Sol−Gel Strategies for Pore Size Control of High-Surface-Area Transition-Metal Oxide Aerogels

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Titania, zirconia, and niobia aerogels were prepared by the sol−gel synthesis from alcoholic metal alkoxide solutions under acidic conditions and the subsequent supercritical drying with carbon dioxide. At a stoichiometric amount of water and a constant alkoxide concentration the nitric acid contents were varied to examine the characteristics of gel formation behavior and the produced aerogel properties. The range of acid content in which transparent polymeric gels were obtained was determined. Under these conditions there was little effect of acid content on the surface area of their calcined aerogel samples. On the other hand, the pore size distributions were significantly affected by the acid contents. The resulting titania, zirconia, and niobia aerogels, after calcination at 773 K for 2 h, had BET surface areas of about 200, 100, and 200 m^2/g, respectively, and relatively narrow pore size distributions in the mesopore region. The results suggest a simple way to control the pore sizes of the high-surface-area aerogel only by adjusting the amount of nitric acid used in the sol−gel synthesis.

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 very large surface associated with these materials made them attractive in the field of catalysis.[1−5] Although aerogels have been known for decades, the literature on the sol−gel synthesis for preparing materials of catalytic interest is not extensive compared with that on the synthesis of glasses and ceramics. Moreover, most of work on this area of research, in the past and even recently, has been done on silica aerogels.[6−8] Much less work has been devoted to transition-metal oxide aerogels which are of general catalytic interest. It has been shown in previous reports that some transition-metal oxide aerogels can be synthesized successfully via acid-catalyzed sol−gel route using metal alkoxides.[9−15] However, the particular effect of acid contents on the physical properties of the prepared non-silica aerogels has not been systematically studied even though it is well recognized that pH is the dominant factor that determines the resulting silica gel structure.[16−18]

In this work, for three typical transition-metal oxides of titania, zirconia, and niobia, the effects of acid contents on the gelation behavior and the textural properties of the aerogels prepared were systematically investigated. This paper briefly describes our synthesis and characterization of these transition-metal oxide aerogels with high specific surface areas and narrow pore size distributions which can be potential catalyst supports. We shall then present how to control the pore sizes of the resulting aerogels by adjusting acid content, one of the sol−gel synthesis parameters.

Experimental Section

Titania, zirconia, and niobia aerogels were prepared by the sol−gel synthesis from alcoholic metal alkoxide solutions under acidic conditions and the subsequent supercritical drying with carbon dioxide. Table 1 lists the sol−gel parameters used to prepare the alcogels in this work. Titanium(IV) *n*-butoxide, zirconium(IV) *n*-propoxide, and niobium(V) ethoxide were purchased from Aldrich Chemical Co. and used as raw materials. First, an alcoholic solution of metal alkoxide was prepared in a dry glovebox. Then another solution containing the same alcohol, nitric acid, and distilled water was added to the metal alkoxide solution under continuous stirring. At the gelling point the stirring was stopped, and the alcogel was aged for different times to obtain the structural rigidity required for supercritical drying. Generally titanium and niobium alcogels were aged for 3 h. On the other hand, zirconium alcogels were

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(1) Kistler, S. S. *Nature* **1931**, *127*, 741.

(2) Kistler, S. S.; Swann, S., Jr.; Appel, E. G. *Ind. Eng. Chem*. **1934**, *26*, 388.

(3) Pajonk, G. M. *Appl. Catal.* **1991**, *72*, 217.

(4) Ko, E. I. *CHEMTECH* **1993**, *23* (4), 31.

(5) Armor, J. N.; Carlson, E. J.; Zambri, P. M. *Appl. Catal.* **1985**, *19*, 339.

(6) Teichner, S. J.; Nicolanon, G. A.; Vicarini, M. A.; Gardes, G. E. *Adv. Colloid Interf. Sci.* **1976**, *5*, 245.

(7) Maret, D.; Pajonk, G. M.; Teichner, S. J. *Catalysis on the Energy Scene*; Kaliaguine, S., Mahay, A., Eds.; Elsevier Science: Amsterdam, 1984; p 347.

(8) Rao, A. V.; Pajonk, G. M., Parvathy, N. N. *J. Mater. Sci.* **1994**, *29*, 1807.

(9) Schneider, M.; Baiker, A. *J. Mater. Chem.* **1992**, *2*, 587.

(10) Schneider, M.; Maciejewski, M.; Tschudin, S.; Wokaun, A.; Baiker, A. *J. Catal.* **1994**, *149*, 326.

(11) Sudoh, K.; Hirashima, H. *J. Non-Cryst. Solids* **1992**, *147, 148*, 386.

(12) Bianchi, D.; Gass, J. L.; Khalfallah, M.; Teichner, S. J. *Appl. Catal. A* **1993**, *101*, 297.

(13) Maurer, S. M.; Ko, E. I. *J. Catal.* **1992**, *135*, 125.

(14) Campbell, L. K.; Na, B. K.; Ko, E. I. *Chem. Mater.* **1992**, *4*, 1329.

(15) Ward, D. A.; Ko, E. I. *Chem. Mater.* **1993**, *5*, 956.

(16) Pope, E. J. A.; Mackenzie, J. D. *J. Non-Cryst. Solids* **1986**, *87*, 185.

(17) Zerda, T. W.; Artaki, I.; Jonas, J. *J. Non-Cryst. Solids* **1986**, *81*, 365.

(18) Himmel, B.; Gerber, T.; Burger, H. *J. Non-Cryst. Solids* **1987**, *91*, 122.

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

metal ion (M^+)	precursor	solvent	M^+/solvent (mmol/mL)	H_2O/M^+ (mol/mol)	HNO_3/M^+ (mol/mol)
Ti^{4+}	$Ti(OC_4H_9{}^n)_4$	methanol	0.625	4.0	0.005–0.1
Zr^{4+}	$Zr(OC_3H_7{}^n)_4$	1-propanol	0.625	4.0	0.70–2.5
Nb^{5+}	$Nb(OC_2H_5)_5$	methanol	0.625	5.0	0.02–0.35

aged for 12–80 h, depending on the concentration of nitric acid. The solvent 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 heated in a tube furnace in a helium flow of 135 mL/min to 573 K, and then in oxygen flowing at 95 mL/min the temperature was increased to 773 K, which was the standard calcination procedure in this study. The sample was heated at a rate of 5 K/min to the desired temperature and held at the temperature for 2 h. After this calcination step, it was slowly cooled to room temperature and stored in a desiccator. The first heat treatment for removal of any organic residues was found to be a crucial step for obtaining a high-surface-area metal oxide aerogel. The xerogel samples were obtained by drying the alcogels prepared under the same sol–gel conditions in a vacuum oven at 343 K overnight.

After supercritical drying and calcination, textural characterization of the aerogel sample was performed on a Micromeritics ASAP 2000 instrument. The BET surface area, pore volume, and pore size distribution of the aerogel samples were obtained from nitrogen adsorption–desorption at 77 K. The mesopore size distributions were calculated applying the Barrett–Joyner–Halenda method[19] to the desorption branch of the isotherms. Prior to the measurements, all samples were outgassed under vacuum at 383 K overnight. Powder X-ray diffraction (XRD) patterns were obtained with a Norelco diffractometer using Cu Kα radiation.

Results and Discussion

Sol–Gel Synthesis. Since transition-metal alkoxides are in general very reactive, the modification of them with acid is commonly employed to retard the hydrolysis and condensation reaction rates in order to obtain homogeneous gels rather than precipitates. Our preliminary tests under various sol–gel conditions showed that the amount of nitric acid in the starting compositions played an important role in determining the gel morphology and the textural properties of the resultant aerogel. Not only is the gelation rate affected, but the gel formation behavior also influenced by this variable. Figure 1 shows the appearance of the sol–gel products prepared by various amounts of nitric acid addition with a stoichiometric water/alkoxide ratio. According to the physical appearance of the resultant products, four different types of behavior can be classified, although these regions were significantly different for three metal alkoxides. The sol–gel reaction under weakly acidic conditions led to the formation and precipitation of particulate materials and the solution became turbid. Such precipitate formation and self-condensation could be avoided by introducing a higher amount of nitric acid. Increasing the acid content could give translucent gels which contained precipitates within the gel network and at much higher acid content transparent polymeric gels with good bounce could be obtained. However, when an excessive amount of acid was used in titania and zirconia systems, the sol–gel solution formed very soft and transparent gel and exhibited fluidity even after aging for an extended period. The amount of nitric acid to maintain the clarity of zirconium(IV) *n*-propoxide in 1-propanol in this study was slightly higher than that reported by Yoldas.[20] On the contrary, a series of niobia alcogels prepared under these highly acidic conditions showed a different aging behavior. If more than 0.25 mol of nitric acid/mol of niobium ethoxide was used, the stability of the resulting gel was reduced and it became increasingly cloudy in the course of aging, probably due to the formation of precipitates in its gel network. Similar observation was reported for titania systems if more than 0.3 mol of nitric or hydrochloric acid/mol of alkoxide was used.[21,22]

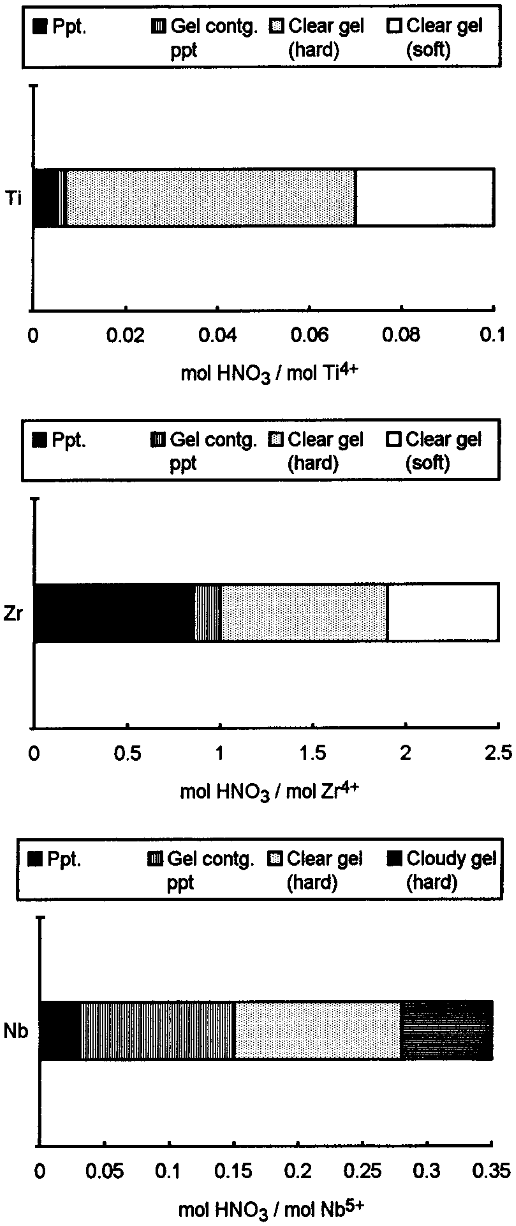

Figure 1. Appearances of sol–gel products prepared with various amount of nitric acid.

As shown in Figure 2, the gelling time increased with the nitric acid concentration. Generally titanium and niobium sol–gel solutions gelled within a few minutes. On the other hand, zirconium alkoxide solutions gelled

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(19) Barrett, E. P.; Joyner, L. G.; Halenda, P. P. *J. Am. Chem. Soc.* **1951**, *73*, 373.

(20) Yoldas, B. E. *J. Mater. Sci.* **1986**, *21*, 1080.

(21) Yoldas, B. E. *J. Mater. Sci.* **1986**, *21*, 1087.

(22) Terabe, K.; Kato, K.; Miyazaki, H.; Yamaguchi, S.; Imai, A. *J. Mater. Sci.* **1994**, *29*, 1617.

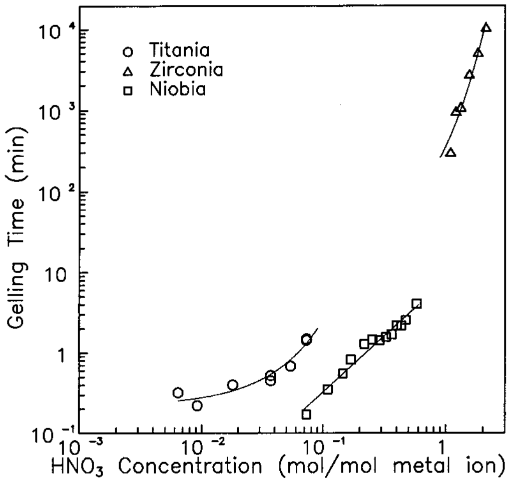

Figure 2. Effect of acid content on the gelling time.

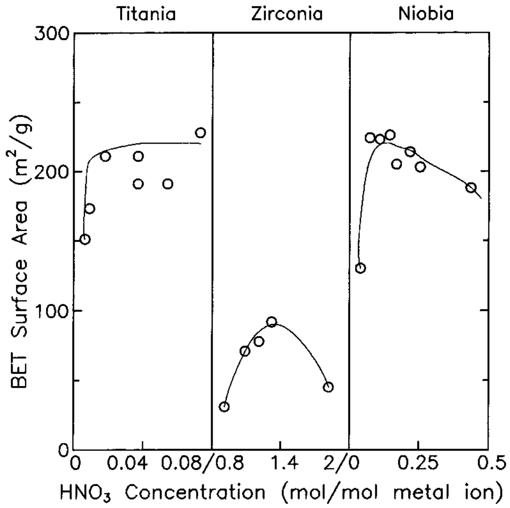

Figure 3. Effect of acid content on the surface area of transition metal oxide aerogels after calcination at 773 K for 2 h.

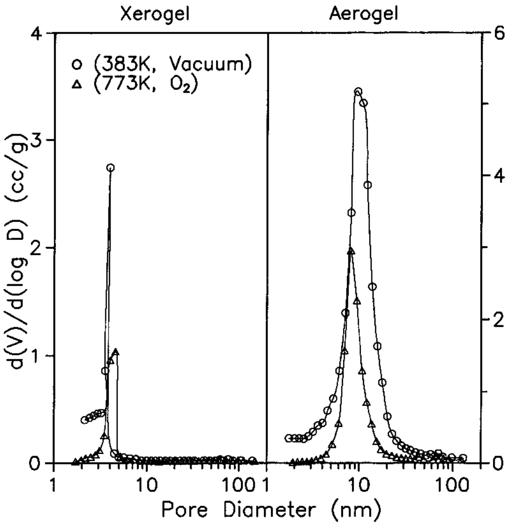

Figure 4. Pore size distributions of titania aerogel and xerogel samples before and after calcination at 773 K for 2 h.

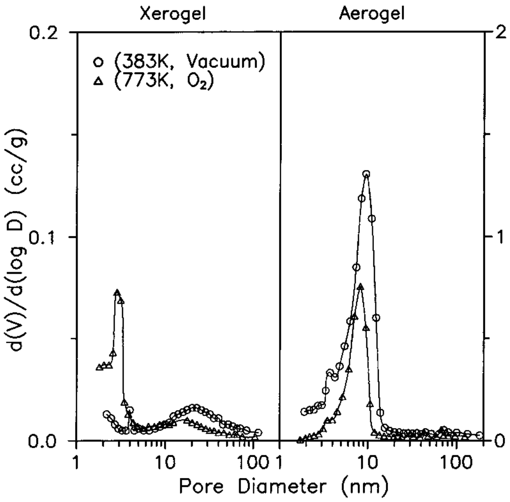

Figure 5. Pore size distributions of zirconia aerogel and xerogel samples before and after calcination at 773 K for 2 h.

in hours or days, depending on the concentration of nitric acid. Since sol–gel chemistry involves nucleophilic reactions, the positive charge of the metal atom can be an important factor for deciding the reactivity of metal alkoxides towards hydrolysis and condensation. According to the results by Livage et al.,[23,24] the order of the partial positive charge on the cation decreases as Zr(+0.65) > Ti(+0.63) > Nb(+0.53). The greater reactivity of zirconium ion required much higher acid content, and thus the alcogel for zirconia had a long gel time. As a general rule, the longer and the bulkier the alkoxide group, the lower the rate constant of hydrolysis and/or condensation.[23,25] Taking this rule into consideration, it could be explained that the reactivity of titanium butoxide was comparable to that of niobium ethoxide.

Physical Properties. As shown in Figure 3, over the range for the formation of transparent polymeric gels, varying the amount of nitric acid added had no marked effect on the surface area of their calcined aerogels. This observation is similar to the result for titania aerogels reported by Schneider and Baiker.[9] Over this range, a transparent and firm alcogel leads to the highest surface area. On either side of this range, the surface area dropped off probably due to the collapse of weaker gel network during all subsequent processing steps; the sol–gel reaction with lower acid contents led to nonuniform weak gels containing precipitates, whereas higher acid contents retarded the condensation kinetics to form weakly branched soft gels. Similar observation has been previously reported by Ward and Ko for the synthesis of high-surface-area titania[14] and zirconia[15] aerogels. In the sol–gel preparation of niobia, beyond this range of acid content, the cloudiness of the gel obtained increased gradually with increasing acid content, leading to a gradual decrease in surface area of the calcined niobia aerogel. The resulting titania, zirconia, and niobia aerogels, after calcination at 773 K for 2 h, had high surface areas of about 200, 100, and 200 m^2/g, respectively.

All the transition-metal oxide aerogels obtained from transparent polymeric gels were mesoporous with relatively narrow pore size distributions as shown in Figures 4–6. These figures show three representative patterns of high-surface-area aerogels calcined at 773 K. The pore size distribution did not vary much as the

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

(24) Livage, J.; Henry, M.; Sanchez, C. *Prog. Solid State Chem.* **1988**, *18*, 259.

(25) Hench, L. L.; West, J. K. *Chem. Rev.* **1990**, *90*, 33.

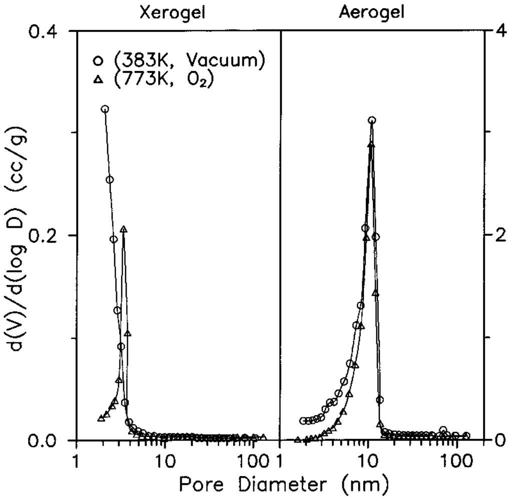

Figure 6. Pore size distributions of niobia aerogel and xerogel samples before and after calcination at 773 K for 2 h.

aerogel sample was heated up to 773 K. These results suggest that the aerogels obtained from clear and firm gels have the rigid porous framework with better thermal stability. The pore size modes were shifted according to aerogel preparation conditions. Generally titania aerogels have symmetric pore size distributions while zirconia and niobia aerogels have asymmetric ones including smaller mesopore sizes. Some of low-surface-area zirconia aerogel samples showed very broad pore size distributions. Sometimes, even bimodal distributions were observed. Although Maurer and Ko's niobia aerogel sample prepared under similar synthetic conditions, after calcination at 773 K, had a surface area of 190 m^2/g, it did not have a narrow pore size distribution.[13]

It is also noted from these figures that the xerogel samples were exclusively microporous. It was found that relatively large pores were collapsed selectively as the gel shrank and micropores were formed at the last stage of conventional drying. Since the xerogel had relatively poor thermal stability, after calcination at 773 K, it had a significant change in the pore size distribution due to the collapse of its original pore structure. Likewise a marked advantage of supercritical drying is clearly demonstrated by the quite different textural characteristics of aerogel and xerogel samples, as these samples came from the same alcogel and differed only in the drying method.

In contrast to the effect on the surface area stated above, increasing the amount of nitric acid used in the sol–gel synthesis resulted in the apparent shift in the pore diameter distribution to larger size. Figure 7 shows that average pore size decreased proportionally with increasing acid content in the case of high-surface-area aerogel samples prepared from transparent polymeric gels. The average pore size of titania aerogel can be controlled from 10 to 22 nm only by varying the concentration of the added nitric acid. Like the part shown in dotted line, for the cloudy niobia gels containing precipitates, with a further increase of acid content the increase of turbidity was observed and the pore size increased accordingly. To date, little attention has been paid to such a dependence of acid content on the pore size of the resulting transition-metal oxide aerogel.

The above findings can be explained by extending widely known sol–gel chemistry of silicon alkoxides under different pH conditions.[23,26,27] Under acidic conditions, hydrolysis is more rapid than condensation and the Si–OH containing monomers slowly condense by cluster–cluster growth into linear or weakly branched polymeric gel network. In a basic environment, the condensation reaction is favored and consumes any Si–OH containing monomers that are generated. These conditions promote the formation of highly branched silica species by monomer–cluster growth. Eventually, the clusters covalently link together through their surface silanol groups, leading to a colloidal gel. In reality, there is not a sharp dividing line between the characteristics of a polymeric and colloidal gel, rather a broad continuum is thought to exist.

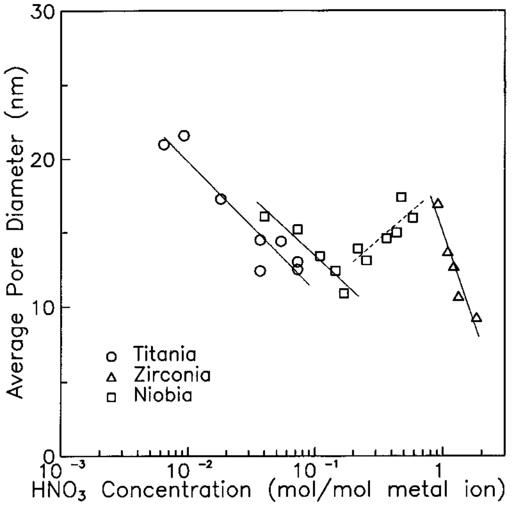

Figure 7. Effect of acid content on average pore diameters of transition metal oxide aerogels after calcination at 773 K for 2 h.

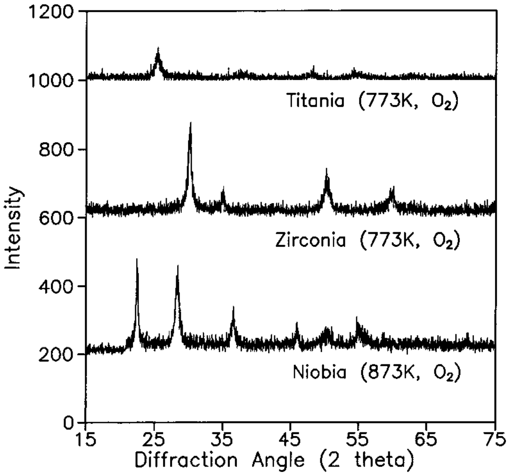

Figure 8. X-ray diffraction patterns of transition metal oxide aerogels after calcination at 773 K (for titania and zirconia) or 873 K (for niobia) for 2 h.

From the same approach the porous network structure of our high-surface-area transition-metal aerogels can be determined by the amount of acid catalyst used in the sol–gel synthesis. Presumably the more branched the gel network is, the larger interconnected particle may be formed and the resulting pore size will become larger. Increasing the acid contents leads to a lower

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(26) Schmidt, H.; Scholze, H. *Aerogels*; Fricke, J., Ed.; Springer-Verlag: Berlin, 1986; p 49.

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

Table 2. Preparation Conditions and Textural Characteristics of the Representative Aerogel and Xerogel Samples before and after Calcination at 773 K for 2 h[a]

	sol−gel synthesis			dried sample			calcined sample		
sample	HNO_3	*t*(g)	*t*(a)	*A*(s)	*V*(p)	*d*(a)	*A*(s)	*V*(p)	*d*(a)
aerogel TiO_2	0.073	1.48	3	769	1.89	9.8	228	0.71	12.5
xerogel TiO_2	0.073	1.50	3	320	0.28	3.5	105	0.16	6.2
aerogel ZrO_2	1.32	18 h	26	272	0.49	7.1	92	0.21	9.2
xerogel ZrO_2	1.32	17 h	26	8	0.01	7.3	22	0.02	4.2
aerogel Nb_2O_5	0.169	0.82	3	397	0.80	8.0	205	0.56	10.9
xerogel Nb_2O_5	0.169	0.75	3	227	0.12	2.0	26	0.03	4.1

[a] HNO_3, the amount of nitric acid used in the sol−gel synthesis (mol/mol metal ion); *t*(g), gelling time (min); *t*(a), aging time (h); *A*(s), BET surface area (m^2/g); *V*(p), pore volume (cc/g); *d*(a), average pore diameter (nm).

degree of cross-linking in the gel network, and thus the average pore size decreases. This observed trend, however, cannot be applied to inhomogeneous systems such as cloudy niobia gels prepared under highly acidic conditions. Under the optimal conditions for obtaining transparent alcogels, changing the amount of nitric acid used could not affect the inherent porous network structure of the polymeric gels, and no noticeable variations in the surface area of the resulting aerogels were observed. As stated earlier, the surface area of the calcined aerogels may be strongly dependent on their structural stability against shrinkage and collapse of the gel network during all subsequent processing steps. Therefore, based on this simple sol−gel strategy, the pore size can be precisely tailored, suggesting applications as catalytic materials.

From the X-ray diffraction results of the aerogels, it was found that all the samples remained amorphous up to 573 K. As shown in Figure 8, after calcination at 773 K, the titania aerogel was in a pure anatase form with poor crystallinity, whereas the zirconia aerogel in a tetragonal phase. The calcined niobia aerogel was still amorphous up to 773 K and crystallized into the TT form[28] after heating at 873 K for 2 h. Table 2 summarizes the amount of nitric acid added for the sol−gel synthesis, gelling time, aging time, and some textural properties of the representative aerogel and xerogel samples examined in this study.

Conclusions

We have synthesized high-surface-area titania, zirconia, and niobia aerogels by optimizing the acid contents in the sol−gel syntheses from alcoholic metal alkoxide solutions. Over the range for the formation of transparent polymeric alcogels, the average pore sizes of the calcined aerogel samples decreased proportionally with increasing the acid contents. On the other hand, there was little effect of acid content on the surface area of the samples over this range. We now present a simple way for controlling the average mesopore sizes of transition-metal oxide aerogels without changing their surface areas only by adjusting acid content. To control the wider range of the pore sizes, the effect of the various factors governing the sol−gel reactions on the resulting structural properties is currently being investigated in our laboratory.

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(28) Shafer, H.; Gruehn, R.; Shulte, F. *Angew. Chem., Intl. Ed. Engl.* **1966**, *5*, 40.