2 for 2 hours.

Fig. 5. Effect of aging time on the pore size distributions of niobia aerogels aged at room temperature for (○), 3 hours; (△) 2 days; (□) 15 days; (●) 66 days. All samples were calcined at 773 K in O_2 for 2 hours.

The corresponding surface area increased with no noticeable change in pore volume, but remained almost constant with more extended aging. The effect of aging conditions on the textural properties of zirconia aerogels is shown in Table 3. The rate of aging was observed to increase with temperature. As shown in Fig. 4, only a two-day aging process including aging at 308 K for one day resulted in a narrow pore size distribution. The resulting pore size distribution remained almost unchanged with very little shift to larger pores.
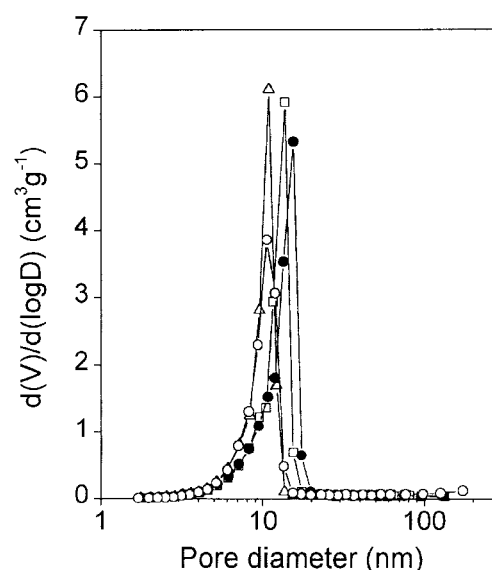
This aging behavior is probably due to the use of a higher amount of nitric acid in the zirconia sol-gel processing. More acidic conditions strongly inhibit the condensation process and are generally known to induce textural modification during aging [Iler, 1979; Brinker and Scherer, 1990]. Thus, the pore size distribution of zirconia aerogels did not shift towards larger pores with aging.

3. Niobia Aerogel

Compared to titania and zirconia, a medium amount of nitric

acid was necessary to obtain transparent niobia alcogels leading to high-surface-area niobia aerogels. Their aging behavior was also studied in a similar way. As shown in Table 4 and Fig. 5, aging did not affect textural properties of the niobia aerogels to any significant extent. The pore size distribution of niobia aerogels very slowly shifted to larger pores with aging. Out of transition metal oxide aerogels studied here, niobia exhibited the slowest aging rate for textural changes due to further condensation. Indeed, the overall porous structure remained almost unchanged after extended aging.

4. Silica Aerogel

It is well known that silicon alkoxides are much less reactive in comparison to the corresponding transition metal alkoxides. The base-catalyzed gelation of tetraethylorthosilicate (TEOS), widely used as a cheaper and less toxic precursor, could be drastically accelerated by using NH_4OH buffered with NH_4F [Russo and Hunt, 1986; Mrowiec-Bialon et al., 1997]. The catalyst systems with fluoride anions are known to be effective for reducing the gelation time from hours or even days to minutes [Iler,
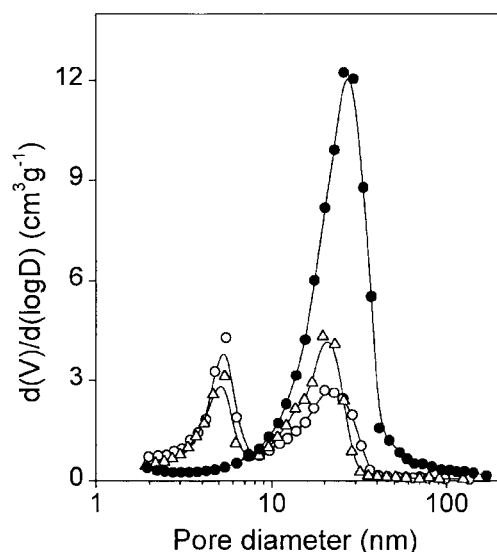
Fig. 6. Effect of aging time on the pore size distributions of silica aerogels aged at room temperature for (○), 1 day; (△) 5 days; (●) 11 days. All samples were prepared with 0.04 mol NH_4F/mol TEOS and calcined at 773 K in O_2 for 2 hours.

1979; Pope and Mackenzie, 1986].

The effect of aging time on the pore size distribution of silica aerogels prepared by the sol-gel process using NH_4OH and NH_4F is shown in Fig. 6. The use of NH_4F in the sol-gel process for rapid gelation initially resulted in an aerogel having bimodal pore size distribution with maxima at ca. 5 and 20 nm. With increasing the aging time, the peak of smaller pores progressively decreased while that of larger pores increased accordingly. Further aging for more than 10 days finally led to a unimodal pore size distribution. The resulting pore size distribution was fairly narrow and symmetric.

In order to understand the aging behavior in more detail, we varied the aging time of silica alcogels prepared under different NH_4F concentrations. As a result, with the higher concentration of NH_4F, the corresponding shorter gelation time required the longer aging time to obtain well-defined unimodal pore size distributions of the resulting silica aerogels. Fluoride anions induced a dramatic decrease in gelation time, but the porous texture of the corresponding silica alcogel was not likely to be stabilized at the time of gelation. The microstructure of alcogels prepared using NH_4OH and NH_4F was expected to be in a metastable condition, giving rise to a bimodal pore size distribution. However, subsequent aging at room temperature allowed reorganization of the porous structure, resulting in a unimodal pore size distribution. The structural changes that occurred during aging increased the pore volumes and average pore diameters of the resulting aerogels, whereas the surface areas remained

virtually unaffected.

CONCLUSIONS

The effect of aging on textural properties of titania, zirconia, niobia, and silica aerogels has been studied. Aging of the alcogels was observed to modify their porous texture in a different manner. For titania aerogels prepared by the sol-gel process under weakly acidic conditions, the pore size distribution shifted to larger pores with aging, probably due to further condensation. Niobia aerogels prepared under medium acidic conditions exhibited no noticeable textural changes after aging. For zirconia aerogels prepared under highly acidic conditions, the highest surface area with a narrow pore size distribution could be obtained only after extended aging. For silica aerogels prepared by the rapid sol-gel process using NH_4OH and NH_4F, subsequent aging of the alcogels resulted in the progressive transformation from metastable bimodal pore size distribution to well-defined unimodal one.

The rate of aging was found to be much slower than that of gelation. There may be differences in the rate of aging, but the stable porous texture of the corresponding aerogel for given sol-gel conditions can be finally obtained by prolonged aging.

REFERENCES

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

Hench, L. L. and West, J. K., "The Sol-Gel Process," *Chem. Rev.*, **90**, 33 (1990).

Iler, R. K., "The Chemistry of Silica," Wiley, New York (1979).

Mrowiec-Bialon, J., Pajak, L., Jarzebski, A. B., Lachowski, A. I. and Malinowski, J. J., "Morphology of Silica Aerogel Obtained from the Process Catalyzed by NH_4F and NH_4OH," *Langmuir*, **13**, 6310 (1997).

Pope, E. J. A. and Mackenzie, J. D., "Sol-Gel Processing of Silica: II. The Role of the Catalyst," *J. Non-Cryst. Solids*, **87**, 185 (1986).

Russo, R. E. and Hunt, A. J., "Comparison of Ethyl versus Methyl Sol-Gels for Silica Aerogels Using Polar Nephelometry," *J. Non-Cryst. Solids*, **86**, 219 (1986).

Smith, D. M., Davis, P. J. and Brinker, C. J., "In-situ Pore Structure Analysis During Aging and Drying of Gels," *Mat. Res. Soc. Symp. Proc.*, **180**, 235 (1990).

Suh, D. J. and Park, T.-J., "Sol-Gel Strategies for Pore Size Control of High-Surface-Area Transition Metal Oxide Aerogels," *Chem. Mater.*, **8**, 509 (1996).

Vega, A. J. and Scherer, G. W., "Study of Structural Evolution of Silica Gel Using ^1H and ^{29}Si NMR," *J. Non-Cryst. Solids*, **111**, 153 (1989).