Effects of surface-group length on liquid defiltration in a MCM-41

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The confined liquid in mobile crystalline material (MCM)-41 modified by short surface groups can defiltrate as the external pressure is reduced, while in MCM-41 modified by long surface groups it cannot, which can be attributed to the variation in effective nanopore size and the associated energy barrier to molecular motion. © 2008 American Institute of Physics. [DOI: 10.1063/1.2963486]

I. INTRODUCTION

For the past decade, it has been an active area of research to explore mechanisms and processes that govern nanofluidic behaviors.1 As liquid molecules are confined in a nanopore or a nanotube, their structures can be fundamentally different from that of a bulk phase. If the tube or pore size is relatively large, the liquid can form a few layers of various effective densities.2 If the tube or pore size is relatively small, the liquid molecules tend to have a chainlike structure.3 At a finite temperature, liquid molecules can rapidly transport across a short nanotube.4 If the tube is long or the pore is deep, an external mechanical, thermal, or electric field can greatly promote the molecular motion.5

If the inner surface of a macroscopic channel is nonwettable, a sufficiently high pressure must be applied to overcome the capillary effect so that the liquid can be forced into it. When the pressure is reduced, the liquid column would flow out of the channel, driven by the surface tension.6 When the channel size approaches the atomic length scale, the infiltration becomes relatively difficult. Even when the solid surface is nominally wettable, a large free space must be provided; otherwise, liquid molecules cannot enter the nanoenvironment no matter how high the external pressure is.7 Once the liquid molecules are confined inside a nanopore, they may or may not defiltrate when the external pressure is removed,8 the reason of which is still under investigation. In a classic porosity analysis, nondefiltration is often attributed to the “ink-bottle effect” and/or the hysteresis in the contact angle.9 For nanoporous materials, a few researchers argued that gas nanophase and pore texture play critical roles.10 Depending on the host/guest species and structures, a single gas molecule may either block or promote liquid infiltration, and if a small number of gas molecules can form a stable cluster, they would cause defiltration as the external pressure decreases. This theory predicts that in the microporous and mesoporous ranges, defiltration is easier if the nanopore size is smaller, which captures a substantial set of experimental data.11

II. EXPERIMENTAL

In this article, we report a recent experimental finding that is contradictory to the results of the analyses discussed above. The nanoporous material was mobile crystalline material (MCM)-41 synthesized by using sodium silicate (water glass), cetyltrimethyl ammonium bromide, sodium hydroxide, ammonium hydroxide, and water. Their molar ratio was 4:1:1:0.3:200. The mixture was stirred vigorously for 1 h, and then its pH value was kept at 10 by adding acetic acid,12 followed by the addition of 15% sodium chloride solution and further stirring for 3 min. After the solution became clear, it was thermally treated in an autoclave at 95 °C for 72 h. Finally, through calcination at 550 °C for 6 h, the template was removed and the MCM-41 particles were obtained. Via a Barret–Joyner–Halenda analysis, the average nanopore size was measured as 2.6 nm and the specific nanopore surface area was 1050 m²/g.

In order to modify nanopore surfaces, 1 g of MCM-41 was first vacuum dried at 100 °C for 2 h and then immediately immersed in 40 ml of dry toluene, followed by injection of 1 ml of chloro(dimethyl)octylsilane or chlorotrimethylsilane (for C₈ or C₁ treatment, respectively). After refluxing at 90 °C in a hot mantle for 24 h, the MCM-41 was washed with dry toluene and dried in vacuum at 50 °C. During the surface treatment, hydroxyl sites were deactivated and C₈ or C₁ groups were attached to nanopore surfaces. The MCM-41 modified by C₈ groups was end capped by C₁ groups for three times, following a procedure similar to the chlorotrimethylsilane (C₁) treatment.

With 7 g of saturated sodium chloride solution, 0.3 g of the surface-modified MCM-41 was sealed in a stainless steel cylinder by a steel piston. The sodium chloride was added to amplify the surface group effect and to promote defiltration.14 By using a 5580-type Instron machine, the piston was compressed into the cylinder at the rate of 0.5 mm/min, applying a quasihydrostatic pressure on the liquid phase. After reaching the specified pressure level, the piston was moved back at the same speed. Similar loading-unloading cycles were repeated for multiple times. Typical liquid intrusion curves are shown in Figs. 1 and 2.

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III. RESULTS AND DISCUSSION

Since C₈ groups are hydrophobic, the modified nanopore inner surfaces are nonwettable to the liquid phase. At a relatively low pressure, it is more energetically favorable for the liquid molecules to stay outside. As a result, the initial section of the loading path is quite rigid. When the pressure reaches 25 MPa, the energy barrier is overcome and the pressure-induced infiltration begins, leading to the formation of an infiltration plateau. Unlike in a gas absorption process, the infiltration of liquid starts with the largest nanopores. As the pressure increases, the liquid infiltrates into smaller nanopores. If the pressure is lowered, the unloading slope is about the same as that in the low-pressure section of the loading path, and thus only a small portion of the compressed system volume is recovered. Clearly, the confined liquid does not defiltrate. That is, the repelling effect of the high-pressure gas phase is not detectable, likely due to the continuous energy and mass exchanges between the confined liquid and gas phases. As the pressure is increased again, the second loading cycle nearly overlaps with the unloading part, and at about the same pressure at which the first unloading is performed, the infiltration resumes. The slope of infiltration plateau at the second loading is close to that of the linear sections of loading path. Eventually, when the pressure reaches 48 MPa, most of the nanoporous space is occupied and the infiltration plateau ends. When the load is reduced, the unloading path is parallel to the sections of the loading path outside the infiltration plateau and the first unloading path, suggesting that no defiltration takes place.

The loading path of the MCM-41 modified by C₁ groups is of similar characteristics (Fig. 2). In low-pressure and high-pressure sections, the slope of infiltration curve reflects the compressibility of bulk liquid and the compliance of testing machine. In the pressure range of 40–50 MPa, an infiltration plateau exists. Upon unloading, when the pressure is higher than 30 MPa, the unloading path is quite regular, with the slope close to that of the linear sections of loading path. When the pressure is lower than 30 MPa, the slope considerably decreases. With the same pressure variation, the rate of system expansion becomes much larger, which should be attributed to the defiltration of confined liquid. When all the confined liquid is released back to the bulk phase, at the pressure of 18 MPa, the unloading path becomes linear again, overlapping with the loading part. The widths of infiltration and defiltration plateaus are the same, as they should be, because the volume of nanopores does not vary. When the external pressure is removed, the system returns to its initial configuration. When loading-unloading cycles are applied again, similar liquid intrusion curves can be obtained repeatedly.

The surface reactions of C₁ and C₈ groups are similar. By reacting with a hydroxyl site, with the by-product of HCl, a carbon chain is attached to the surface. The bond strengths and the end/side groups of C₁ and C₈ chains are the same, causing similar degrees of hydrophobicity. The major difference is the chain length. The length of a C₁ group, OSi(CH₃)₃, is only about 0.3 nm, while the length of a C₈ group, OSi(CH₃)₂(CH₂)₇CH₃, is much longer (~1.1 nm). Thus, the effective nanopore size of the MCM-41 modified by C₁ groups is nearly 2 nm, and that of the MCM-41 modified by C₈ groups is around 0.5 nm. In a relatively large nanopore, the confined liquid is more similar to a continuum fluid. Along the radius direction, the liquid molecules form a few layers. While the interface layer can be quite immobile, the solid-liquid interaction at inner layers can be relatively weak. Consequently, as the external pressure is decreased, the excess solid-liquid interfacial tension would provide a sufficient driving force of defiltration for the liquid molecules in the interior. Once the molecular density in the central part of the nanopore is lowered, the molecules in the interface layer can diffuse either along the surface or along the radius direction, resulting in the eventual complete defiltration. That is, the interface liquid molecules form a "lubricating" layer between the solid surface and the far field. In a relatively small nanopore, as depicted in Fig. 3, there may be only a small number of liquid molecules in a cross section. Under this condition, all the confined liquid is exposed to the solid surface. Even if the solid is hydrophobic, to move out of a nanopore, a liquid molecule must overcome the energy barrier among tetrahedral sites. In between adjacent surface groups, liquid molecules are at a metastable state. If thermal motion is insufficient to raise the system’s free energy so that the confined liquid becomes mobile, it cannot be released from the nanopores even though the potential outside the nanopores is lower. This phenomenon is in agreement with...
the prediction of a molecular dynamics simulation that, in a relatively small structureless nanopore, as the pore size decreases the liquid conductivity increases.

Note that the infiltration pressure of the C8 group modified MCM-41 is lower than that of the C1 group modified MCM-41, which conflicts with the prediction of the classic Laplace–Young equation, indicating again that the continuum theory breaks down in nanoenvironment.

IV. SUMMARY

In summary, contradictory to the previous analyses, the confined liquid can defiltrate from nanopores of MCM-41 modified by C1 groups, while it is “locked” in MCM-41 modified by C8 groups. This can be attributed to the chain-like structure of liquid molecules in small nanopores and the associated energy barrier among tetrahedral sites, suggesting that the molecular configuration of confined liquid is an indispensible factor that must be taken into account for studies of unloading behaviors.

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