

## Anomalously Low Surface Area and Density in the Silica-Alumina Gel System

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*A range of composition/processing conditions that yield xerogel surface areas 2 orders of magnitude lower than expected along with low skeletal densities has been discovered. For xerogel compositions in the vicinity of 50 wt% Al<sub>2</sub>O<sub>3</sub>, surface areas are 1 to 5 m<sup>2</sup>/g and skeletal densities are 2.1 to 2.2 g/cm<sup>3</sup>, as compared to the expected values of ≈300 m<sup>2</sup>/g and ≈2.6 g/cm<sup>3</sup>, respectively. This be-*

*havior is observed over a wide range of heat treatment temperatures (373 to 1073 K) and appears to be the result of closed porosity which evolves during gel drying. [Key words: gels, alumina, silica, surface area, processing.]*

**T**HE synthesis of silica-alumina gels is of interest to primarily two groups of researchers, those interested in the synthesis and characterization of catalyst supports or catalysts and those interested in the synthesis of mullite (2SiO<sub>2</sub>·3Al<sub>2</sub>O<sub>3</sub>). With regard to catalytic activity, the chemical composition of interest corresponds to ≈15 wt% alumina, whereas the composition of mullite is ≈72 wt% alumina. The initial motivation for this work was to synthesize gels ranging in composition from pure Al<sub>2</sub>O<sub>3</sub> to pure SiO<sub>2</sub> in order to study the effect of Si/Al on such sur-

face properties as acid strength distribution. As a side note of that program, we have discovered a range of compositions that yield gel surface areas 2 orders of magnitude lower than expected, along with low skeletal densities. Although this low-surface-area/density behavior does not appear to have been previously reported, these properties are extremely attractive for a number of applications such as sealants and protective coatings.

A number of different reaction schemes for synthesizing silica-alumina gels have been reported in the literature, including the coprecipitation of sodium silicate and sodium aluminate,<sup>1,2</sup> hydrolysis and condensation of a mixture of aluminum isopropoxide and tetraethyl orthosilicate (TEOS),<sup>3-5</sup> reaction of silica sols with dissolved aluminum salts,<sup>3,6,7</sup> and mixing of silica and alumina sols.<sup>8</sup> For all of these procedures, the N<sub>2</sub> BET surface areas of the dried gels (xerogels)

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were over 100 m<sup>2</sup>/g, typically exceeding 300 m<sup>2</sup>/g. One exception was noted for a mullite gel dried at 393 K which resulted in a surface area of 2.8 m<sup>2</sup>/g.<sup>7</sup> However, after heat treatment at 523 K, the surface area increased to over 100 m<sup>2</sup>/g.

#### EXPERIMENTAL PROCEDURE

For samples synthesized at Montana State University (MSU), the silica sol was prepared at ambient temperature using reagent-grade tetraethyl orthosilicate<sup>†</sup> (TEOS) and distilled water adjusted to pH 2 with HCl. The TEOS/H<sub>2</sub>O molar ratio was 1:25. The sol was stirred overnight (approximately 16 h) until the solution became homogeneous. A saturated aqueous solution of reagent-grade aluminum nitrate<sup>‡</sup> was added to the stirring silica sol; then reagent-grade ammonium hydroxide<sup>§</sup> (28% to 30% NH<sub>3</sub>) was added dropwise until the solution gelled at pH 6. For samples prepared at the University of New Mexico (UNM), synthesis conditions were identical except the TEOS was Fisher reagent grade. The TEOS/H<sub>2</sub>O/HCl molar ratios were 1:25:0.002. Complete details of the xerogel synthesis and preparation are shown stepwise in Table I.

True density measurements were made via helium displacement at ≈295 K using a pycnometer.<sup>¶</sup> Nitrogen specific surface area at 77 K was determined from a BET analysis using a molecular cross-sectional area of 0.162 nm<sup>2</sup>. Nitrogen adsorption isotherms were measured at UNM on the samples synthesized at MSU using a flow type analyzer<sup>\*\*</sup> (designated MSU). The samples synthesized at UNM

were studied with an automated volumetric analyzer<sup>††</sup> (designated UNM). The MSU samples were outgassed in a dry nitrogen stream at 673 K, and the UNM samples were outgassed under vacuum at several temperatures. For standard samples, surface areas were within 5% for these two different surface area analysis systems. Thermal gravimetric analysis was conducted over the temperature range of 298 to 1073 K using an analyzer<sup>‡‡</sup> with dry nitrogen sweep gas and a heating rate of 25 K/min. Phase analysis was conducted using a powder X-ray diffractometer.<sup>§§</sup> Pore/particle morphology was examined using a transmission electron microscope.<sup>¶¶</sup> Low-field NMR spin-lattice relaxation experiments of pore water were conducted at 303 K and 20 MHz using a pulse spectrometer.<sup>\*\*\*,9</sup> Mercury intrusion measurements were made with a mercury porosimeter.<sup>†††</sup> Chemical composition of the MSU samples was inferred from percent Al determinations using a flame atomic absorption spectrometer.<sup>††††</sup> Percent Si and Al for the

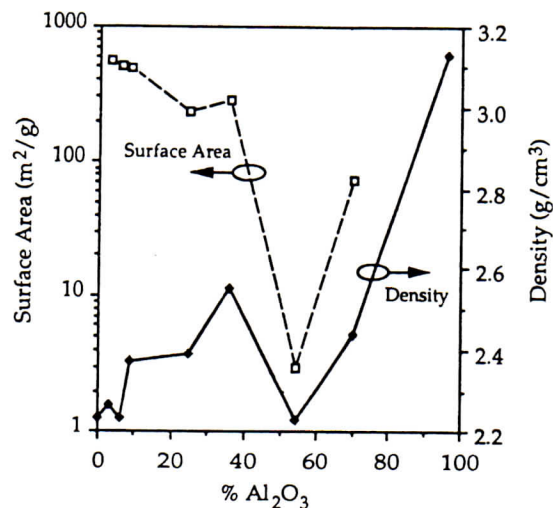


Fig. 1. Surface area and density versus composition for silica-alumina xerogels synthesized at MSU. Anomalously low surface area and density are apparent in the region of 50 wt% alumina.

UNM samples was determined using wavelength-dispersive XRF. Compositions are approximately ±5% for the MSU samples and ±2% for the UNM samples.

#### RESULTS

The variation of surface area and density as a function of measured alumina content for samples synthesized at MSU and heat-treated at 673 K for 3 h is presented in Fig. 1. A duplicate set of samples were synthesized at UNM using the same synthesis scheme but different sources of starting chemicals (see Fig. 2). The reduction in surface area seen in both plots is dramatic. Based on the uncertainty in compositional analysis, we do not attribute any significance to the different compositions corresponding to the surface area minimum between Figs. 1 and 2. This anomalously low surface area does not appear to have been reported previously by researchers working in the silica-alumina gel system.<sup>1-4,6,7</sup> The very low surface area in the region of ≈50% might

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<sup>\*\*</sup>Quantasorb, Quantachrome Corp.  
<sup>††</sup>Autosorb-1, Quantachrome Corp.  
<sup>‡‡</sup>990, E. I. du Pont de Nemours & Co., Wilmington, DE.  
<sup>§§</sup>Scintag, Santa Clara, CA.  
<sup>¶¶</sup>2000 FX, JEOL, Tokyo, Japan.  
<sup>\*\*\*</sup>CPS-2, Spin-Lock, Toronto, Ontario, Canada.  
<sup>†††</sup>Autoscan-33, Quantachrome.  
<sup>††††</sup>AA-975, Varian Associates, San Carlos, CA.

Table I. Synthesis and Preparation of Silica-Alumina Xerogels

Synthesis
Silica Sol
With 1 part (by volume) TEOS
Add 2 parts (by volume) distilled water adjusted to pH 2 with hydrochloric acid (molar ratio of water to TEOS is ≈25:1)
Stir overnight
Hydrogel
Add saturated aluminum nitrate solution to stirring silica sol (molar ratio of water to aluminum nitrate ≈33:1)
Add 2N ammonium hydroxide until mixture gels at pH 6
Wash gel with 10 volumes distilled water for 1 h
Centrifuge
Filter gel (washing twice with distilled water) and allow air to be pulled through gel for 1 h
Dry at 383 K overnight
Preparation
Xerogel
Grind xerogel with mortar and pestle
Wash xerogel using 1 L of distilled water per 2 g of powder for 1 h
Filter xerogel powder
Dry at 383 K overnight

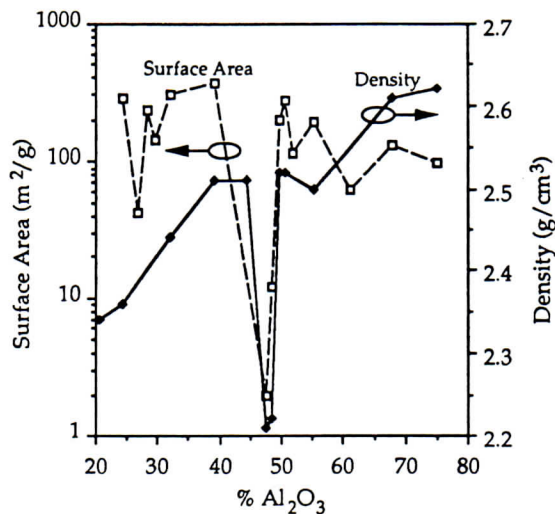


Fig. 2. Surface area and density versus composition for silica-alumina xerogels synthesized at UNM. Anomalously low surface area and density are apparent in the region of 50 wt% alumina.

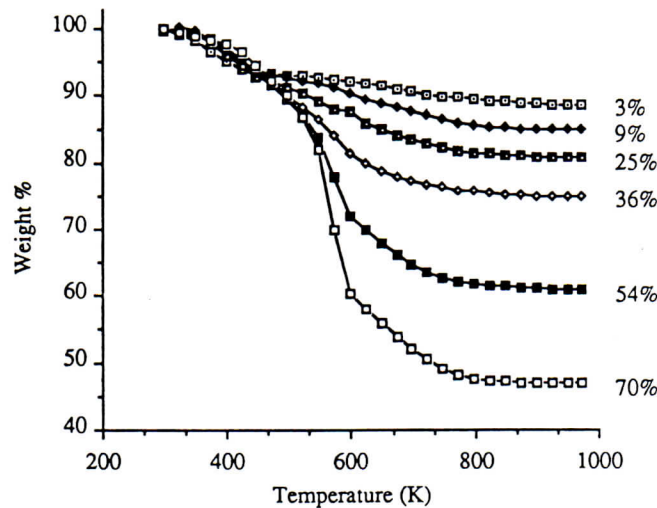


Fig. 3. Weight loss determined by TGA for 3 to 70 wt% alumina xerogels synthesized at MSU. The curves show increasing weight loss with increasing alumina content but do not correlate with surface area and density.

suggest that large crystallites formed. However, X-ray diffraction indicated that the sample is amorphous.

True density of the samples was determined via helium displacement. The value of  $2.23 \text{ g/cm}^3$  for the pure silica sample is in agreement with densities for amorphous silica reported by Iler.<sup>10</sup> The pure alumina sample had a density of  $3.13 \text{ g/cm}^3$ , which is between values reported for aluminum oxide hydroxide (boehmite) and  $\gamma$ -alumina. If the density followed a rule of mixtures, the densities of the various mixtures should vary between 2.23 and  $3.13 \text{ g/cm}^3$ . This rule is generally obeyed, as can be seen in Figs. 1 and 2, except in the region with very low surface area.

Thermogravimetric analysis (TGA) was performed on one series of gels in order to observe if any significant differ-

ences in weight loss was noted between the low- and high-surface-area materials. Weight loss curves are presented in Fig. 3 for a wide range of alumina contents and indicate a clear trend of increasing weight loss with increasing percent alumina (probably a result of nitrate decomposition). No correlation with specific surface area is observed. Since the TGA measurements indicate similar behavior between high- and low-surface-area materials of similar composition, experiments to assess whether a 673 K heat treatment is necessary to achieve the observed low-surface-area/density were conducted. Samples were first heated for 3 h at 373 K, and the surface area and density were measured. The process was repeated at increasing 100 K intervals (for 3 h at each temperature) using the same samples. Figure 4 shows the surface area as a function of

heat treatment for two samples of similar composition but exhibiting very different surface areas at 373 K ( $395$  vs  $3.8 \text{ m}^2/\text{g}$ ). For temperatures less than 873 K, the surface area of the low-surface-area 47%  $\text{Al}_2\text{O}_3$  material decreases more dramatically than the surface area of the high-surface-area 39%  $\text{Al}_2\text{O}_3$  material. At higher temperatures, the surface area of the 47%  $\text{Al}_2\text{O}_3$  sample actually increases. This could be the result of opening of previously closed pores. Figure 5 shows the change in density for the heat-treated materials. The density increases for both the high-surface-area/density material and the low-surface-area/density material to a point at 1073 K where they exhibit nearly equal densities (indicating closed pore collapse).

To obtain more detailed information about the pore structure of these materials,

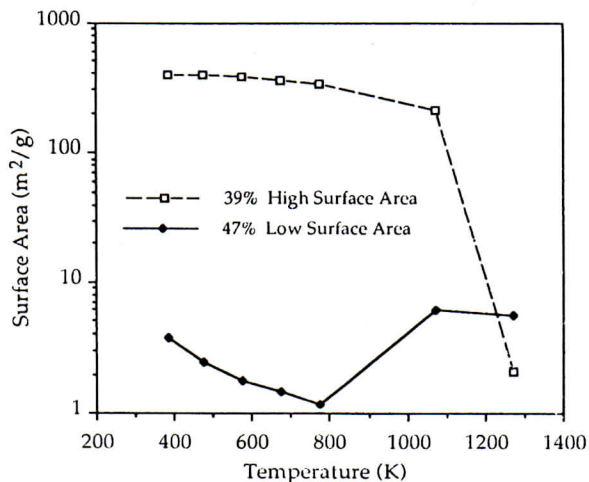


Fig. 4. Surface area for 'high' (39 wt%) surface area/density and 'low' (47 wt%) surface area/density xerogels after various heat treatments.

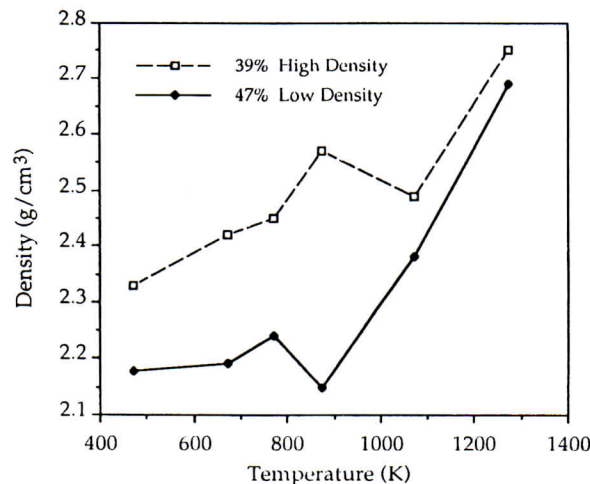


Fig. 5. Density for the 'high' (39 wt%) surface area/density and the 'low' (47 wt%) surface area/density material after various heat treatments.

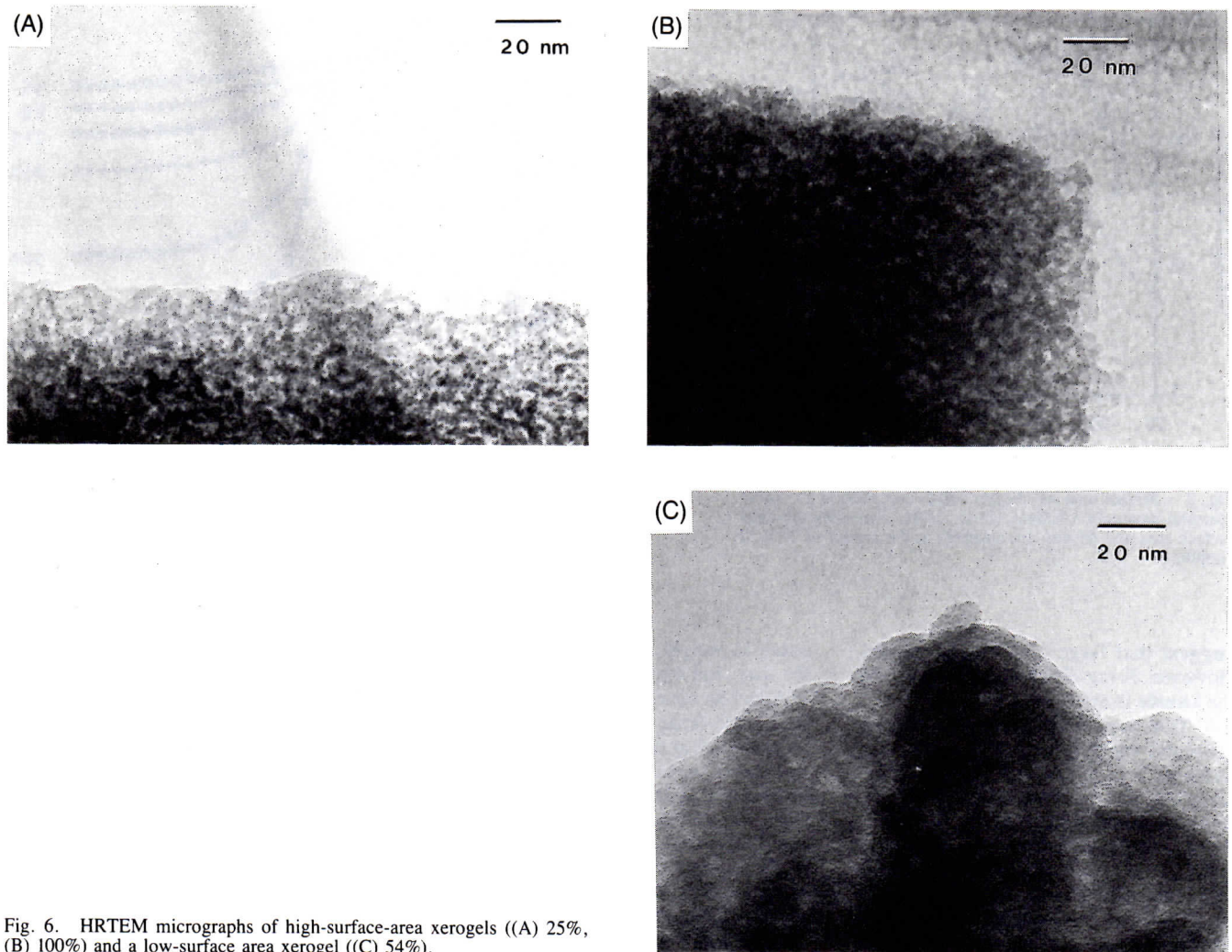


Fig. 6. HRTEM micrographs of high-surface-area xerogels ((A) 25%, (B) 100%) and a low-surface area xerogel ((C) 54%).

low-field NMR spin-lattice relaxation measurements and mercury porosimetry were performed. Using NMR, the pore structure of the wet gel may be ascertained in situ from the relaxation behavior of the pore water.<sup>11</sup> For three samples of composition spanning the low-surface-area/density region (i.e., one low-surface-area and two high-surface-area samples), NMR indicates that the gels before drying all have virtually the same pore structure. In this preliminary study, we did not track pore structure evolution during drying, but NMR measurements of the final dried xerogels (673 K) indicated that no measurable amounts of molecular water were present. Mercury porosimetry results were similar for all samples studied. These results were interpreted as mercury filling around the particles at low pressure and combined sample compression/pore filling at the higher pressures.<sup>12</sup> For amorphous materials with closed pores, the pores can collapse, resulting in a change in sample volume at the high pressures necessary to probe the pore structure of these materials. From a conventional intrusion experiment, it is not possible to distinguish between pore filling and pore collapse.

The coupled results of low surface area and low density are difficult to explain unless the low-surface-area/density samples have a significant concentration of closed pores (i.e., pores which helium cannot access at  $\approx 295$  K). Closed porosity would explain both the low density and surface area observations. The concentration of closed pores would have to be quite significant to explain the density results (15% to 20% by volume of the sample). In order to assess the possibility of closed porosity, high-resolution transmission electron microscopy (HRTEM) was performed on three samples (25%, 54%, 100% alumina) which had been heat-treated at 673 K (Fig. 6). For the two high-surface-area samples (25% and 100%), the presence of pores is clearly indicated, with pore size on the order of 2 nm. However, for the low-surface-area/density material with intermediate chemical composition, a completely different particle morphology is observed, and no structures attributable to porosity are apparent.

Although these results support the presence of closed porosity (at least on the surface of the particles), we cannot pres-

ently explain why closed porosity exists. Since the gels have very similar physical structures before drying (as confirmed using low-field NMR), during drying some phenomena must be occurring which serve to close the pores just after the fluid leaves (no entrapped water is observed in the dried gels). This could partially be the result of the high surface tension of the pore fluid (i.e., water), which serves to collapse the pore throats during the final stages of drying. However, this does not explain the compositional dependence that is observed. Questions that remain for future investigation include why the effect is observed in this alumina content range, what is the effect of different silica and alumina sources, does low surface area/density also imply low permeability, and can this procedure produce low-surface-area films.

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