FINAL TECHNICAL REPORT
BASIC SCIENCE OF NEW AEROGELS
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OBJECTIVE AND RATIONALE FOR THE RESEARCH

The main goal of the proposed research was to explore synthesis of materials at low temperatures and the value of nanocomposites in the area of aerogels. While there is a great deal of interest in single component and/or single phase aerogels, there is but little research on nanocomposite aerogels. The conceptual innovation and discovery of nanocomposites by the co-PI's on this proposal has led to an entirely new field of ceramic research because of the profound effects on enhanced densification of ceramics, lowering in crystallization temperature of ceramics and glasses through isostructural seeding, crystallization of glasses which have been thought to be impossible to crystallize, morphology control, etc. The objective was to exploit the nanocomposite idea in the making of composite aerogels which could lead to step function improvements in the areas of thermal insulation, adsorbents, catalyst substrates, membranes (filters), etc., because these can be tailored to have better thermal, mechanical and porosity properties than the single phase aerogels of SiO_2 , Al_2O_3 , TiO_2 , etc.

SUMMARY

The main goal of this project was achieved and the results can be summarized as follows:

- 1) The feasibility of making monolithic composite aerogels containing silica and natural clay minerals, synthetic clay minerals or zeolites has been demonstrated, using two different processes. Up to 30 weight percent of the mineral phase has been successfully added.
- 2) The addition of natural and synthetic clay minerals or zeolites to silica aerogels has been shown to retard densification. Composite silica aerogels showed significant surface area still present after sintering at 800°C or 1000°C . Surface areas of selected samples before and after sintering are shown in Table 1. For most samples, 1 weight percent of the second phase material was equally effective at retarding densification than 10 weight percent of the second phase material.
- 3) Composite aerogels, in general, had lower hardness values than the control samples of pure silica. Hardness values for pure silica control samples were in the range of 0.04 to 0.086 GPa and composite silica aerogels had hardness values 0.015 and 0.195 GPa. Hardness values were inversely proportional to aerogel pore radius.

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Table 1. Surface areas of selected gels before and after sintering.

Sample ID	Composition*	BET Surface Area As Prepared (m^2/g)	BET Surface Area 1000°C, 2hrs (m^2/g)
M3	10 wt. % kaolinite	926	448
N3	10 wt. % mullite	672	356
Q4	1 wt. % zeolite Y	923	408
R2	1 wt. % attapulgite	865	256
V4	30 wt. % kaolinite	858	298

* The rest is silica

The details of the accomplishments are given below under separate headings and the cumulative list of publications are given at the end.

A. Composite Aerogels of Silica and Minerals of Different Morphologies.
Claire Rutiser, Sridhar Komarneni and Rustum Roy

Monolithic composite aerogels have been prepared from silica/boehmite, silica/montmorillonite, silica/mullite and silica/kaolinite, with 1 and 10 mol% or wt% of the mineral in the final product. The aerogels were sintered at 1000°C for different durations to determine their thermal stability. The various samples lost 50 to 60% of their initial surface area after this treatment but still retained very high surface areas compared to the sintered aerogels prepared from silica only. The incorporation of small amounts of second phases of different morphologies in silica aerogels prevented their densification leading to high surface area materials with high thermal stability.

B. Composite Aerogels: Mechanical, Thermal Stability and Porosity Properties.
Claire A. Rutiser, Sridhar Komarneni and Rustum Roy

Silica aerogels were made from tetramethoxysilane (TMOS) with 1 and 10 weight percent of natural and synthetic phases of different morphologies. The second materials used include attapulgite, sepiolite, zeolite Y, zeolite 4A, Li fluorhectorite, and kaolinite (30%). Two different sol-gel preparation routes were used, leading to monolithic or partially monolithic aerogels in most cases. Vickers hardness indentation testing was carried out on these samples and also on pure silica aerogels. Hardness varied from <0.01 to 0.2 GPa for composite aerogels compared to 0.04 to 0.09 GPa for the control samples of silica aerogels. Hardness for the as-prepared aerogels varied greatly even among samples of the same mineral composition suggesting that gelation time, pH, and other factors may have greater effect on hardness than second phase composition. Surface area and pore size measurements of samples after sintering at 600° to 1000°C showed high surface areas and mesopores.

Composite silica aerogels containing 1 or 10% zeolite superultrastable Y, 1% attapulgite, or 30% kaolinite densified the least during sintering.

C. Single Phase and Diphasic Aerogels and Xerogels of Mullite: Preparation and Characterization.
Sridhar Komarneni and Claire Rutiser

Single phase mullite composition gels have been synthesized using tetraethoxysilane $[\text{Si}(\text{OC}_2\text{H}_5)_4]$ and aluminum nitrate nonahydrate as precursors. Diphasic mullite gels have been prepared using colloidal silica and boehmite as precursors. Xerogels and aerogels of both the above gels have been obtained by ordinary drying in air at 60°C and critical point drying in methanol, respectively. Single phase xerogels show an intense exothermic peak at about 980°C while their counterparts, aerogels, do not show any detectable exotherm by differential thermal analysis (DTA). These results suggest that the structure of single phase gels changed during critical point drying and the structural changes were investigated by solid-state ^{27}Al magic angle spinning nuclear magnetic resonance (MASNMR) spectroscopy. No differences between diphasic xerogels and aerogels could be detected by DTA because there was little or no effect of drying on the discrete silica and alumina phases. The tetrahedral coordination of Al in single phase mullite gel changed to octahedral coordination as detected by MASNMR during critical point drying which suggests that the alumina component segregated. Both single phase and diphasic aerogels of mullite composition showed very high surface areas in the temperature range of 1000°C - 1400°C and these may be useful for high temperature catalytic applications.

D. Single Phase and Diphasic Nanocomposite Aerogels .
Claire Rutiser, Sridhar Komarneni and Rustum Roy

Single phase and diphasic nanocomposite aerogels were prepared in various stoichiometric compositions and their physical properties were evaluated. Single phase aerogels were synthesized using nitrate and TEOS precursors. Nanosized amorphous oxide sols (boehmite, MgO and colloidal silica) were used to prepare diphasic aerogels. Critical point drying was performed for all gels, using ethanol as the principal supercritical fluid. Nitrogen adsorption and desorption isotherms were determined and were used to calculate the specific surface areas and pore size distributions.

A list of the aerogels prepared along with the as-prepared surface areas is given in Table 2. We have successfully synthesized aerogels of $\text{SiO}_2/\text{Al}_2\text{O}_3$ (5 and 10 mole percent Al_2O_3), mullite, SiO_2/MgO (5 and 10 mole percent MgO), cordierite, both aerogels and xerogels of SiO_2/Ag (5 and 10 mole percent silver) and xerogels of $\text{SiO}_2/\text{ZrO}_2$ (5 and 10 mole percent ZrO_2). Low thermal expansion aerogels, of the composition $\text{Ba}_{1.25}\text{Zr}_4\text{P}_{5.5}\text{Si}_{0.5}\text{O}_{24}$, were also synthesized. It may be seen that almost all the aerogels had high surface areas ($> 150\text{m}^2/\text{g}$). This clearly demonstrates the feasibility of using

the above processes to synthesize high-surface area monolithic aerogels as well as their flexibility in achieving various tailored end compositions.

SiO_2 /metal aerogels are of special interest in high temperature catalysis and gas separation applications. Both xerogels and aerogels of the composition SiO_2/Ag (5 and 10 mole percent silver) were successfully synthesized using the single phase nitrate/TEOS process. Both aerogels and xerogels showed similar pore size distributions before heat treatment, with porosity of 20nm or less. After heat treatment at 900°C, 2 h). The volume of nitrogen desorbed was much less after sintering than before, indicating a decrease in the total volume of porosity. The results for this composition (summarized in Table 3) clearly demonstrate the superior surface areas and the enhanced thermal stability of the nanoporosity (< 20nm) in SiO_2/Ag aerogels as compared with xerogels. This demonstrates the efficacy of the supercritical drying process for producing high temperature catalyst substrate materials. The success in synthesizing high surface area SiO_2/Ag aerogels indicates the feasibility of the metal nitrate/TEOS single phase process for synthesizing aerogels incorporating similar metals such as SiO_2/Cu and SiO_2/Ni . etc.

Table 2. List of prepared aerogels and xerogels, along with surface areas as prepared.

Composition	Surface Area (m^2/g)
a) $\text{SiO}_2/\text{Al}_2\text{O}_3$ - diphasic aerogel	
95/5	146
90/10	129
b) $\text{SiO}_2/\text{Al}_2\text{O}_3$ - single phase aerogel	
95/5	418
90/10	318
c) SiO_2/MgO - diphasic aerogel	
95/5	55
90/10	190
d) SiO_2/MgO - single phase aerogel	
95/5	197
90/10	242
e) Mullite - diphasic aerogel	171
f) Mullite - single phase aerogel	434
g) Cordierite - single phase aerogel	302
h) SiO_2/Ag - single phase aerogel	
95/5	374
90/10	250
i) $\text{Ba}_{1.25}\text{Zr}_4\text{P}_{5.5}\text{Si}_{0.5}\text{O}_{24}$	176
single phase aerogel, ultralow thermal expansion	

Table 3. Surface area (m^2/g) and pore size distributions of SiO_2/Ag xerogels and aerogels before and after heat-treatments as determined by N_2 adsorption and desorption isotherms.

Composition	As-Prepared	800°C/2h	900°C/2h
Xerogel, (95/5)	694	136	41.7
Pore size	<5nm	<1.8nm	bimodal, 3.5 & 10.2nm
Aerogel, (95/5)	374	N/A	140
Pore size	<20nm		<20nm
Aerogel, (90/10)	250	N/A	141
Pore size	<20nm		<20nm

CUMULATIVE LIST OF PUBLICATIONS AND PRESENTATIONS
RESULTING FROM CURRENT GRANT

1985-1987

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