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Effect of Physical Structure on the Phase Development of Aluminosilicate Gels

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The surface area and density of aluminosilicate xerogels containing a one-to-one Al/Si molar ratio (47 wt% alumina) can be varied dramatically by changing the pore fluid prior to drying. The surface area of ethanol-washed 47 wt% alumina gels was more than 500 m^2/g, while gels dried from the mother liquor (approximately 75 vol% ethanol, 25 vol% water) had less than 1 m^2/g surface area. Changes in the physical structure of the dried gels had dramatic effects on subsequent phase evolution and densification behavior during heat treatment. NMR, X-ray diffraction, and DTA were used to follow the phase evolution of different gels. Differences in the amorphous gel structure were identified using ^{27}Al and ^{29}Si MAS NMR. Gels of identical composition prepared from the same precursor solutions crystallized to different phases, depending upon the surface area of the gel prior to heating. The high surface material (ethanol washed) formed mullite and amorphous silica, while the low surface area gel (unwashed) crystallized to mullite and cristobalite. These gels were prepared from alkoxide precursors. A low surface area gel with a different degree of chemical homogeneity was prepared by the nitrate method for comparison. Results indicate that the physical structure of aluminosilicate gels, i.e., pore structure and chemical homogeneity, has a dramatic influence on phase evolution. [Key words: aluminosilicates, gels, structure, phases, surface area.]

I. Introduction

It was recently reported that the surface area and skeletal density of aluminosilicate gels are related to both gel composition and the pore fluid present prior to drying.[1–4] For example, the surface area of a 47 wt% alumina gel (balance silica) was varied by nearly three orders of magnitude by washing the gels with different liquids prior to drying.[1] Gels washed with ethanol had surface areas on the order of 500 m^2/g, while gels of identical composition dried from the mother liquor (no washing) had surface areas less than 1 m^2/g.[3] The skeletal density of the gels, as determined by helium pycnometry, was also affected by washing. The formation of closed pores, inaccessible to the probe gases, was responsible for the dramatic drop in surface area and skeletal density.[2] Perhaps the most interesting property of the 47 wt% alumina gels is that a wide range of pore structures can be developed by varying the amount of water used for hydrolysis of the alkoxide precursors or by washing the gels in different fluids prior to drying. Figure 1 shows nitrogen adsorption isotherms of nonporous, microporous, and mesoporous 47 wt% alumina gels. For these materials, "nonporous" does not imply that the gels are completely dense; it means that there is little or no accessible porosity. Such a drastic effect on physical structure might be expected to alter the crystallization and sintering behavior of gel-derived powders. In fact, previous studies have shown that the structural evolution of aluminosilicates is particularly sensitive to the nature of the precursor gel, e.g., colloidal versus polymeric gels.[5]

Yoldas and co-workers,[5–7] Huling and Messing,[8,9] and others[10,11] have studied the effect of precursors and preparation conditions on the structure of aluminosilicate gels. These works compared the phase evolution of gels prepared by different techniques, including colloidal versus polymeric (Yoldas) and a variety of seeded gels (Huling and Messing). Yoldas showed that the microstructure of a heat-treated ceramic was directly related to the physical structure of the gel.[5] Sintered gels prepared from a sol of colloidal boehmite and tetraethyl orthosilicate (TEOS) consisted of dense mullite grains separated by large (~1 μm) pores.[5] Polymeric precursors produced mullite with no intergranular porosity, but a significant number of small pores developed within each

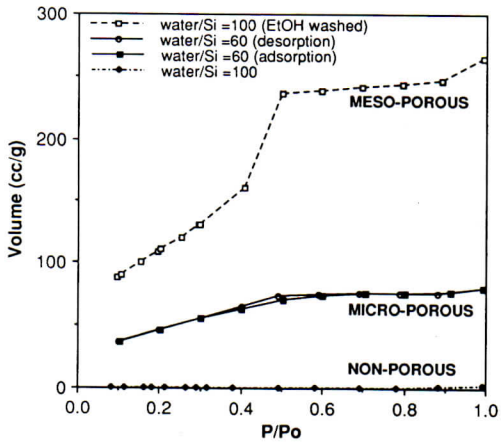

Fig. 1. Nitrogen isotherms for non-, micro-, and mesoporous 47 wt% alumina gels.

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grain.[6] The observed differences in microstructure were attributed to differences in the scale on which the silica and alumina species were mixed during processing.[6] The degree of mixing was controlled by the size of the species in the sol, molecular mixing for polymeric precursors versus mixing limited by particle size for colloids. Huling and Messing tried to control the microstructure of aluminosilicates by "seeding" colloidal gels with polymeric species.[8] Because the polymeric species were mixed on the molecular level in solution, crystallization of mullite began at around 980°C.[9] These crystallites then served as nucleation sites for crystallization in the remainder of the gel.[9] Both studies showed that the physical structure of a gel, in addition to its chemical composition, plays an important part in the phase development and densification. In this paper, the effect of changes in physical structure, specifically pore structure, on phase evolution was investigated. Unlike the previous investigations, the alkoxide-derived gels used in this study were prepared identically, except that the high surface area powder required an ethanol wash prior to drying in order to prevent pore closure during drying. Data for a low surface area material prepared by a nitrate–alkoxide method are provided for comparison. The 47 wt% alumina composition was selected because of a unique drop in surface area and density reported for this composition.[1]

In order to probe the structure of gels as a function of heat treatment temperature, a combination of solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy, X-ray diffraction (XRD), and differential thermal analysis (DTA) was employed. In addition, dilatometry was used to investigate the densification behavior of gel-derived powders. The technique of MAS NMR can be used to probe the structure of both amorphous and crystalline solids. Previous studies have shown the utility of MAS NMR for the characterization of silica,[12–14] alumina,[15,16] and aluminosilicates.[17–20] Because both ^{27}Al and ^{29}Si are NMR active nuclei, each can be probed to provide complementary information. DTA provides information on the reactions occurring during heat treatment and can be interpreted with the aid of published literature.[11,21,22] X-ray diffraction is the method of choice for determining the presence or absence of crystalline phases. Information from these three methods can be combined to understand the overall phase evolution of the 47 wt% alumina gels studied in this paper.

II. Experimental Procedure

Two methods were used to prepare 47 wt% alumina gels, corresponding to an aluminum-to-silicon molar ratio of 1. In the initial stages of this research, powders were prepared from a stoichiometric solution of TEOS[¶] and aluminum nitrate[**] which was gelled by raising the pH to approximately 6 with NH_4OH.[¶] Powders prepared in this manner are designated "nitrate." A detailed description of the solution preparation and the washing procedure has been given previously.[1,2] A second method of preparation used TEOS and aluminum tri-*sec*-butoxide.[††,3,4] Stoichiometric amounts of TEOS and aluminum tri-*sec*-butoxide were added to ethanol[‡‡] to produce the desired 47 wt% alumina precursor solution. Hydrochloric acid[¶] dissolved in additional ethanol was then added to adjust the pH and to produce a solution of 2 wt% solids based on SiO_2 and Al_2O_3. The molar ratio of aluminum to silicon to HCl was approximately 1:1:1. This mixture was refluxed for 24 h. Gels were formed by the addition of 100 mol of water per mole of silicon in solution. Materials prepared in this manner, designated "ASB," had an accessible surface area less than 1 m^2/g after drying at 100°C for 24 h. High surface area powders of the 47 wt% alumina gels were prepared by washing the ASB gels with ethanol prior to drying, resulting in the replacement of the original pore fluid with essentially pure ethanol. The high surface area powders are designated "ASB-washed." Prior to analysis, all gels were dried at 100°C for 24 h. Samples were then calcined at 400°C. Further heat treatments were carried out sequentially to temperatures ranging from 1000° to 1400°C in 100°C increments. All heat treatments were carried out in a tube furnace using 10°C/min heating and cooling rates and a 2-h hold at temperature. Because of limited sample size, a single gel was used for each series of heat treatments. That is, a gel was heated to the first temperature of interest, cooled, and then after analysis the same sample was heated to the next higher temperature. The gels used for X-ray diffraction, surface area, and NMR analyses received identical heat treatments.

The surface area of all samples was determined by reduction of nitrogen adsorption data[§§] using the BET method with five adsorption points over the range of relative pressures from 0.05 to 0.30. The cross-sectional area of nitrogen was assumed to be 0.162 nm^2/molecule. X-ray diffraction was used to determine the crystalline phases present in the fired gels. Patterns were collected on a powder diffractometer[¶¶] using a scan rate of 1°/min from 10° to 60° 2θ for Cu$K\alpha$ radiation. DTA data were collected[***] using a 10°C/min heating rate up to 1500°C. Shrinkage measurements were made on a dilatometer[†††] using a 10°C/min heating rate up to 1400°C. Natural abundance ^{27}Al and ^{29}Si MAS NMR experiments were carried out on a wide-bore machine[‡‡‡] equipped with a solids accessory[§§§] and a 7.05 T cryomagnet operating at a proton resonance frequency of 300.1 MHz. ^{27}Al spectra were acquired at 78.2 MHz using 1.5-μs pulses and a 2-s delay. Samples were spun at up to 8 kHz in Torlon[¶¶¶] rotors and referenced to aqueous $Al(H_2O)_6$. Proton decoupled ^{29}Si spectra were acquired at 59.6 MHz using a 4-μs pulse and 30-s recovery delays. Kel-F[****] and Delrin[††††] rotors were spun at 3 to 4 kHz, and chemical shifts were referenced to TMS. Sample rotation speeds for both the ^{27}Al and ^{29}Si NMR samples were sufficient to prevent spinning sidebands.

III. Results and Discussion

(1) Surface Area, DTA, XRD, and Shrinkage

Physical structure differences among these aluminosilicate xerogels were first identified by variations in surface area. In order to test the stability of this phenomenon, surface area was measured as a function of heat treatment temperature for a low surface area ASB gel. Figure 2 compares these data to the surface area as a function of temperature for a nitrate and an ASB-washed gel. The low surface area of the 47% alumina gel was retained through the entire range of temperatures and showed only a slight increase above 800°C. This observed increase in surface area was probably due to an increase in the accessibility of the internal structure caused by the opening of closed pores. Figure 3 illustrates DTA data for nitrate, ASB, and ASB-washed gels. Significant differences were apparent in both peak position and height. The low surface area nitrate gel had a very small peak at 1050°C, while the ASB gel had two peaks, one at 980°C and another at 1025°C. The high surface area ASB-washed powder had a large exothermic peak at approximately 1025°C. The significance of these differences will be discussed more fully in the NMR sections.

[¶]Fisher Scientific Co., Pittsburgh, PA.
[**]Mallinckrodt, St. Louis, MO.
[††]Alfa Products, Ward Hill, NJ.
[‡‡]Midwest Grain Products, Pekin, IL.
[§§]Autosorb 1, Quantachrome Corp., Syosset, NY.
[¶¶]Pad-V, Scintag, Inc., Santa Clara, CA.
[***]DuPont 990, E. I. Dupont de Nemours and Co., Wilmington, DE.
[†††]Edward Orton Jr. Ceramic Foundation, Westerville, OH.
[‡‡‡]GN-300, General Electric Co., Freemont, CA.
[§§§]Chemmagnetics, Fort Collins, CO.
[¶¶¶]Amoco Chemicals Corp., Chicago, IL.
[****]3M, St. Paul, MN.
[††††]E. I. DuPont de Nemours and Co., Wilmington, DE.

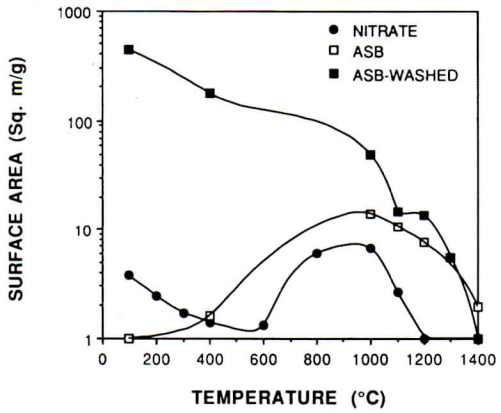

Fig. 2. The log of surface area as a function of temperature for low (nitrate and ASB) and high surface area (ASB-washed) gels.

Diffraction data for nitrate, ASB, and ASB-washed gels heated to 1100° and 1400°C are summarized in Table I. Significant differences were evident. The low surface area nitrate and ASB gels crystallized to a mixture of mullite and cristobalite, while the high surface area gel formed only mullite. Presumably, the high surface area gel also contained some residual amorphous silica-rich material, but the amorphous hump was removed from the X-ray data by background subtraction. Figure 4 compares the shrinkage behavior of nitrate, ASB, and ASB-washed powders. The ASB-washed powder experienced the highest final shrinkage. The two low surface area powders had approximately the same shrinkage at the maximum temperature studied, 1400°C, but the nitrate powder began to densify at a much lower temperature than the ASB.

Variations in the phase evolution of aluminosilicates have been attributed to differences in the level of mixing among the precursors.[5,6] The crystallization of mullite occurred at much lower temperatures for well-mixed aluminosilicates, but mullite formation inhibited the densification of these materials. The reduced crystallization temperature, as indicated by X-ray diffraction, of the ASB-washed gel might be a direct result of a mixing effect. NMR data will further address the question of molecular mixing. The enhanced low-temperature

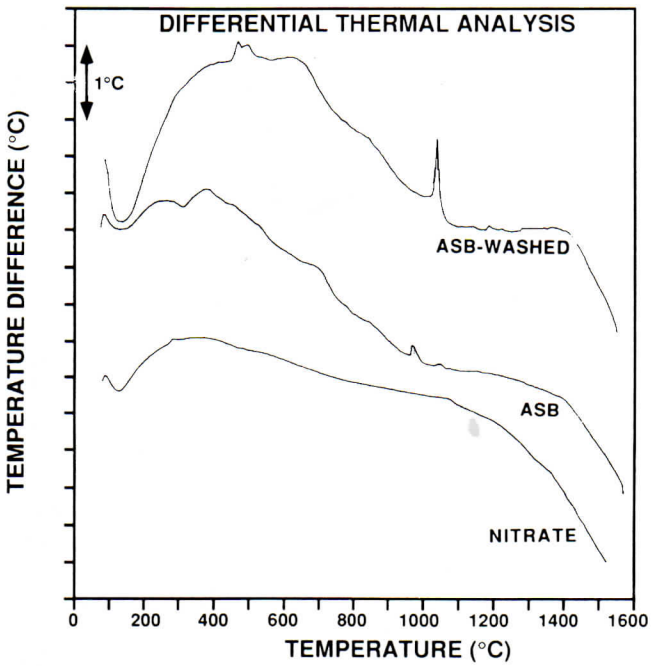

Fig. 3. DTA data for nitrate, ASB, and ASB-washed xerogels.

Table I. Summary of Phase Development as Determined by X-ray Diffraction for Nitrate, ASB, and ASB-Washed Gels Heated to 1100° and 1400°C

Sample	Phase development	
	1100°C	1400°C
Nitrate	Amorphous	Mullite and cristobalite
ASB	Mullite (trace)	Mullite and cristobalite
ASB-washed	Mullite (minor)	Mullite

shrinkage of the nitrate powder can be explained in terms of less-efficient molecular-level mixing of silica and alumina. With a silica-rich region present, the gel could undergo viscous sintering as reported for other hydroxyl-containing silica gels.[23] The higher ultimate shrinkage of the ASB-washed gel was a direct result of the retention of the amorphous silica in that particular sample, as indicated by XRD and NMR. The low surface area materials formed crystalline cristobalite above 1100°C, eliminating the possibility of viscous sintering. The similar final shrinkage observed for both of the low surface area materials is probably a result of the products formed. In an effort to determine the structural effects responsible for these differences in phase evolution and densification, MAS NMR was used.

(2) ^{27}Al MAS NMR

^{27}Al MAS NMR spectra for nitrate, ASB, and ASB-washed xerogel powders are summarized in Table II. Each material was examined after heat treatment to 400°, 1100°, and 1400°C. The 400°C spectra were similar to previously reported results.[2,19,20] The resonances at 0 and 60 ppm have been assigned to octahedral and tetrahedral coordination of aluminum, respectively.[24] An additional resonance at 30 ppm was prominent in the ASB-washed material. Chemical shifts in this region have been assigned to 5-coordinate species.[20,25] It is unlikely that the 5-coordinate species was unique to the ethanol-washed gel, as it has been observed previously in nitrate samples;[2] rather, we suspect that the resonance cannot be discriminated from the background in the nitrate and ASB materials.

Heating to 1100°C produced significant changes in each sample. The tetrahedral resonance in the nitrate sample broadened, extending from 30 to 80 ppm. The relative height and area of the 0 ppm resonance suggest that the octahedral aluminum species were unaffected by heat treatment in this sample. The 1100°C spectrum for the ASB xerogel exhibited increased relative intensity in the 30 to 80 ppm region, reflecting an increased amount of 4-coordinate aluminum, probably due to the incorporation of silicon into the second coordination sphere of Al or incorporation of Al into the Si-O network. Phase development, as seen by ^{27}Al NMR, was most pronounced for the high surface area ASB-washed

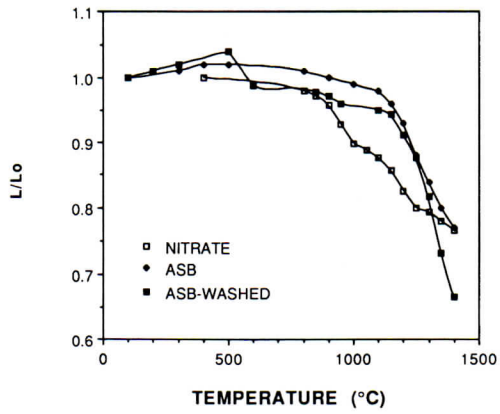

Fig. 4. Shrinkage data for nitrate, ASB, and ASB-washed gels heated at 10°C/min up to 1400°C.

Table II. Summary of ^{27}Al MAS NMR Data for Nitrate, ASB, and ASB-Washed Gels Heated to 400°, 1100°, and 1400°C

Sample	^{27}Al MAS NMR data (ppm)*		
	400°C	1100°C	1400°C
Nitrate	0 (l)	0 (l)	0 (l)
	60 (s, b)	30 to 80 (b)	30 to 70 (m, b)
ASB	0 (l)	0 (l)	0 (l)
	60 (s, b)	60 (s, b)	42 (l)
ASB-washed	0 (l)	0 (l)	0 (l)
	30 (s)	42 (s)	42 (l)
	60 (s, b)	60 (l)	60 (l)

*s small, m medium, l large, b broad.

Table III. Summary of ^{29}Si MAS NMR Data for Nitrate, ASB, and ASB-Washed Gels Heated to 400°, 1100°, and 1400°C

Sample	^{29}Si MAS NMR data (ppm)*		
	400°C	1100°C	1400°C
Nitrate	−80 to −110 (b)	−87 (s, b)	−87 (l)
		−110 (l, b)	−110 (l, b)
ASB	−80 to −120 (b)	−87 (m, b)	−87 (l)
		−110 (l)	−110 (l)
ASB-washed	−80 to −120 (b)	−87 (m)	−87 (l)
		−110 (l)	−110 (l)

*s small, m medium, l large, b broad.

sample. Distinct resonances developed at 60 and 42 ppm, consistent with the development of crystalline mullite.[26] The relative size of the 0 ppm resonance suggests that a significant amount of aluminum remained in the 6-coordinate state, outside the mullite phase. The lack of distinct mullite peaks in the ASB data was probably due to the quadrupolar nature of Al, which makes it especially sensitive to bond-strain effects. If the mullite were composed of small crystallites such that a majority of the aluminum was within a few bond lengths of the crystallite boundary, ^{27}Al NMR might not detect the presence of any crystalline mullite.

By 1400°C, all three xerogels had ^{27}Al NMR spectra consistent with the formation of mullite. The aluminum in the ASB and ASB-washed gels was present almost entirely in the form of mullite, as the NMR spectra were nearly identical to those of pure mullite.[26] Oxygen vacancies in the mullite structure, whose number were determined by the amount of Si^{4+} substituted onto Al^{3+} sites, produced two distinct types of Al tetrahedral sites. These resonances were at 60 and 42 ppm. The ^{27}Al MAS NMR spectrum of crystalline $3Al_2O_3 \cdot 2SiO_2$ has been proposed to consist of three peaks, 60, 42, and 0 ppm, with intensities in the ratio of 0.25:1:1.[26] These peaks correspond to the Al associated with an oxygen vacancy, a 4-coordinate species, and a 6-coordinate species, respectively. The intensity ratios of the tetrahedral Al peaks in the 1400°C ASB and ASB-washed samples preclude unambiguous assignment. The phase development, as seen by ^{27}Al NMR, of the nitrate sample heated to 1400°C was similar to that of the ASB powder at 1000°C (data not given). Both produced NMR spectra consistent with the presence of 6-coordinate Al (0 ppm resonance) outside the mullite phase. The inhibited reactivity of the nitrate sample as compared to the alkoxide-derived gels could be a direct result of the efficiency of mixing in the two solutions.

(3) ^{29}Si MAS NMR

^{29}Si MAS NMR spectra of nitrate, ASB, and ASB-washed powders as a function of temperature are summarized in Table III. The 400°C spectra all showed broad resonances consistent with those seen for other amorphous aluminosilicate gels.[2,24] However, the nitrate xerogel resonance appeared somewhat narrower and shifted to the high field side as compared to the ASB and ASB-washed gels. This suggests that less aluminum was incorporated into the second coordination sphere of silicon, and therefore the gel network, for the nitrate material. This is consistent with the ^{27}Al NMR data which also showed less-efficient molecular mixing for the nitrate samples. The same mixing effects might be responsible for the delayed appearance of crystalline mullite in the diffraction data for the nitrate gels as well as their enhanced shrinkage. Additional effects related to thermal analysis data will be discussed below.

Heat treatment to 1100°C produced splitting in the resonance of the nitrate gel. Peaks developed at −88 and −110 ppm. The small, broad, −88 ppm resonance spans the range of chemical shifts, −75 to −95 ppm, that have been assigned to silicon atoms with one to four aluminum atoms in the second coordination sphere (due to the formation of Si–O–Al bonds).[17] Using standard Q notation this would be Q^4 (1 to 4 Al).[‡‡‡‡] The −110 ppm resonance has been assigned to Q^4 (0Al) silicon species in amorphous silica.[2] The peak splitting that occurred with heat treatment supports the model that aluminosilicate gels undergo phase separation into an alumina-rich and a silica-rich phase prior to mullite formation.[21] Both the ASB and the ASB-washed xerogels underwent similar phase separations by 1100°C, but narrower aluminosilicate resonances (−87 ppm) were apparent. The sharp ^{29}Si resonance at −87 ppm is consistent with the formation of crystalline mullite,[26,27] which agrees with results of ^{27}Al NMR and XRD. It was also apparent from the NMR data that a significant amount of the silica existed outside the aluminosilicate network because of the presence of the −110 ppm resonance. Of course, this was expected since the 47 wt% alumina gels are silica-rich with respect to the mullite composition (72 wt% Al_2O_3, 28 wt% SiO_2).

Phase separation similar to that observed in this work by ^{29}Si NMR has been previously suggested to occur around 980°C for other mullite precursors, leading to the development of an exothermic peak in DTA.[21] The two DTA peaks seen for the ASB powder could have been produced by individual phase separation and mullite crystallization events. The single, more intense peak for the ASB-washed sample might be a combination of phase separation and mullite crystallization. The lack of a distinct exotherm in the nitrate gel is probably due to the fact that it was poorly mixed initially, broadening the exotherm into the background. Interestingly, the ^{29}Si and XRD spectra of the ASB powder (Table III and I, respectively) showed the presence of some crystalline aluminosilicate, while the ^{27}Al NMR spectrum of the same material did not. Again, this is probably due to the lower resolution of aluminum as a result of its quadrupolar nature. As might be expected from the XRD, DTA, and NMR data, the 1100°C phase development was most complete in the ASB-washed sample. The presence of the distinct silica-rich amorphous phase may have aided the low-temperature densification of the nitrate gel as compared to the ASB material, but after phase separation and crystallization, the ASB gel sintered to nearly the same density as the nitrate.

By 1400°C, all of the powder samples showed the presence of crystalline aluminosilicate, −87 ppm, and residual silica, −110 ppm. In fact, taken alone, the ^{29}Si data show little difference in the speciation of Si within the nitrate, ASB, and ASB-washed powders after the 1400°C heat treatment. However, XRD data clearly showed that crystalline cristobalite was present in the nitrate and the ASB gels. The cristobalite may not have appeared in the ^{29}Si spectra if the relaxation time was significantly longer than the 30-s pulse delay times employed. The broadening of the −110 ppm ^{29}Si NMR peaks in the nitrate and ASB samples may have been caused by the

[‡‡‡‡]The superscript of the Q identifies the number of network-forming (bridging) oxygens of the silicon. Q^0 corresponds to a monomeric silicon species such as $Si(OH)_4$ while Q^4 would indicate a fully condensed Si–O–Si network.

fact that these gels contain a significant amount of amorphous silica in addition to cristobalite. This amorphous silica would not have shown up in the XRD data because of automated background subtraction. The complementary data provided by ^{27}Al MAS NMR (Table II) suggest that the aluminum speciation varied between the nitrate and the alkoxide-derived gels. However, the aluminum present outside the mullite phase in the nitrate sample did not incorporate into the silica phase. This would have shifted the −110 ppm ^{29}Si NMR peak toward −88 ppm. The nitrate gels appeared to have less-developed crystallinity, by both ^{27}Al NMR and XRD, than either the ASB or the ASB-washed gel. Again, this was probably due to the degree of liquid phase mixing that the precursor solutions experience.

IV. Summary and Conclusions

The physical structure of alkoxide-derived aluminosilicate xerogels was changed by exchanging the pore solvent prior to drying. ASB gels dried from the mother liquor had a surface area of less than 1 m^2/g, while ethanol-washed gels had over 500 m^2/g surface area. This change in physical structure had dramatic effects on the phase evolution and densification of the gels. Low surface area nitrate and ASB gels crystallized to mullite and cristobalite, while the high surface area ASB-washed gel formed only mullite. Additional effects were observed by MAS NMR because of the degree of solution mixing of aluminum and silicon species using nitrate as opposed to alkoxide precursors. Phase separation and less-efficient molecular level mixing also led to enhanced low-temperature densification of the nitrate gel as compared to the ASB material, but the retention of amorphous silica at higher temperatures may have helped the ASB-washed gel attain the highest density of the three. The data presented show that the degree of mixing of the Al and Si species prior to heating can have a dramatic effect on the thermal behavior of these gels. More importantly, differences in physical structure, surface area, and skeletal density induced in gels prepared by identical methods can have dramatic effects on the phase evolution of aluminosilicates.

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