

Preparation of Hydrophobic Monolithic Silica Aerogels through Surface Modification Using Hexamethyldisilazane in Supercritical CO₂

Can Erkey* and Ayşe Meric Kartal

Department of Chemical and Biological Engineering, Koc University, 34450 Sariyer, Istanbul, TURKEY, cerkey@ku.edu.tr, Fax: +90 (212) 338 1548

There are several advantages to using supercritical CO₂ (scCO₂) as solvent in chemical modification of the metal oxide surfaces. In particular, the low viscosity and low surface tension of the SCFs leads to enhanced deposition kinetics over conventional solution methods. The application areas include polymer modification, construction of low-energy hydrophobic surfaces, preparation of stationary phases for reversed-phase chromatography, making biocompatible surfaces, and forming monolayers for lithography, micropatterning, and sensors where alkylsilanes are generally used as the modifying agent.

In this study, we rendered the surface of monolithic silica aerogels hydrophobic using hexamethyldisilazane (HMDS) as surface modification agent and scCO₂ as solvent. The silica aerogels were prepared by two step (acid-base) sol-gel method using 50 wt.% tetraethylorthosilicate (TEOS) and ethanol as solvent. The effect of temperature (in the range of 40-60 °C) and pressure (in the range of 52-138 bar) on the rate of modification reaction was investigated at various HMDS concentrations. The treatment leads to a hydrophobic surface coating on the modified aerogels with an average thickness of 600 µm. The contact angles were found to be greater than 100° at different HMDS concentrations in the fluid phase and it was found that the hydrophobicity was restricted to the surface of the monoliths. In addition, phase behavior of the binary mixture HMDS and CO₂ was studied in a high pressure view cell. Bubble points were determined by varying the pressure at a fixed temperature and composition at temperatures 40, 50 and 60 °C. As the concentration of HMDS increased, the bubble point pressure tended to decrease. The bubble point curves were modeled using the Peng-Robinson equation of state and compared well with the experimental data.

INTRODUCTION

Surface chemical modification of silica aerogels by HMDS have been studied recently using four different methods which can be classified as the co-precursor method [1,2], the derivatization method [1-3] and deposition of HMDS on aerogel surface from the gas phase and the supercritical phase [4,5]. The aim of all the studies was to replace the hydrogen (H) in the surface silanol (Si-OH) groups by a hydrolytically stable organofunctional group like Si-R (e.g. R=CH₃) in order to prevent the adsorption of water and hence the deterioration of the aerogel structure. The co-precursor method involves the incorporation of HMDS or various other organosilanes such as monoalkyl, dialkyl, trialkyl, aryl, alkoxy/chloro silanes as hydrophobic reagents in standard sol-gel synthesis. Venkateswara Rao et al. used two different hydrophilic precursors (TEOS and tetramethylorthosilicate (TMOS)) for a fixed molar ratio of hydrophobic to hydrophilic precursor as 0.5 [1]. HMDS gave the highest contact angle (135°) for both of the hydrophilic precursors when compared to the other hydrophobic precursors. However, the optical transmittance was as low as 5%. In another study, the mole ratio of the hydrophobic to hydrophilic precursor was varied from 0.1 to 0.6, resulting in a decrease in optical transmittance from 65% to 5% and an increase in contact angle from 110° to 136° [2]. It can be concluded that in order to increase hydrophobicity, the transmittance has to be sacrificed for the co-precursor method. Furthermore, an increase in HMDS amount increases the hydrophobicity while decreasing the optical transmittance and causing cracks in the monoliths. If improved transmittance is required, derivatization method seems to be more useful with an increase up to 70% and 88% for TMOS based and TEOS based aerogels respectively [1]. Similarly, in other studies derivatization method yields monolithic and transparent aerogels with a contact angle of 109° [2], and aerogels with a transparency of 75% and a contact angle of 143° [3]. The derivatization method is different from the co-precursor method since HMDS is introduced after the gel formation by immersing the prepared gel in a mixture of a solvent and HMDS for more than 12 hours at a temperature above 40 °C [1-3]. The major drawbacks of this method are the possible effect of the side product ammonia (NH₃) and the removal of unreacted HMDS with several heat treatments above 50 °C.

For the deposition of HMDS on the aerogels, a reaction of surface silanol groups and organosilanes were realized in a gaseous or supercritical environment using solvents such as nitrogen (N₂) [4] or scCO₂ [5]. The modification reaction in N₂ [4] was a continuous process with a feed stream of various HMDS concentration at relatively high temperatures (150-450 °C). It was reported that the duration of silation and formation of the gaseous byproducts (methane, ammonia, hexamethyldisiloxane (HMDSO) and nitrogen) were dependent on the temperature, e.g. methane was produced above 300 °C. The chemical modification reaction in scCO₂ was carried out in batch mode [5], ammonia was produced as a product of the reaction of silica and HMDS. Ammonia then reacted with CO₂ to form ammonium carbamate which was weakly physisorbed on the surface hydroxyl groups, and was easily removed with evacuation or by purging. The reaction was carried out in a cell at 50 °C and at 200 bar by injection of 50µl HMDS which was previously dissolved in scCO₂ in a mixing cell. It was observed that ammonium carbamate blocks a portion of the surface silanol groups from participating in the reaction with HMDS. It Ammonium carbamate is removed by purging but the amount of chemisorbed species are reduced because of the blocking. It was found that this could be prevented by setting the CO₂ pressure at low values (below 90 bar) since at low pressures ammonium carbamate formation is not favored. Thus, such pressure adjustment provides advantage for the usage of scCO₂ in chemical modification reactions.

In this study, we studied the chemical modification of the surface of silica aerogels from a supercritical phase using CO₂ as the solvent. In addition, the hydrophobicity was characterized by contact angle tests and the dimensions and the properties of the surface coating were investigated. Furthermore, the phase behavior of HMDS and CO₂ was studied through determination of bubble point pressures for different mole fractions of HMDS. The experimental data was compared with the results from the Peng-Robinson equation of state (PREOS) model.

MATERIALS AND METHODS

Silica aerogels in this study were synthesized using TEOS (Aldrich with purity: 98.0 %) as the precursor, HCl (Riedel-de Haen with purity: 37%) as the hydrolysis catalyst and NH₄OH (Aldrich 2.0M in ethanol) as the condensation catalyst. A 50 wt % solution of TEOS in ethanol (Merck with purity: 99.9%) was prepared. Subsequently, water and acid catalyst were added to start hydrolysis under continuous stirring. Condensation started with the addition of the base catalyst and the sol was taken into syringe molds (5ml cylindrical) for complete gelation. The overall mole ratio of TEOS to water was 1:4, HCl to TEOS was 500:1, and NH₄OH to TEOS was 80. These mole ratios were kept constant in the aerogel synthesis. After gelation was finished, the monolith alcogel was taken out from the mold and placed in an aging solution which was 50 vol. % ethanol and water, and left in furnace at 50 °C for 20 hours. The aim of the aging step was to improve the mechanical strength of the material. After the aging step was completed, the aging solution was replaced with pure ethanol and the alcogels were kept for two more days in pure ethanol in order to remove all the impurities other than ethanol.

The alcogels were dried supercritically using the experimental apparatus given in Figure 1. After the alcogels were placed in the main vessel with ethanol, the vessel was heated to 40 °C and charged with CO₂ from a syringe pump up to 103 bar. Subsequently, ethanol was extracted continuously at a constant flow rate of 50ml/h which was adjusted by the needle valve. At the end of the extraction process, the vessel was depressurized slowly and the aerogels were obtained.

The surface modification of the hydrophilic aerogels was achieved by the injection of HMDS (purchased from Alfa Aesar with purity: 98%) from the 10ml high pressure vessel to the main vessel. The experimental apparatus can be seen in Figure 1. For a typical experiment, a certain amount of HMDS was placed in the 10ml vessel within a vial and the vessel was charged with CO₂. The vessel was kept at 103 bar at room temperature overnight until all the HMDS placed in the vial was dissolved in CO₂. Subsequently, the small vessel was brought to 276 bar by charging with CO₂ from the syringe pump. The CO₂ – HMDS mixture at 276 bar at room temperature was injected into the main vessel by opening the valve between the small and the main vessel. After the reaction of HMDS with the aerogel surface, the extraction of excess HMDS at 103 bar at temperatures between 40-60 °C with a flowrate of 30ml/h, was carried out and then the vessel was depressurized at the reaction temperature. The surface modification reactions were carried out at various pressures (52-138 bar) and at various temperatures (40-60 °C). The thickness of the observed surface coating on the modified aerogels was measured from the photographic image. In addition to this, the surface contact angle was also measured from the photographic image of the water droplet at the surface of the modified aerogels.

The same experimental apparatus which is described in Figure 1 was used for the phase behavior study of the binary mixture HMDS and CO₂. The small vessel was removed

from the set-up and the phase changes were studied in the main high pressure view cell as the CO₂ is introduced. The temperature was kept constant at 40 °C and the pressure was increased until the bubble point is reached. The pressure was recorded when the last single bubble is observed for various HMDS concentration. The same procedure was repeated for temperatures 50 °C and 60 °C as well. The concentration in terms of mole fraction of HMDS and CO₂ can be determined by recording the mass of HMDS which is put into the vessel and the mass of the CO₂ that enters the vessel. Finally, pressure-mole fraction of CO₂ (P-x) and pressure temperature (P-T) diagrams were constructed for different temperatures.

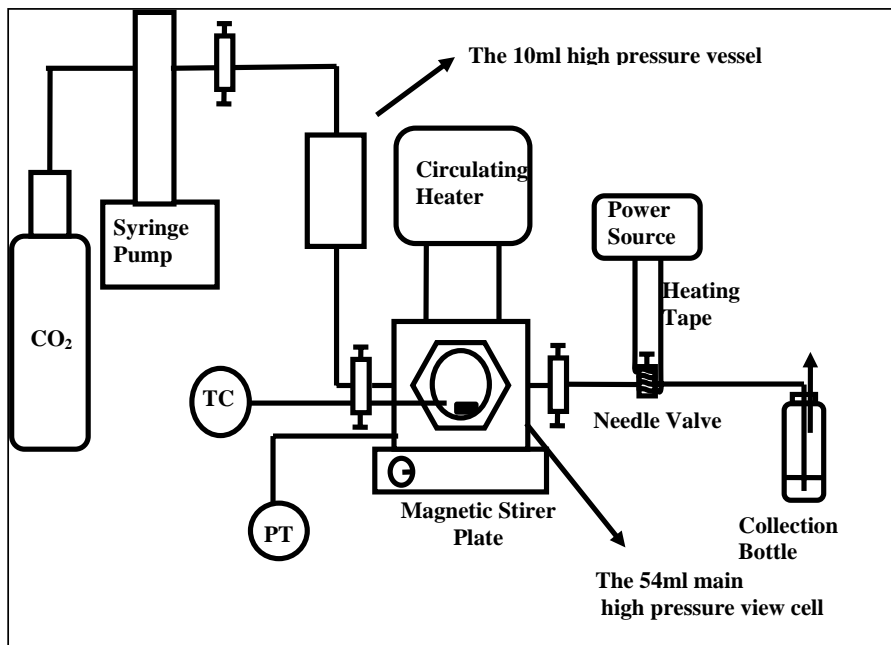


Figure 1: Schematic representation of the supercritical drying process, surface modification process and phase behavior study of binary mixture HMDS and CO₂.

In addition to the experimental data, vapor-liquid equilibria of binary mixture HMDS and CO₂ can be modeled through Peng-Robinson equation of state (PREOS) using the pure component properties given in Table 1.

Table 1: Pure component properties [6] used in PREOS

Substance	Critical temperature (K)	Critical pressure(bar)	Acentric factor
CO ₂	304.19	73.82	0.23
HMDS	544	19.2	0.51

RESULTS

All of the silica aerogels that are used in the surface modification are prepared as described in the materials and methods section. The diameter and the thickness of the monolithic aerogels were 10mm and 2mm, respectively. In order to preserve the monolithic

shape of the aerogels during surface modification, the amount of HMDS injected to the vessel was an important parameter. Therefore, the amount of HMDS placed in the 10ml vessel and the extraction time are adjusted. For an uptake time of 1 hour, the studied amounts of HMDS in the 10ml vessel were 2 ml, 0.2 ml and 0.5 ml. It was observed that all aerogel sample surfaces became opaque independent of the amount of the HMDS. For 2ml HMDS, the aerogels pulverized as a result of multiple cracks. For 0.2 ml HMDS, the aerogels were still monolithic with no cracks but a simple contact angle test showed that the surface of the aerogel was destroyed by the water droplet, revealing that it was not modified sufficiently. For 0.5 ml HMDS, it was possible to obtain both hydrophobic and monolithic aerogels when the extraction time was more than 3 hours. Below 3 hours, the obtained monoliths had still cracks in it while above 3 hours, no cracks are observed.

The hydrophobicity of the aerogels was restricted to the surface coating of the aerogels which had a thickness of 600 μ m as shown in Figure 2. The opacity and the hydrophobicity decreases further down this depth. A contact angle above 100° could be measured. It was observed that the contact angle decreased with time down to 95°. The poor quality of the surface coating can be attributed to self-polymerization of the organosilane giving rise to polymerized surface coating as concluded in other studies [5]. Reaction temperature is a factor which controls the competition between the surface reaction and self-polymerization.

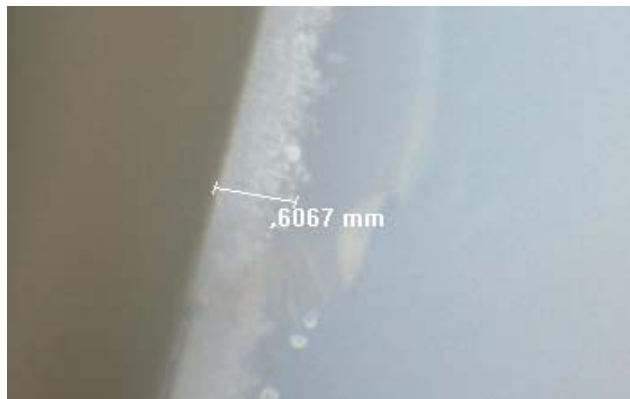


Figure 2: Surface coating of the modified aerogel

The phase behavior of binary mixture HMDS and CO₂ was studied by determining bubble points at a fixed temperature and at varying HMDS concentrations from 0.03 mol% to 0.47 mol% for 40 °C and from 0.13 mol% to 0.25 mol% for 50 °C and 60 °C. The bubble point pressure tends to decrease as the HMDS concentration is increased as shown in Figure 3 for 40 °C. Also, at a fixed composition, the bubble point pressure tends to increase as the temperature is increased as it is seen in Figure 4 for a 0.14 mol% HMDS.

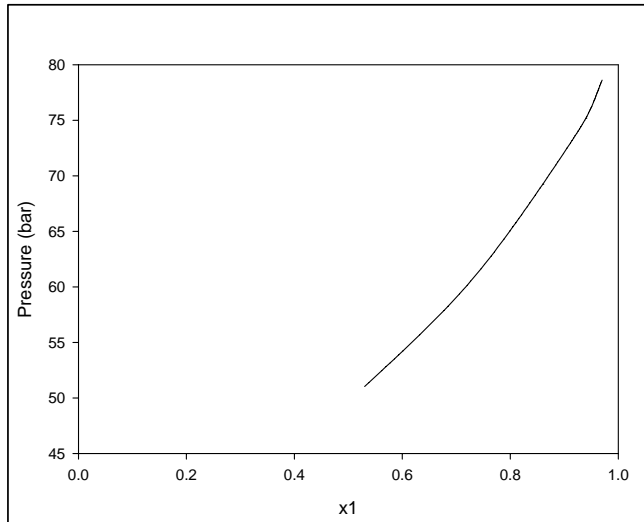


Figure 3: The variation of bubble point pressures with CO2 mol% at 40°C.

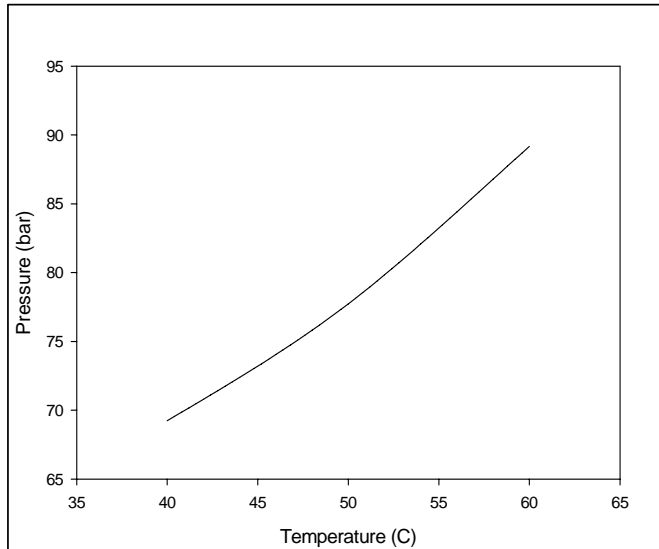


Figure 4: The variation of bubble point pressure with temperature at a fixed HMDS concentration of 0.14mol%.

CONCLUSION

We have demonstrated the surface chemical modification of silica aerogels by using HMDS in CO₂ at pressures 52-138 bar and at temperatures 40-60 °C. The hydrophobicity of the silica aerogels were analyzed by the contact angle test and the values above 100° could be achieved. The HMDS treatment has caused the formation of a white opaque surface coating of thickness 600µm. The treatment was found to be restricted to the thickness of the coating. It was concluded that the CO₂ was a good solvent for HMDS treatment and the silation reaction can be carried out in a relatively short time such as 1hour.

Furthermore, we have determined the bubble point data of binary mixture HMDS and CO₂ for various mole fractions at fixed temperature, and for various temperatures at fixed mole fractions. The bubble point pressure decreases as the mole fraction of CO₂ decreases for a fixed temperature and it increases as the temperature increases. PREOS was found to represent the data successfully.

REFERENCES

[1] Venkateswara Rao, A., Bhagat, S.D., Barboux, P., Journal of Non-Crystalline Solids, Vol.350, **2004**, p.216.

[2] Venkateswara Rao, A., Kalesh, R.R., Journal of Sol-gel Science and Technology, Vol.30, **2004**, p.141.

[3] Shewale, P.M., Venkateswara Rao, A., Parvathy Rao, A., Applied Surface Science, Vol.254, **2008**, p.6902.

[4] Slavov, S.V., Sanger, A.R., Chuang, K.T., J. Phys. Chem. B, Vol. 104, **2000**, p.983.

[5] Combes, J.R., White, L.D., Tripp, C.P., Langmuir, Vol.15, **1999**, p.7870.

[6] Yaws, C.L., Handbook of thermodynamic diagrams, Gulf Pub. Co., **1996**.