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% Al₂O₃, surface areas are 1 to 5 m²/g and skeletal densities are 2.1 to 2.2 g/cm³, as compared to the expected values of ≈300 m²/g and ≈2.6 g/cm³, respectively. This behavior 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.]

The 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 (2SiO₂·3Al₂O₃). 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 Al₂O₃ to pure SiO₂ in order to study the effect of Si/Al on such surface 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,¹ hydrolysis and condensation of a mixture of aluminum isopropoxide and tetraethyl orthosilicate (TEOS),² reaction of silica sols with dissolved aluminum salts,³ and mixing of silica and alumina sols.⁴ For all of these procedures, the N₂ BET surface areas of the dried gels (xerogels)
were over 100 m²/g, typically exceeding 300 m²/g. One exception was noted for a mullite gel dried at 393 K which resulted in a surface area of 2.8 m²/g. However, after heat treatment at 523 K, the surface area increased to over 100 m²/g.

**Experimental Procedure**

For samples synthesized at Montana State University (MSU), the silica sol was prepared at ambient temperature using reagent-grade tetrachloro orthosilicate¹ (TEOS) and distilled water adjusted to pH 2 with HCl. The TEOS/H₂O 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 nitrate⁴ was added to the stirring silica sol; then reagent-grade ammonium hydroxide⁵ (28% to 30% NH₃) 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/H₂O/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. Nitrogen specific surface area at 77 K was determined from a BET analysis using a molecular cross-sectional area of 0.162 nm². Nitrogen adsorption isotherms were measured at UNM on the samples synthesized at MSU using a flow type analyzer** (designated MSU). The samples synthesized at UNM were studied with an automated volumetric analyzer¹¹ (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 analyzer¹² with dry nitrogen sweep gas and a heating rate of 25 K/min. Phase analysis was conducted using a powder X-ray diffractometer.¹³ Pore/particle morphology was examined using a transmission electron microscope.¹⁴ Low-field NMR spin-lattice relaxation experiments of pore water were conducted at 303 K and 20 MHz using a pulse spectrometer.³³-⁹ Mercury intrusion measurements were made with a mercury porosimeter.¹¹⁵ Chemical composition of the MSU samples was determined by percent Al determinations using a flame atomic absorption spectrometer.¹¹ Percent Si and Al for the 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.¹⁴,²³ The very low surface area in the region of ≈50% might

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**Table 1. Synthesis and Preparation of Silica-Alumina Xerogels**

<table>
<thead>
<tr>
<th>Step</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Synthesis</strong></td>
<td></td>
</tr>
<tr>
<td>Silica Sol</td>
<td>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</td>
</tr>
<tr>
<td>Hydrogel</td>
<td>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</td>
</tr>
<tr>
<td>Preparation</td>
<td>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</td>
</tr>
</tbody>
</table>
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 g/cm$^3$ for the pure silica sample is in agreement with densities for
amorphous silica reported by Iler. The
pure alumina sample had a density of
3.13 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 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 mea-
surements indicate similar behavior between
high- and low-surface-area materials of
similar composition, experiments to assess
whether a 673 K heat treatment is neces-
sary 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 tempera-
ture) 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 m$^2$/g).
For temperatures less than 873 K, the
surface area of the low-surface-area 47%
Al$_2$O$_3$ material decreases more dramati-
cally than the surface area of the high-
surface-area 39% Al$_2$O$_3$ material. At
higher temperatures, the surface area of
the 47% Al$_2$O$_3$ sample actually increases.
This could be the result of opening of pre-
viously closed pores. Figure 5 shows the
change in density for the heat-treated ma-
terials. 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,
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. 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. 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 =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 presently 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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REFERENCES