Nanocomposite Aerogels by Methanol Supercritical Drying

S. Komarneni

*Intercollege Materials Research Laboratory and
Department of Agronomy, The Pennsylvania State University
University Park, PA 16802, USA*

This review paper deals with the synthesis and characterization of nanocomposite aerogels. The use of 1 to 10 mole % Al_2O_3 as a second phase prevented densification of silica and led to high surface areas and mesoporosity at 1000°C in nanocomposite aluminosilicate aerogels. Composite aerogels have also been prepared from silica and different natural and synthetic minerals. These second phases also prevented densification of silica and led to high surface area materials which may be useful as catalyst substrates. High surface area ($\sim 1220 \text{ m}^2/\text{g}$) hydrophobic aerogels have been prepared for potential natural gas storage. [aerogel, nanocomposite, supercritical drying, hydrophobic aerogels]

1. Introduction

There is an enormous worldwide interest in aerogels because of their useful properties such as low thermal conductivity, low density, low dielectric constant, high surface area, etc. Aerogels are coherent porous solids of low density which are usually prepared by supercritical drying [1] but can also be prepared by subcritical drying [2] in some cases. Aerogels have some disadvantages such as poor mechanical properties, poor thermal stability and poor hydrophobicity. Our recent research has focused on improving the above properties of the aerogels by nanocompositing so that they can be used in various applications such as insulation, catalysis and adsorption.

2. Experimental

Preparation of Gels. Tetramethoxysilane (TMOS) and boehmite (Remet Chemical Corporation, Chadwick, NY) were used to prepare nanocomposite aluminosilicate aerogels of 99% SiO_2 + 1% Al_2O_3 and 90% SiO_2 + 10% Al_2O_3 (all mole %). First TMOS was hydrolyzed using a TMOS/ H_2O molar ratio of 4. Boehmite was then added, stirred and transferred to Pyrex glass tubes before gelation. After gelation, the gels were exchanged with methanol before supercritical drying. Pure SiO_2 gels were also prepared from TMOS for comparison.

Composite aerogels were also prepared from TMOS and 1 to 10 wt% of minerals such as montmorillonite, kaolinite, mullite and different zeolites by first hydrolyzing TMOS followed by the addition of mineral phase. The gels were prepared in Pyrex glass tubes and exchanged with methanol. Hydrophobic silica gels were prepared from TMOS by cohydrolyzing with different amounts of ethyltrimethoxysilane (ETMS) (Fig. 1). After gelation, the gels were exchanged with methanol.

Fig. 1. Experimental procedure for TMOS-ETMS gels.

Supercritical Drying. The various gels were first aged in methanol to remove residual water from gel pores. A 50 ml Hastalloy "C" autoclave was then used for supercritical drying. Tubes containing the gels were placed in the autoclave and 15 ml of methanol was added to maintain methanol vapor pressure during the heating period to prevent the premature loss of pore fluid from the gel. The autoclave was sealed and pre-pressurized with nitrogen to 1200 psi and critical point drying was done in a three-stage operation. The first stage involved heating the autoclave to 260°C while keeping the pressure around 1200 psi. For the second stage, the above pressure and temperature were maintained for 15 minutes and then the supercritical methanol was purged with argon. After 15 minutes of purging, the pressure in the autoclave was released and the vessel was cooled slowly. Thus monolithic aerogels were obtained.

Heat Treatments. Some of the aerogels were heated in a furnace up to 1400°C in order to test their thermal stability i.e., porosity properties upon heat treatment to various temperatures.

Characterization. Many of the samples were characterized by powder X-ray diffraction for phase identification upon heat treatment. All the samples were characterized by BET N₂ adsorption-desorption isotherms from which surface areas and pore-size distributions were determined using an Autosorb-1 apparatus. Some of the samples were characterized by water absorption-desorption isotherms in order to determine their hydrophilic or hydrophobic behavior. Water isotherms were determined by a home-built device [3].

3. Results and Discussion

Nanocomposite Aerogels in the SiO₂-Al₂O₃ System.

As prepared 99% SiO₂ + 1% Al₂O₃ aerogels showed surface areas of 907 m²/g and median pore size of 6.5 nm. Upon heat treatment at 1000°C/2h this aerogel showed a surface area of 621 m²/g and median pore-size of 5.6 nm. The as-prepared 90% SiO₂ + 10% Al₂O₃ aerogel showed a surface area of 620 m²/g and a median pore-size of 7.5 nm while the aerogel heated at 1000°C/2h showed a surface area of 489 m²/g with a median pore size of 6.5 nm.

Thus high surface area and mesoporosity were preserved in the above nanocomposite aerogels even after heat treatment at 1000°C while the pure silica gel was found to densify and lose its porosity properties under the same heat treatment conditions [4]. The nanocompositing of silica gel with alumina as a second phase prevented densification by retarding viscous sintering and led to high surface areas of 489-621 m²/g and mesopores in the range of 5.6 to 6.5 nm in diameter after thermal treatment at 1000°C (Fig. 2). These thermally stable nanocomposite aerogels are expected to find applications in separations, insulation, catalysis at high temperatures.

Fig. 2. Pore-size distribution of 0.9 SiO₂-0.1 Al₂O₃ nanocomposite aerogel.

Composite Aerogels with Minerals. Composite aerogels were obtained with 1 to 10 wt% natural and synthetic minerals of different morphologies such as montmorillonite, kaolinite, mullite and zeolites. These composite aerogels sintered at 1000°C lost 50-60% of their initial surface area but still retained very high surface areas when compared to pure silica aerogel treated under identical conditions. These results also showed that small fractions of second phases composited with silica gels retarded densification by retarding viscous sintering leading to high surface area materials with high thermal stability (Table 1).

Table 1. Nitrogen BET surface areas of aerogels [5].

Composition	As Prepared	Sintered at 800°C/2h	Sintered at 1000°C/2h
	-----m ² /g-----		
Silica	712	721	<1
Silica + 1% Zeolite Y	923	828	408
Silica + 10% Zeolite Y	422	548	322

Hydrophobic silica aerogels. Aerogels of high surface area and density and hydrophobicity were achieved with ETMS modification of TMOS gels. The exposed ethyl groups and methoxy groups impart hydrophobicity to these aerogels. Figure 3 shows the water adsorption isotherms of ETMS-TMOS aerogels with different amounts of ETMS. An ETMS content of as little as 10% imparted extreme hydrophobicity to the silica aerogel [6].

Fig. 3. Water adsorption isotherms of ETMS-TMOS aerogels with 10 to 50 mole % ETMS [6].

The best aerogel composition was found to be 25 mole % ETMS and 75 mole % TMOS which had a surface area of 1221 m²/g with hydrophobic property. These aerogels are expected to be useful in natural gas storage application.

References

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