Influence of Ti addition on boehmite-derived aluminum silicate aerogels: structure and properties

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Abstract Aluminosilicate aerogels offer potential for extremely low thermal conductivities at temperatures greater than 900 °C, beyond where silica aerogels reach their upper temperature use limits. Aerogels have been synthesized at two Al:Si ratios, a 3Al:1Si mullite composition, and an 8Al:1Si alumina rich composition. Boehmite (AlOOH) is used as the Al source, and tetraethoxysilane as the Si precursor. The influence of Ti as a ternary constituent, introduced through the addition of titanium isopropoxide in the sol–gel synthesis, on aerogel morphology and thermal properties is evaluated. Four different boehmite precursor powders are evaluated. Morphology, surface area and pore size, and thermal transformation vary with the crystallite size of the starting boehmite powder, as does incorporation of titanium and evolution of Ti-containing crystalline phases. The addition of Ti influences sol viscosity, gelation time, surface area and pore size distribution, as well as phase formation on heat treatment.

Keywords Aerogel · Boehmite · Aluminum silicate · Titanium isopropoxide · Al₂TiO₅ · Mullite

Abbreviations

| Abbreviation | Description |
|--------------|-------------|
| DTA          | Differential thermal analysis |
| BET          | Brunauer, Emmett, Teller surface area |
| FESEM        | Field emission scanning electron microscopy |
| FTIR         | Fourier transform infrared spectroscopy |
| ICP          | Inductively coupled plasma spectroscopy |
| TEOS         | Tetraethoxy silane |
| TGA          | Thermogravimetric analysis |
| TIP          | Titanium isopropoxide |
| XRD          | X-ray diffraction |

1 Introduction

Aluminosilicate aerogels are of interest as constituents of thermal insulation systems with potential for use at temperatures higher than those attainable with silica aerogels, which densify and sinter at temperatures above 800 °C [1–3]. It is anticipated that the effectiveness of aluminosilicate aerogels as thermal insulators will be influenced by their composition (Al:Si ratio), backbone structure, morphology, pore size distribution, and physical and skeletal densities.

Several sol–gel methods have been reported in the preparation of aluminosilicates, including use of aluminum alkoxides [4], aluminum salts, including AlCl₃, plus propylene oxide (PO) as a gelling agent[5, 6], and colloidal dispersions of aluminum hydroxides, such as boehmite [7–9].
Use of soluble precursors produces gel networks with significant Al–O–Si tetrahedral bonding [7, 9], while the colloidal approach primarily maintains the AlO₆ octahedral structure characteristic of boehmite [10, 11]. The difference in backbone structure has been shown in our laboratory (F. Hurwitz, unpublished) to lead to differences in crystallization behavior. The transformation to mullite, which takes place in the AlCl₃/PO system at 980–1,005 °C, is shifted to temperatures above 1,300 °C in the boehmite-derived system.

Published work by a number of researchers has demonstrated that addition of Ti to alumina and mullite systems affects mechanical strength, grain size and coefficient of thermal expansion [12]. TiO₂, when added to SiO₂, can act as a radiation opacifier, reducing heat transfer at higher temperatures [13].

The current study incorporates titanium as a ternary constituent in the aluminosilicate aerogels synthesized from boehmite precursors as the Al source, and tetraethylorthosilicate (TEOS) as the Si source. The objectives of the work are to establish a fundamental understanding of the relationship among constituent ratios and synthesis parameters on aerogel structure and thermal properties, including densification and sintering, and to evaluate the effect of Ti addition on these properties.

Titanium isopropoxide was selected as the Ti source, allowing introduction of Ti into the backbone structure of the gel at the molecular level.

2 Experimental

2.1 Synthesis

Several boehmite (AlOOH) powders, designated as P2, P2W, L4 and T25, were donated for this study by Sasol North America. Tetraethoxysilane (TEOS) and titanium isopropoxide (TIP) were purchased from Sigma–Aldrich, Inc. Reagent grade nitric acid was purchased from Fisher Scientific.

Aluminosilicate aerogels were prepared by a method similar to that of Aravind [8] at Al:Si ratios of 8Al:1Si and 3Al:1Si. Al₂TiO₅ was synthesized as a model compound. TEOS was hydrolyzed with a stoichiometric amount of water using a nitric acid catalyst in 200 proof ethanol, and the mixture was vigorously stirred for 60 min. In those formulations incorporating Ti, TIP was added to the hydrolyzed TEOS at the end of the 60-min hydrolysis time, at levels needed to achieve 2.5–10 mol % titanium. The boehmite powders were dispersed in 0.9 M nitric acid solution or in water, and sonicated using a Misonix 4000 ultrasonic processor with a 419 tip for 2 min at 60 % amplitude for batch sizes with 48 mmol total metal (Al + Si + Ti). The dispersed boehmite was combined with the hydrolyzed TEOS plus TIP solution. The combined sol was poured into polyethylene molds and held at either ambient temperature or 55 °C for 24 h, following which the hydrogels were extracted into 200 proof ethanol, and then supercritically dried using CO₂.

2.2 Characterization

Supercritically dried aerogels were characterized by physical measurement to determine shrinkage and physical density. Nitrogen adsorption/desorption was used to determine surface area using the method of Brunauer, Emmett and Teller (BET) as well as pore size distribution. Chemical bonding structure of starting powders and aerogels were characterized by Fourier transform infrared spectroscopy (FTIR) using KBr pellets. Field emission scanning electron microscopy (FESEM) was performed on uncoated samples using low accelerating voltage (typically 1 kV) to characterize pore morphology. Thermal analysis of the aerogels was conducted using simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in helium to identify mass loss and phase transitions. X-ray diffraction analysis (XRD), obtained from Cu Kα radiation, was used to characterize both starting boehmite powders and aerogels, and to correlate phases in heat-treated samples with DTA transitions. Multiple regression techniques were employed for data analysis using JMP statistical software.

3 Results and discussion

Boehmite, AlO(OH), has an octahedral AlO₆ structure, with crystallites arranged in layers having a characteristic d spacing [10]. XRD characterization, shown in Table 1, shows a variation in crystallite size, determined from the width of the (021/040) X-ray peak, among the starting powders, with d spacing for the most part varying inversely with crystallite size. The P2W powder has the smallest crystallite size at 2.6 nm, while the 4.9 nm P2 powder has the largest d spacing.

The as-received powders are aggregated, and sonication has been found effective in dispersing the aggregates. In acid solution, the Al–OH species are protonated [11] and

| Table 1 Crystallographic characteristics of boehmite precursors |
|---------------------------------------------------------------|
| **Boehmite powder** | **2θ (degree)** | **d-spacing (Å)** | **Crystallite size (nm)** |
|---------------------|----------------|-----------------|--------------------------|
| P2W                 | 14.094         | 6.279           | 2.6 ± 0.1                |
| P2                  | 14.074         | 6.287           | 4.9 ± 0.2                |
| T25                 | 14.168         | 6.246           | 6.9 ± 0.1                |
| L4                  | 14.393         | 6.149           | 13.0 ± 0.1               |

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can undergo condensation with other Al–OH groups, or with Si–OH or Ti–OH species, with reaction likely taking place at the surface of small aggregates. The aerogel retains the boehmite crystallographic structure of the starting powders, as confirmed by XRD.

The T25 precursor was the most acidic when suspended in nitric acid solution or water (pH 1.5 in acid/4.5–5.5 in water), compared with P2 (pH 1.5–2.5/6–6.5), P2W (pH 2.5–3.5/6.0) and L4 (4–5.5 dispersed in acid), with pH increasing with increased quantities of boehmite in the 8Al:1Si formulations. The L4 powder did not disperse well in water (particles were observed to settle). After combining the colloidal powder dispersion with the hydrolyzed TEOS solution, P2W and T25 sols had a pH of 3.0 in acid, and 4.4–5.0 in water; P2 showed a pH of 3.8 in acid and 3.5–4.0 in water. Addition of TIP did not affect the pH of the final sol. The sols were allowed to gel with no further adjustments to pH.

Addition of Ti to Si containing gels increased viscosity of the combined sol and decreased gelation time; in some cases this resulted in trapping of bubbles in the hydrogel. At 10 mol % Ti, gelation occurred within 1–2 min at room temperature, capping the upper limit of Ti incorporation by this method. At Ti levels of 2.5–5 mol % sols remained sufficiently fluid to be poured into molds. The Al2TiO5 composition gelled more slowly than those containing Si. Addition of TIP to silicon containing L4 boehmite formulations resulted in sols that did not gel. However, Al2TiO5 formulations using L4 powders gelled successfully, producing an aerogel with a surface area of 332 m2/g and 8.5 nm average pore size, compared with the higher surface area of 434 m2/g and 7.6 nm average pore size obtained using P2.

Elemental analysis by inductively-coupled plasma (ICP) spectroscopy indicated Ti incorporation of 4.3–4.8 mol % for P2, P2W and T25 formulations targeting 5 % Ti.

Fourier transform infrared spectroscopy spectra (Fig. 1) exhibit peaks at 3,296, 3,094, 1,070, 728, 624 and 474 cm−1 that are present in the P2 starting powder. These peak positions are very similar to the peak positions of 1,074, 757, 632 and 483 cm−1 reported by Chen [14] for boehmite. Bands at 3,296 and 3,094 cm−1 are characteristic of the –OH stretch in AlOOH [15]. There also is a shoulder near 3,400 cm−1 which can be attributed to the presence of free –OH groups. Little free-OH is present in aerogels synthesized from the L4 precursor. The peak at 1,132 cm−1 seen in the starting powder is shifted to 1,120 cm−1 as a result of its overlap with the SiO4 band at 1,100 cm−1 [16]. Si–O bonds also contribute to the band at 917 cm−1, which decreases in intensity as more Al is added.

Ti incorporation is associated with increased intensity of the peak at 945 cm−1, which has been assigned to Ti–O–Si bonding [17]. Silanol groups also may contribute to the vibrations in this region; however, the peak is much smaller in formulations without Ti. AlO4 groups appear to predominate, based on the preservation of the 1,070, 728, 624 and 474 cm−1 of the boehmite powder, indicating that the octahedral AlO6 structure is maintained in the aerogel. The small band near 870 cm−1, not found in the boehmite powder, indicates the presence of some AlO4 species [18]. The small intensity of the AlO4 band, together with the preservation of the boehmite structure, would support a conclusion that SiO groups are incorporated on the outer surface of the boehmite crystallites.

T25 produced very soft and difficult to handle hydrogels, many of which broke under their own weight during aging. Determination of combined shrinkages of gelation and supercritical drying were difficult to determine accurately in the T25 system due to the resulting non-uniform diameters of the cylindrical monoliths, but were nominally 4.5–8.5 %. Multiple regression analysis of the combined shrinkages due to gelation and supercritical drying for the P2 and P2W aerogels (Fig. 2) shows statistically significant influences of precursor, Al:Si ratio, gelation temperature, and to a lesser extent, Ti incorporation. Minimum shrinkage of 2.5 % is attained for the P2W system, 3Al:1Si ratio, 55 ºC gelation temperature with no Ti addition.

Physical densities were nominally 0.06–0.07 g/cm3, with densities for P2W being the lowest on a statistical basis. Adding Ti has no statistical influence on density. Pore volumes ranged from 96 to 98 %.

3.1 Surface area and pore size distribution

Brunauer, Emmett, Teller surface area was influenced by the boehmite precursor, Al:Si ratio and Ti addition. The statistical model of BET surface area as a function of these Al:Si ratios, 3:1 and 8:1, and for Ti additions of 0 or 5 %. The precursor powder is also shown to have a statistically significant influence on surface area, with the highest

Fig. 1 FTIR comparison of P2 aerogels with and without Ti. Peaks marked with asterisk are characteristic of boehmite
surface areas attained using the smallest crystallite size P2W powder, followed by P2 and T25, further supporting the evolution of aerogel structure as deriving from the self-assembly of the boehmite crystallites, with morphology reflecting the original crystallite size. Dispersion of powders in water versus acid solution did not have a significant effect (Fig. 3).

Pore volume also is a function of precursor. Highest pore volumes (0.93 cm$^3$/g) are achieved using P2 or P2W powders. The largest effect in increasing pore volume with all three precursors comes from the addition of Ti (Fig. 4). The increment in pore volume can be attributed to the appearance of larger pores, increasing the breadth of the pore size distribution, plotted in Fig. 5, and the aerogel microstructure, shown in Fig. 6.

3.2 Effects of thermal exposure

Thermogravimetric analysis of samples heated in He shows an initial mass loss below 150 °C, which increases with the degree of Ti incorporation (Fig. 7). Semiquantitative

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**Fig. 2** Statistical analysis of shrinkages in P2 and P2W aerogels shows the influence of Al:Si ratio, gelation temperature and incorporation of Ti on the combined shrinkages of gelation and supercritical drying. $R^2 = 0.74$. Comparison is for two levels of Ti:0 and 5 mol %. Values for each parameter to minimize shrinkage are indicated by *dotted red line* (Color figure online).

**Fig. 3** Influence of precursor, Al:Si ratio and 5 % Ti addition on BET surface area, based on multiple regression analysis data for P2W, P2 and T25 aerogels at Al:Si ratios of 3 and 8. $R^2 = 0.84$.

**Fig. 4** Pore volume is shown to increase with Ti addition. $R^2 = 0.83$.

**Fig. 5** Pore size distributions in P2 and P2W formulations, with and without Ti. Incorporation of Ti leads to formation of larger pores and increases pore volume.
analysis by XRD shows that the composition of the Al$_2$TiO$_5$ formulation after heat treatment to 600 °C is 60 % TiO$_2$, 40 % (Al$_2$O$_3$)$_{1.33}$, or 27.9 % Ti, as compared with a formulated Ti composition of 26.3 %, suggesting that Ti species are not lost in this region. The loss below 150 °C therefore is likely attributable to continued condensation with evolution of isopropoxide and water. The mass change near 300 °C in the Al$_2$TiO$_5$ composition corresponds with anatase formation, and is discussed below. The largest mass loss for the aerogels with 0–10 % Ti occurs at 350–400 °C, corresponding with the evolution of water accompanying the transformation from boehmite (γ-AlOOH) to γ-alumina, as confirmed by XRD.

A comparison of DTA traces for P2 3Al:1Si aerogels with and without Ti addition, and for a P2-derived Al$_2$TiO$_5$, is provided in Fig. 8. The sharp peak at 290 °C is seen in other Al–Ti containing sol–gel derived materials [19], and is shown by XRD to correspond with the formation of anatase. The maxima at 405 °C in the aluminosilicate aerogels corresponds with the transition from γ-AlOOH to γ-alumina, as confirmed by X-ray diffraction; in the Al$_2$TiO$_5$ formulation, this maximum is shifted to 380 °C.

Formation of a variety of transitional aluminas is possible in the 900–1,200 °C range [20], and is reflected in variations in the DTA curves at 1,170 °C and above. The small, sharp phase transformation seen at 1,315 °C in the samples without Ti, corresponding with mullite formation, is shifted to 1,205 °C with 5 % Ti addition. Two small, sharp peaks at 1,160 and 1,370 °C are found in the Al$_2$TiO$_5$ formulation. Samples analyzed after exposure to 1,170 °C contained γ-Al$_2$O$_3$ and rutile, with a small amount of anatase (nominally 3 %) remaining. After exposure to 1,425 °C, Al$_2$TiO$_5$ is the prominent phase, accompanied by γ-Al$_2$O$_3$ and TiO$_2$ (rutile).

A comparison of the influence of 5 % Ti addition on the microstructure of post DTA tested samples heated to 1,425 °C is shown in Fig. 9. The P2 3Al:1Si sample without Ti maintains a fine-grained, microporous structure after thermal exposure (Fig. 9b), while the one with 5 % Ti addition (Fig. 9d) is characterized by larger grains. XRD analysis reveals mullite in both thermally
exposed samples. In the sample without Ti, mullite is the only phase present; with Ti addition, the sample is primarily mullite, with nominally 2 % TiO₂ present as rutile. The larger grain size in the Ti-containing sample likely is the result of the lower temperature transformation to mullite in the sample with Ti, leading to the

Fig. 9 Microstructural comparison of as supercritically dried aerogels with samples after DTA runs to 1,425 °C. a P2 3Al:1Si, as supercritically dried; b P2 3Al:1Si post-DTA; c P2 3Al:1Si with 5 % Ti; d sample with 5 % Ti after DTA exposure

Fig. 10 Changes in microstructure of P2-derived Al₂TiO₅ with thermal exposure. a as supercritically dried; b at 600 °C; c at 1,170 °C; at 1,425 °C. Note that images of samples exposed to higher temperatures are shown at lower magnifications
sample experiencing longer time at temperature after mullite formation.

Changes in microstructure of the P2-derived Al₂TiO₅ formulation with thermal exposure to 1,425 °C are seen in Fig. 10. as supercritically dried aerogel (Fig. 10a) shows fine pore structure, with a surface area of 434 m²/g. Fine pores are maintained after conversion to c-Al₂O₃, as evidenced by the microstructure at 600 °C (Fig. 10b). At 1,170 °C, the formation of a TiO₂ rutile phase is seen. After 1,425 °C exposure, grain growth is evident, along with the formation of Al₂TiO₅ (Fig. 10d).

When L4 is used as the precursor in the Al₂TiO₅ formulation, the 1,425 °C heat treated sample exhibits Al₂TiO₅, c-Al₂O₃ and TiO₂ (rutile) present in the P2 material, but also contains large crystallite size inclusions of a lanthanum aluminum titanium oxide (La₃TiAl₆O₁₉), as seen in Fig. 11. La is present in the L4 precursor powder, at a level of 1.5–2 wt%.

4 Conclusion

The sol–gel approach to forming aluminosilicate aerogels using boehmite and TEOS has been demonstrated to be compatible with the introduction of Ti at the molecular level using titanium isopropoxide to form ternary Al–Si–Ti aerogels. Aerogels were formed successfully using Sasol N.A. P2, P2W and T25 powders. The ternary system using the L4 powder did not gel. Surface area, pore structure, shrinkage and density were strongly influenced by the choice of boehmite precursor powder. Highest surface areas and lowest shrinkage were achieved using the smallest particle size P2W powder at an Al:Si ratio of 3:1.

In the ternary system, Ti incorporation was limited to 10 mol % due to large increases in viscosity and decreased gelation time with TIP addition. The rheological changes present an interesting opportunity for dispersing powders or nanotubes in the aerogel and enabling gelation to occur without these materials settling, providing more homogeneous dispersions of a reinforcing phase.

The synthesis approach can be used to produce Al₂TiO₅ compositions containing 33 % of the total metal as Ti for applications in which higher Ti loadings are desirable. This formulation was demonstrated using both P2 and L4 powders.

Ti incorporation also influences phase transformation. The ternary Ti containing materials undergo transformation to mullite, accompanied by loss of pore structure and densification, at somewhat lower temperature than the corresponding aluminosilicates without Ti.

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