

SYNTHESIS OF HYDROPHILIC AND HYDROPHOBIC XEROGEL

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ABSTRACT

Highly porous hydrophilic and hydrophobic silica xerogels were synthesized by surface modification of silica hydrogels at ambient pressure drying. The silica hydrogels were prepared by a sol–gel polymerization of an inexpensive silica precursor (sodium silicate) under atmospheric conditions. In order to minimize shrinkage due to drying, the hydrogel surface was modified using trimethylchlorosilane (TMCS) in the presence of ethanol/n-hexane solution before ambient pressure drying (APD). Properties of the final product were investigated using Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR). Highly porous hydrophilic xerogels were obtained after heat-treating the modified xerogels. At temperatures above 400°C the surface alkyl groups (-CH₃) were significantly oxidized and, consequently, the properties of the resulting xerogels were altered. Products obtained via the proposed inexpensive approach have superior properties and the method exploits an inexpensive silica source (sodium silicate).

Key words: aerogels, xerogels, surface modification,

INTRODUCTION

Aerogels are the most highly porous nanostructured materials. They exhibit large surface area (~1200 m²/g), high porosity (80–98%), low bulk density (~0.03 g/cm³), extremely low thermal conductivities (0.005 W/mK), and unique acoustic properties (sound velocities as low as 100 m/s) [1,2]. Because of these properties, aerogels are utilized as thermal super-insulators in solar energy systems, refrigerators, and thermal flasks [3]. Despite these applications, the high production costs have thus far prevented their commercial use.

Meanwhile, applications for porous silica xerogels continuously expand as their production costs decrease and their properties improve. Hydrophobic and hydrophilic silica xerogels with superior physical properties such as high surface area and large pore volume have potential applications in fields such as adsorbents, separations, biomedicine, sensors, drug delivery systems, catalyst carriers, thermal insulation, glazing, paints, and oil spill clean-up [4–8].

Conventional silica xerogels have relatively high density, low surface area, and small pore volume, restricting their applications. Recent observations suggest that the properties of porous materials improve following modification with silica gels (alcogel or hydrogel) during synthesis before the ambient pressure drying (APD) [9–13]. Moreover, silylating hydrogels and drying at ambient pressure can give less-dense silica xerogels. During the drying process,

non-polar alkyl groups (which repel each other) replace surface OH groups, resulting in the “spring back-effect”, which preserves the silica gel network and, hence, the porosity [14].

Surface modification of silica hydrogels by alkyl groups has been reported to preserve the porous network even after drying at ambient pressure [15]. Prakash et al. [16] have synthesized silica aerogel films at ambient pressure via solvent exchange and surface

modification processes. Solvent exchange is a lengthy and tedious process because it simply depends on diffusion of the solution within the gel. Hence, it takes several days to produce silica aerogels at ambient pressure. Schwertfeger et al. [17] developed a new synthesis for sodium silicate-based silica aerogel at ambient pressure. Since then, many researchers have focused on synthesizing sodium silicate-based silica aerogels at ambient pressure.

Nevertheless, the solvent exchange process, which is required for silica aerogel synthesis at ambient pressure, makes it a tedious process. Recently, Shi et al. [18] reported a new method, called

one-step solvent exchange and surface modification process. This method is based on combining different solvents (trimethylchlorosilane (TMCS), n-hexane, and ethanol) for surface modification.

EXPERIMENTAL

The schematic presentation of the silica aerogels catalyzed with various acids is shown in Fig. 1. Wet gels were prepared from commercial sodium silicate precursor of specific gravity 1.05 diluted from specific gravity of 1.39 (Na_2SiO_3 , Marvin-Ltd, Bulgaia, $\text{Na}_2\text{O}:\text{SiO}_2 = 1:3.13$) using citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) as catalyst keeping molar ratio of $\text{Na}_2\text{SiO}_3:\text{H}_2\text{O}$ constant at 1:150. The sols were prepared by adding acid dropwise in sodium silicate solution while stirring and were kept for gelation at 50°C in a temperature controlled oven to form a gel. The formed gels were aged for 3 h at 50°C to give strength to the gel network. To study the effect of acid, the monolithic gels were first cut into very small pieces then washed with 50 mL water four times so that the sodium salt trapped in the pores of gel will come out and once with methanol in 24 h respectively. The subsequent surface chemical modification was carried out using a mixture of methanol (MeOH), n-hexane (Merck, Germany) and trimethylchlorosilane (TMCS, Fluka, Pursis grade, Switzerland) in volume ratio of 1:1:1 over a period of 24 h. After completion of surface modification, the gels were exposed to ambient air for 24 h. Dry gels obtained by ambient drying were heated at 50 to 400°C for 1 h each, and were taken out for characterization after cooling of oven to room temperature as hydrophobic silica aerogels.

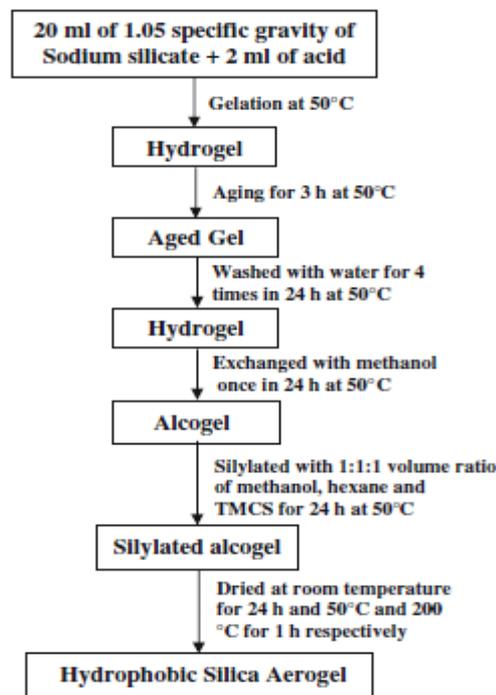


Fig. 1. Schematic representation of the silica aerogels catalyzed with citric acid

RESULTS AND DISCUSSION

Sodium silicate (Na_2SiO_3) has been and probably will always be the cheapest source of relatively pure silicic acid from which silica gel can be made. Sodium silicate reacts with water to give silicic acid and then the silicic acid polymerizes and forms silica gel as shown in the following reactions:

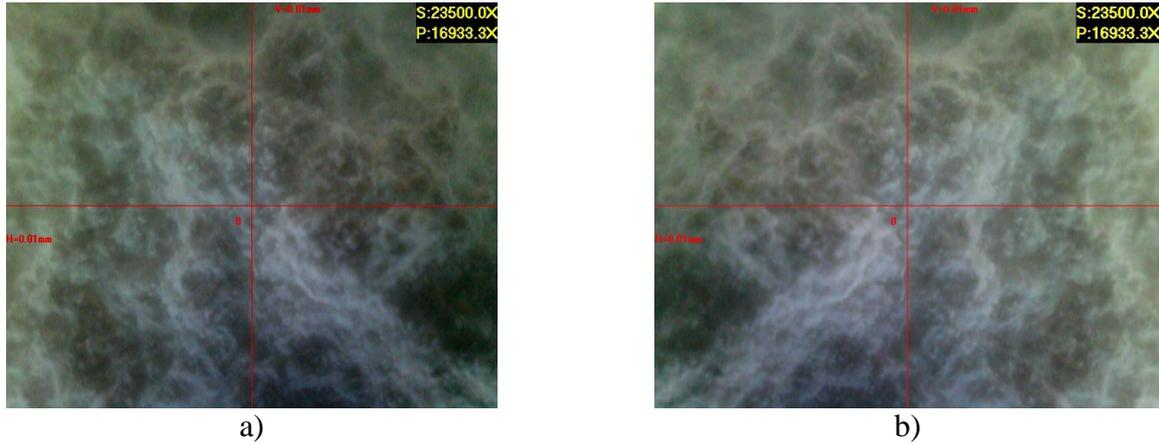


Fig.2. Micrographs of the silica aerogels prepared using acid a) citric acid-2 M, b) citric acid-3 M

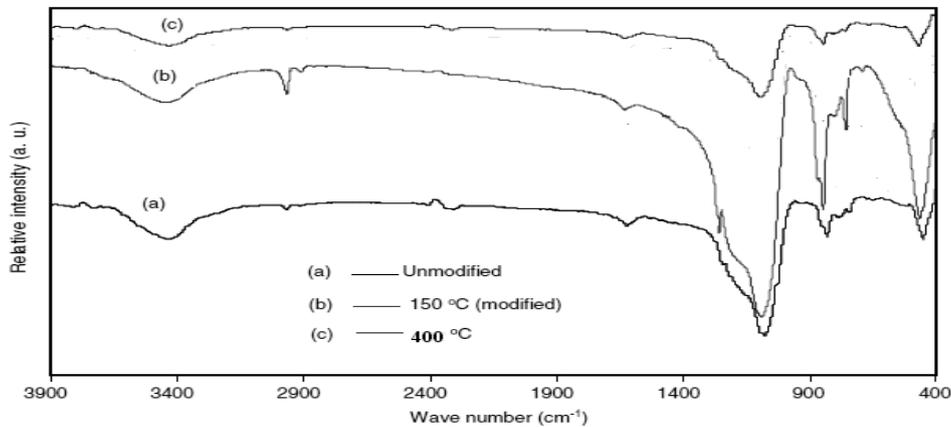


Fig.3. IR spectra of unmodified silica gel together with those modified with TMCS

The absorption peak centered at 976 cm^{-1} corresponds to the OH groups adsorbed on the silica surface, the bending of H-O-H bonds, and the stretching of the Si-OH bonds. The peaks centered at 1070 and 495 cm^{-1} correspond to the Si-O-Si bonds and are the most informative of the silica network structure. The two weak peaks at 976 and 960 cm^{-1} for the unmodified silica gel represent the Si-OH stretch vibrations, indicating that there is no modification of the silica gel surface. Moreover, there are no C-H peaks in the IR spectra of the unmodified silica gel. Si-OH and Si-H₂O peaks are present in the IR spectra and show the hydrophilic nature of the unmodified gel. A strong peak at 1256 cm^{-1} for the modified samples indicates significant surface modification by TMCS. The OH and Si-OH peaks are conspicuous for the unmodified xerogel. Fig.3 also shows the IR spectra for heat treated, TMCS modified xerogel. The peak at 1256 cm^{-1} , which was present in modified xerogel, clearly disappears after heat treatment at 400°C . This change indicates that the attached group (-CH₃) gets oxidized at that temperature, converting the hydrophobic gel into its hydrophilic counterpart.

CONCLUSIONS

Hydrophobic and hydrophilic sodium silicate based silica xerogels were obtained by simultaneous solvent exchange and surface modification of wet silica gel with trimethylchlorosilane (TMCS) followed by ambient pressure drying. A hydrophilic xerogel with better physicochemical properties was obtained by heating the TMCS modified silica gel at 400°C . The silica wet gel was obtained by a novel fast gelation of colloidal silica sol. The surface modifying agent (TMCS) as

well as the heattreatment process has a strong effect on the properties of the final product. Products obtained via the proposed inexpensive approach have superior properties and the method exploits an inexpensive silica source (sodium silicate).

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