

# Effects of surface treatment of MCM-41 on motions of confined liquids

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## Abstract

To apply mobile crystalline material 41 (MCM-41), which has a larger specific surface area than many other nanoporous silicas, for energy absorption, chlorotrimethylsilane treatment is performed to adjust the structure of inner surfaces of nanopores. As the treatment time is sufficiently long, the pore surface can be changed from hydrophilic to hydrophobic, leading to an energy absorption efficiency a few times higher than previously developed nanoporous-material-functionalized liquids. A strong effect of addition of electrolyte on infiltration pressure is observed.

## 1. Introduction

Mobile crystalline material 41 (MCM-41) is a commonly used nanoporous material [1]. It is usually synthesized by a templating mechanism [2]. Through phase separation, a continuous network surrounding template molecules is formed first. Then, by combustion and/or extraction, the template is removed, leaving the empty space inside the network material as nanopores [3]. Depending on the length of template molecules, the pore size can be adjusted in the range of 2–20 nm. In MCM-41, the pore walls are usually formed by amorphous silica, and the pore structure is hexagonal and quasi-one-dimensional. One remarkable feature is its very large porosity, typically 60%–80%, resulting in an ultrahigh specific surface area.

Recently, intensive studies were performed on applying nanoporous materials for energy absorption [4–9]. The nanoporous material must be first hydrophobicized. When it is immersed in water, due to capillary effect the number of liquid molecules that diffuse into the nanopores is negligible, and thus under ambient pressure the nanopores remain empty. As an external pressure is applied, the effective ‘strain’ energy in the liquid phase becomes increasingly high. Eventually, when the pressure reaches a critical value, the capillary effect can be overcome and it is more energetically favorable for the liquid molecules to enter the nanopores, where the ‘strain’ energy can be released since the solid network is much stiffer than the liquid. Based on the classic Young’s equation, the

critical pressure can be assessed as  $p_{in} = 2\Delta\gamma/r$ , where  $\Delta\gamma$  is the effective excess solid–liquid interfacial tension and  $r$  is the pore size. In a number of nanoporous materials, as the pressure is lowered, the desorption curve is quite different from the absorption curve. Particularly, the confined liquid defiltrates from the nanopores only when the pressure is much lower than  $p_{in}$ , or does not defiltrate at all. As a result, a significant portion of the stored ‘strain’ energy is effectively dissipated; that is, the compression of the nanoporous-material-functionalized (NMF) liquid is hysteretic. Such a system has great potential for developing high-performance protection or damping devices, e.g. armours and bumpers. The amount of dissipated energy associated with the irreversible compression process can be estimated as  $E^* = \Delta\gamma \cdot A$ , where  $A$  is the total nanopore surface area. Usually, at a hydrophobic solid surface  $\Delta\gamma$  is 10–100 mJ m<sup>-2</sup>, and for a mesoporous material  $A$  is around 100–300 m<sup>2</sup> g<sup>-1</sup>. Thus,  $E^*$  is at the level of 10 J g<sup>-1</sup>, which is higher than that of conventional energy absorption materials, such as rubbers or reinforced polymers [10], by orders of magnitude.

Since the energy absorption efficiency is amplified by  $A$ , it is attractive to use MCM-41, which has larger specific pore surface areas compared with most other nanoporous silicas, to develop NMF liquids. Since the nanopore surface of MCM-41 is formed by amorphous silica, it is wettable to water, and the capillary mechanism discussed above does not work directly. Surface treatment must be performed to modify the structures of inner pore walls so that they can be effectively hydrophobic.

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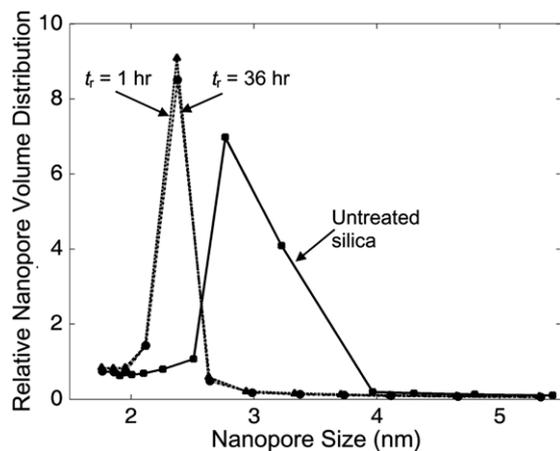


Figure 1. BJH analysis results of the MCM-41.

## 2. Experimental

The synthesis technique of MCM-41 silica has been well established [11]. In this study, the network material was obtained from Sigma-Aldrich (CAT No. 643645). The as-received material was in powder form, with the average particle size of about  $50\ \mu\text{m}$ . The solid line in figure 1 shows the result of a Barret–Joyner–Halenda (BJH) analysis, which was performed using a Micromeritics TriStar-3000 Analyzer. About 100 mg of the sample was dehydrated at  $100\ ^\circ\text{C}$  for 2 h in a nitrogen flow. The sample mass was determined through comparison of dry sample tubes with and without silica. The gas adsorption analysis was carried out using nitrogen at 77 K. According to the measured isotherms, the specific pore surface area was  $1060\ \text{m}^2\ \text{g}^{-1}$  and the specific pore volume was around  $1.0\ \text{cm}^3\ \text{g}^{-1}$ . The average pore diameter was 2.8 nm.

About 2 g of MCM-41 was sealed in a round bottom flask, and heat treated at  $100\ ^\circ\text{C}$  for 24 h in a vacuum oven. Then, 40 ml of toluene and 1.0 ml of chlorotrimethylsilane was injected while the solution was slowly stirred. Its molecular size was relatively small; so that the molecules could diffuse into the nanopores relatively easily. At the nanopore surface, they would react with hydroxyl sites, forming hydrophobic  $\text{OSi}(\text{CH}_3)_3$  surface groups [12, 13]. The byproduct of hydrochloric acid must be washed away. The surface treatment reaction was performed by first stirring the mixture for 10 min at room temperature and then refluxing it at  $90\ ^\circ\text{C}$ . The refluxing time,  $t_r$ , ranged from 1 to 48 h. Prior to the treatment, the toluene had been dehydrated using anhydrous calcium sulfate. The opening of the condenser was protected by a drying pipe filled with anhydrous calcium sulfate (the drierite). After the surface treatment, the silica was vacuum filtered, washed with dry toluene, vacuum dried, washed again with warm water, and finally vacuum dried at  $100\ ^\circ\text{C}$ .

After the surface treatment, 0.25 g of MCM-41 was immersed in 7 g of distilled water and sealed in a steel cylinder by a steel piston with reinforced gasket. The piston was compressed into the cylinder by a type 5569 Instron machine at the rate of  $0.5\ \text{mm}\ \text{min}^{-1}$ . After the infiltration plateau was fully formed, which is discussed in detail shortly, the piston was moved back at the same speed. The loading–unloading process was repeated a few times. From the second cycle, the

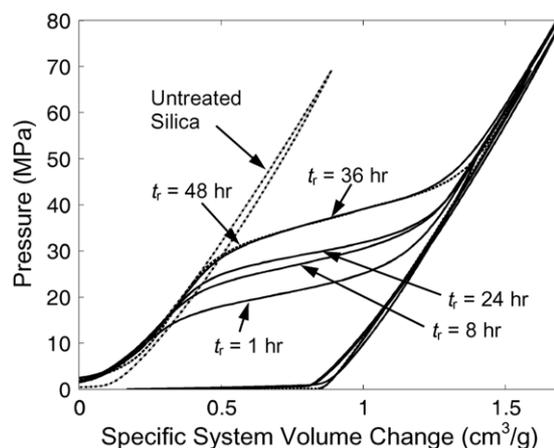


Figure 2. Typical sorption isotherm curves of the MCM-41 samples.

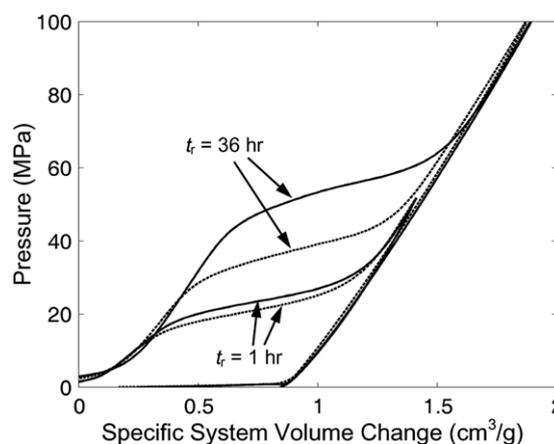


Figure 3. Effects of addition of sodium chloride. The dashed lines indicate the behaviour of pure water based systems, and the solid lines are for sodium chloride solution based systems.

pressure–volume curves were quite linear, indicating that the liquid defiltration never took place. Thus, in the following discussion we focus on the first loading. Figure 2 shows typical sorption isotherm curves of MCM-41 of various surface treatment times. For a few silica samples, the pressure induced infiltration experiment was also performed by using saturated sodium chloride solution. Figure 3 shows typical sorption isotherm curves.

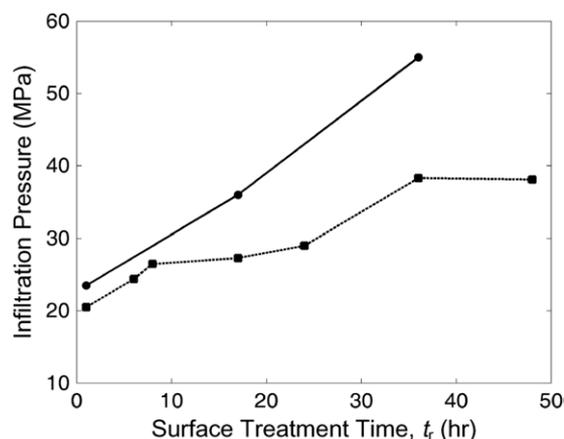
## 3. Results and discussion

Without surface treatment, MCM-41 silica is hydrophilic, and thus can be soaked by water spontaneously under ambient pressure. Under this condition, as external pressure is applied, the compression of the liquid phase and the filled silica particles is quite linear, as shown by the dash–dotted line in figure 2. Such a system does not have any energy absorption capacity. When the MCM-41 is surface treated, a layer of silane groups is formed at the inner walls, and the pore surfaces become effectively nonwetttable to water. The dashed line and the dash–dotted line in figure 1 show the pore volume distributions of two surface treated silica samples. It can be seen that the effective nanopore size decreases by about 0.4 nm, close to the double chain length of  $\text{OSi}(\text{CH}_3)_3$ ; that is, as the pore

surface is covered by the silane groups, the pore volume that can be accessed by guest molecules is reduced. However, the decrease in effective pore size is quite insensitive to the treatment time. For instance, as  $t_r$  increases from 1 h to 36 h, the pore volume distribution curve is almost the same, suggesting that the accessible pore volume is not dependent on the silane group density. It should be attributed to it being energetically unfavourable for gas/water molecules to enter the confining space between adjacent silane groups, and thus they tend to stay in the interior of the nanopore, making the silane group layer 'solid-like'. This phenomenon is in agreement with the experimental observation that, regardless of the difference in treatment time, for all the surface treated silicas the width of the infiltration plateau, which reflects the specific volume of the nanopores that are filled by confined liquid, is about  $0.8 \text{ cm}^3 \text{ g}^{-1}$ , smaller than the BJH measurement result.

The silane group density has a pronounced influence on the infiltration pressure. As shown by the solid lines in figure 2, only when a sufficiently high pressure is applied, can the capillary effect be overcome and pressure induced infiltration takes place, starting with the relatively large nanopores and ending with the smallest nanopores. It can be seen that after being surface treated for 1 h, the silica becomes quite hydrophobic so that the infiltration pressure is 20.5 MPa. In this study, the infiltration pressure,  $p_{in}$ , is defined as the pressure at the middle point of the infiltration plateau, which is taken as the section of sorption isotherm curve where the slope is smaller than 50% of that of the untreated silica system. Using Young's equation, the excess solid-liquid interfacial tension can be assessed as  $\Delta\gamma = p_{in} \times r/2 = 15 \text{ mJ m}^{-2}$ , with  $r$  being set to 1.4 nm, which looks plausible compared with macroscopic measurement results of contact angles. As  $t_r$  increases, more and more chlorotrimethylsilane molecules could enter nanopores and complete the reaction at hydroxyl sites, and thus the density of the hydrophobic surface groups becomes larger. Consequently, the repelling force applied on confined water molecules by pore wall rises, causing a larger  $\Delta\gamma$ . When the treatment time is 8 h,  $p_{in}$  increases to 26.5 MPa and the effective  $\Delta\gamma$  is  $18 \text{ mJ m}^{-2}$ . As  $t_r$  increases to 36 h,  $p_{in}$  rises to 38 MPa and the effective  $\Delta\gamma$  becomes  $27 \text{ mJ m}^{-2}$ . However, when  $t_r > 36 \text{ h}$ , its influence on infiltration pressure is negligible. For instance, the sorption isotherm curve of the silica treated for 48 h (the dashed line in figure 2) is almost identical to that of the silica treated for 36 h; that is, the surface group layer saturates. According to figure 4, the  $p_{in}$ - $t_r$  relationship is quite nonlinear.

Figure 3 shows the influence of addition of electrolyte. Sodium chloride is chosen because it is neutral and has relatively small cation and anion sizes. The solution is saturated so as to maximize the electrolyte effects. As the liquid is ionized, its molecular structure is changed. Around cations, water molecules form clusters, while anions are often unsolvated. As a result, the effective polarity may increase, and thus the degree of nonwettability to a nonpolar surface tends to be higher. In a previous study on a nanoporous silica gel, it was noticed that adding sodium chloride would cause a large increase in degree of defiltration but only a secondary increase in infiltration pressure [14]. For the MCM-41, however, no defiltration could be observed even when the



**Figure 4.** The infiltration pressure as a function of the surface treatment time. The dashed lines indicate the behaviour of pure water based systems, and the solid lines are for sodium chloride solution based systems.

sodium chloride solution is saturated and the external pressure is fully removed, probably due to the difficulty in formation, clustering and growth of gas nanophases in the quasi-one-dimensional nanopores. One interesting phenomenon is that the increase in infiltration pressure is significant, especially when the surface coverage is relatively high. When  $t_r = 1 \text{ h}$ , with the addition of sodium chloride, the infiltration pressure rises by about 3 MPa, 15% of that of a pure water based system. When  $t_r = 36 \text{ h}$ ,  $p_{in}$  of a sodium chloride solution based system rose by 27 MPa, nearly 75% higher than that of a pure water based system. The large increase in infiltration pressure and the non-defiltration of the surface treated MCM-41 suggest that defiltration is not dominated by the solid-liquid interfacial tension, which is compatible with previous discussions of the gas phase effect [15].

In the previously analysed silica [14], the silica pore surface was first modified by  $\text{C}_8$  groups and then the remaining silanol (Si-OH) sites were end-capped using chlorotrimethylsilane. Thus, the pore surface was covered by both  $\text{C}_8$  chains and  $\text{OSi}(\text{CH}_3)_3$  chains; the density of the former was much higher. In the current study, as discussed above, the pore surface of the MCM-41 was covered by only  $\text{OSi}(\text{CH}_3)_3$ . While both surface groups have similar hydrophobic effects to water molecules, they behave differently if ions exist. The  $\text{C}_8$  group is effectively more polar, which lowers its interfacial tension with an electrolyte solution. Since the functional end groups of  $\text{C}_8$  and  $\text{OSi}(\text{CH}_3)_3$  chains are the same, the difference of their interactions with sodium chloride solution must be related to their length, the details of which are still under investigation.

As the MCM-41 is fully surface treated, in saturated sodium chloride solution, the infiltration pressure is about 55 MPa. The specific energy absorption efficiency associated with the loading-unloading cycle can be calculated as the area enclosed by the sorption isotherm curve, which is around  $45 \text{ J g}^{-1}$ , nearly 4 times larger than that of nanoporous silica gel [14]. The high energy absorption efficiency should be attributed to the high degree of hydrophobicity caused by the high surface coverage and the short chain length, as well as the large specific pore surface area.

#### 4. Concluding remarks

In summary, it is noted in a pressure-induced infiltration experiment that guest species cannot enter the confining space among the surface groups at nanoporous surfaces of MCM41, and therefore the accessible pore volume is quite insensitive to the surface group density. The degree of hydrophobicity, which dominates the infiltration pressure, however, increases considerably with the surface treatment time. While the C<sub>8</sub> chain and the OSi(CH<sub>3</sub>)<sub>3</sub> chain have the same functional end groups, their interfacial tensions with sodium chloride solution are abundantly different, probably because of the difference in chain length. The non-defiltration of confined liquid in surface treated MCM-41 silica suggests that defiltration is not governed by solid–liquid interfacial tension.

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