

Effects of Nanopore Size on Properties of Modified Inner Surfaces

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By analyzing sorption isotherm curves of surface treated MCM-41 samples, it is noticed that if the nanopore size is relatively small, the end group dominates the solid–liquid interaction and the influence of the side group is relatively weak, which can be attributed to the confinement effect of nanopore walls.

1. Introduction

Modifying properties of inner surfaces of nanoporous materials is of relevance to drug delivery, absorption and adsorption, separation and purification, catalysis, and so forth.^{1–5} If the surface of a nanopore is wettable, it can be filled by liquid spontaneously, with the filling rate being dominated by both surface diffusion and normal flow.⁶ If the nanopore surface is nonwetable, an external driving force, very often a quasi-hydrostatic pressure, must be applied to overcome the capillary effect.^{7–9} An additional control mechanism is therefore available in the second case.

Nanoporous materials can be synthesized using carbons, silica, alumina, polymers, metals and alloys, and so forth.¹⁰ Many of these materials are intrinsically hydrophilic. To adjust the infiltration behaviors of liquids, the inner surfaces of nanopores must be modified by hydrophobic groups. Unlike treatments for large solid surfaces, the molecular size of the treatment agent for a nanoporous material must be sufficiently small, so that it can diffuse into the nanopores relatively easily. Over the years, a number of techniques have been developed.^{11,12} However, many unique nanometer-scale phenomena remain unexplained. For instance, although it has been well-known that, to make the nanopores nonwetable to water, the end groups must be hydrophobic, the effect of the side groups and its dependence on the nanopore size are still inadequately understood. In the past decade, a few computer simulations have provided useful insights,^{13,14} while relevant experimental data are still scarce.

2. Experimental Section

In the current study, we investigated a MCM-41 silica. The network material was obtained from Sigma-Aldrich (cat no.: 643645). According to a Barret–Joyner–Halenda (BJH) analysis using a TriStar 3000 analyzer, the specific surface area was 1060 m²/g and

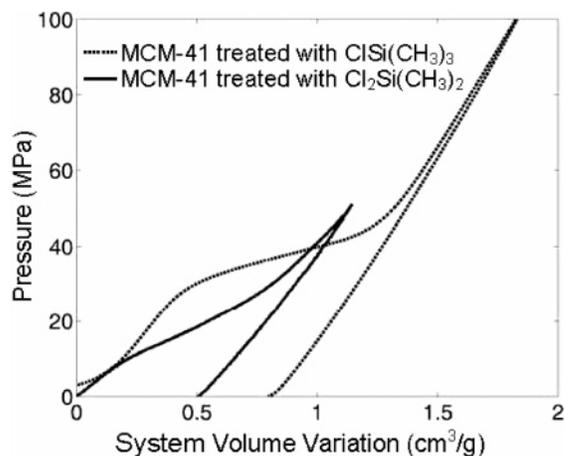


Figure 1. Typical sorption isotherm curves of surface treated MCM-41 in distilled water.

the average nanopore size was 2.8 nm, with a standard deviation of $\sigma = 0.3$ nm. The largest and smallest nanopore sizes were 3.7 and 1.9 nm, respectively. The nanopore volume was about 1.0 cm³/g. Nearly 2 g of the silica particles was first vacuum-dried at 100 °C for 24 h and then immersed in 40 mL of dry toluene in a sealed round-bottom flask. When the liquid was slowly stirred, 1 g of chlorotrimethylsilane ((CH₃)₃SiCl) or dichlorodimethylsilane ((CH₃)₂-SiCl₂) was injected into the flask. The surface treatment was performed by refluxing the mixture at 90 °C for 2 days. The byproduct of chloride acid and the residual reactants were removed by washing the silica particles with dry toluene and warm water.

The surface treated MCM-41 was immersed in a liquid phase and sealed in a stainless steel cylinder by a piston. The liquid phase was either distilled water or saturated aqueous solution of sodium chloride. In an Instron 5580 machine, the piston was compressed into the cylinder at 0.5 mm/min, and once the inner pressure was relatively high, it was moved back at the same rate. At such a slow loading rate, the pressure could be regarded as quasi-static, since no detectable variation in the sorption isotherm curves was observed when the loading rate was changed in the range of 0.1–1 mm/min. Figures 1 and 2 show typical sorption isotherm curves. The inner pressure was calculated as the piston force divided by its cross-sectional area. The specific system volume variation was calculated as the intrusion volume of the piston normalized by the mass of MCM-41.

3. Results and Discussion

The untreated MCM-41 is hydrophilic, and thus, it can be soaked by water under ambient pressure. Since the nanopores are filled, no further infiltration can take place as the pressure is increased. Thus, the pressure–volume curve is quite linear. When it is treated with chlorotrimethylsilane, as depicted in Figure 3a, the (CH₃)₃SiCl molecules would react with the hydroxyl

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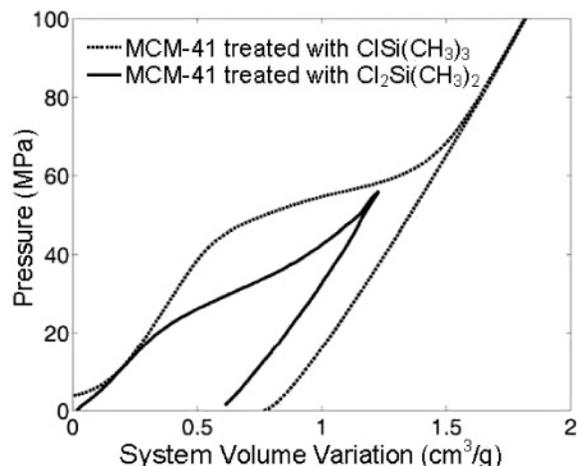


Figure 2. Typical sorption isotherm curves of surface treated MCM-41 in saturated aqueous solution of sodium chloride.

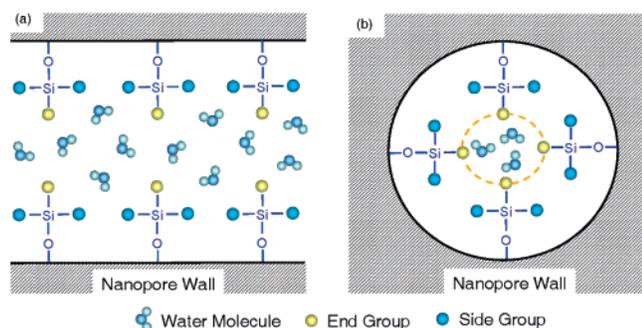


Figure 3. Schematic of liquid molecules in a surface treated nanopore: (a) side view and (b) end view.

sites at the nanopore walls and form surface groups of $(\text{CH}_3)_3\text{SiO}$.¹⁵ In each surface group, there are one end group and two side groups. All of them are methyl groups, which are hydrophobic. When the MCM-41 is surface treated with dichlorodimethylsilane, the $(\text{CH}_3)_2\text{SiCl}_2$ molecules would form surface groups via a similar reaction. However, while the end group and one side group are still methyl, the other is a chloro group, which is hydrophilic.

Figure 1 shows that after the surface treatment the nanopore surfaces are nonwetttable to water. The dashed line indicates the behavior of the MCM-41 treated with $(\text{CH}_3)_3\text{SiCl}$. As the piston is compressed into the steel cylinder, when the piston displacement is relatively small, the inner pressure is insufficient to overcome the capillary effect, and the system is quite rigid. When the pressure increases to $p_{\text{in}} = 26$ MPa, water molecules are forced into the nanopores and the pressure induced infiltration (PII) begins. If the nanopore size were uniform, PII would continue at the same pressure level. In the experiment, because of the nanopore size distribution, the pressure must be increased to force water molecules into smaller nanopores. At the onset of PII, by using the classic Young's equation, $\Delta\gamma = p_{\text{in}}(d/4)$, the effective interfacial tension, $\Delta\gamma$, can be estimated as 24 mJ/m^2 , with d being set to 3.7 nm , the largest nanopore size measured in the BJH experiment. When the pressure increases to about 46 MPa , the system becomes rigid again, indicating that the nanopores are filled. Under this pressure, if d is taken as 1.9 nm (the smallest nanopore size), $\Delta\gamma$ is 22 mJ/m^2 , close to the previously calculated value. That is, $\Delta\gamma$ is quite independent of

the nanopore size. The infiltration volume, which can be assessed as the width of the infiltration plateau between the starting and ending points of PII, is about $0.82 \text{ cm}^3/\text{g}$. It is nearly 20% smaller than the BJH measurement result of the specific nanopore volume, which should be attributed to the hydrophobic surface groups occupying the near-surface nanoporous space. After the infiltration is completed, as the pressure is lowered, the confined liquid does not defiltrate, owing to the difficulty in nucleation of the gas nanophase.¹⁶ Thus, if the loading–unloading cycle is repeated, PII can no longer be observed. Note that if the surface treatment time is further increased, the sorption isotherm curve would not vary much, suggesting that the surface group density has been saturated. Clearly, with the hydrophobic end group and side groups, water molecules cannot access the hydrophilic silica surface, and consequently, it becomes energetically unfavorable for them to enter the nanopores without the aid of external pressure.

For the MCM-41 treated with $(\text{CH}_3)_2\text{SiCl}_2$, while a similar PII characteristic can be observed, the infiltration pressure is quite different. The PII starts at a relatively low pressure of 8 MPa and ends at about 43 MPa . The low infiltration pressure indicates a low degree of hydrophobicity, primarily due to the hydrophilic chloro side group, qualitatively in agreement with the treatment results of large solid surfaces.¹⁷ At the onset of PII, the effective interfacial tension can be calculated as 7.4 mJ/m^2 , only about 30% of that of $(\text{CH}_3)_3\text{SiCl}$ treated MCM-41. The associated infiltration volume is slightly smaller than that of the $(\text{CH}_3)_3\text{SiCl}$ treated MCM-41, probably because liquid molecules may diffuse into the relatively less hydrophobic nanopores, especially the largest nanopores, under ambient pressure.

A remarkable phenomenon is that the decrease in $\Delta\gamma$ is highly nonuniform when the nanopore size varies, which is reflected by the large slope of the infiltration plateau of the solid line in Figure 1. At the end of PII, for example, the effective interfacial tension can be estimated as 20 mJ/m^2 , slightly lower than that of $(\text{CH}_3)_3\text{SiCl}$ treated silica by only 5%. This may be related to the confinement effect of nanopore walls. As depicted in Figure 3b, when d is relatively small, while along the axial direction the surface configuration does not change (Figure 3a), along the radius direction the end groups are “crowded” in the central part of the nanopore, which leads to a shielding effect. That is, as the lateral distance between adjacent end groups decreases, the access of liquid molecules to the side groups is “blocked”. Thus, the interfacial tension between the confined liquid and the effective pore surface (the dashed line in Figure 3b) is dominated by the end group. Note that this discussion can be extended to other nanometer-scale structures, such as networks of nanowires/nanorods and stacks of nanolayers, as long as the accessibility of liquid molecules to surfaces is affected by the geometrical factors.

With the addition of sodium chloride in the liquid phase, as shown in Figure 2, the main characteristics of the sorption isotherm curves of $(\text{CH}_3)_3\text{SiCl}$ treated and $(\text{CH}_3)_2\text{SiCl}_2$ treated silica samples remain similar. However, the infiltration pressures increase significantly. For the $(\text{CH}_3)_3\text{SiCl}$ treated MCM-41, at the onset and the end of PII, the pressures are 40 and 69 MPa , respectively, both of which correspond to an interfacial tension around 35 mJ/m^2 , higher than that of the water based system by nearly 50%. For the $(\text{CH}_3)_2\text{SiCl}_2$ treated MCM-41, the pressures are 18.5 and 50 MPa , respectively. The former corresponds to an interfacial tension of 17 mJ/m^2 (130% higher than that of the

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water based system), and the latter corresponds to 25 mJ/m² (25% higher than that of the water based system). It can be seen that when all the end and side groups are methyl groups, the interfacial tension is independent of the nanopore size. The increase in $\Delta\gamma$ caused by the addition of sodium chloride is quite uniform across the entire infiltration plateau, while the extent is larger than that at large solid surfaces,⁹ probably because the nanopore size is comparable with the Debye distance and therefore the ordinary double layer structure cannot be formed. In a nanopore modified by (CH₃)₂SiClO, hydrophilic chloro groups would interrupt the distribution of solvated ions and thus the liquid structure can be heterogeneous. The details of the configuration of solvated ions and their interactions with surface groups are still under investigation. Nevertheless, it is clear that, as the nanopore size is small, at the high-pressure end of the infiltration plateau, the influence of side group is much less pronounced compared with the low-pressure end, indicating that the shielding effect of the end group can be important.

4. Concluding Remarks

To summarize, by treating a MCM-41 with either (CH₃)₃SiCl or (CH₃)₂SiCl₂, the nanopore wall can be hydrophobic, allowing pressure induced infiltration. In relatively large nanopores, the influences of the end group and the side groups are comparable with each other. If the nanopore size is relatively small, due to the shielding effect of the end groups, the influences of the side groups are suppressed. With the addition of sodium chloride in the liquid phase, while the solvated ion structure in the nanopores can be fundamentally different from that in the bulk phase, similar size effects can still be observed.

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