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Energy Absorption Behaviors of Nanoporous Materials
Functionalized (NMF) Liquids

A Dissertation submitted in partial satisfaction of the
Requirements for the degree of Doctor of Philosophy

in

Materials Science and Engineering

by

Tae Wan Kim

Committee in charge:

Professor Yu Qiao, Chair
Professor Sungho Jin
Professor Yuhwa Lo
Professor Vlado Lubarda
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2011

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Chair

University of California, San Diego

2011

To my wife, Mirim Ha
and my son, Jaeshin Kim

Never underestimate your power to change yourself;

Never overestimate your power to change others.

- H. Jackson Brown, Jr.

Dream as if you'll live forever;

Live as if you'll die today

- James Dean

If you can dream it,

You can do it

- Walt Disney

Winners never quit and quitters never win

- Vince Lombardi

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Chapter 4, in part, is a reprint of the material as it appears in Electrically controlled hydrophobicity in a surface modified nanoporous carbon. Kim, Taewan; Lu, Weiyi; Lim, Hyuck; Han, Aijie; Qiao, Yu, *Applied Physics Letters*, vol 98, 053106, pp 1-3, 2011. The dissertation/thesis author was the primary investigator and author of this paper.

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ABSTRACT OF THE DISSERTATION

Energy Absorption Behaviors of Nanoporous Materials
Functionalized (NMF) Liquids

by

Tae Wan Kim

Doctor of Philosophy in Materials Science and Engineering

University of California, San Diego, 2011

Professor Yu Qiao, Chair

For many decades, people have been actively investigating high-performance energy absorption materials, so as to develop lightweight and small-sized protective and damping devices, such as blast mitigation helmets, vehicle armors, etc. Recently, the high energy absorption efficiency of nanoporous materials functionalized (NMF) liquids has drawn considerable attention. A NMF liquid is usually a liquid suspension of nanoporous particles with large nanopore surface areas ($100 - 2,000 \text{ m}^2/\text{g}$). The inner surfaces of nanopores must be non-wettable to the liquid phase.

The liquid can enter the nanopores only when a sufficiently high external

pressure is applied. During the pressure induced infiltration, mechanical work is converted to solid-liquid interfacial energy. At the equilibrium state, $E = \Delta\gamma \cdot A$, where $\Delta\gamma = rP_{in}/2$, $\Delta\gamma$ is the effective solid-liquid interfacial tension, A is the nanopore surface area, r is the effective pore radius, and P_{in} is the infiltration pressure.

In order to understand the energy absorption behaviors of NMF liquid, we investigate nanofluidic behaviors in hydrophobic nanoenvironments, which is different from continuum fluids in terms of structures, length scale, time scale geometry surface properties, electrolyte, effective flow rate, profile, etc.

The current research on NMF liquids is focused on 1) the anion effects on the ion transport pressure, 2) the inner surface group length effects, 3) electrically responsive energy absorption behaviors, 4) the relation between the functional surface group density and the energy absorption behaviors, 5) primary particle size effects, 6) the repeatability of the energy absorption behaviors, and 7) simple, cost-efficient synthetic methods of a nanoporous silica.

1 INTRODUCTION

1.1 Background of Nanoporous Materials

Nanoporous materials are of great interest for various applications, ranging from catalysis, adsorption, sensing, and separation, owing to their high surface areas, tunable pore sizes, adjustable frameworks, and surface properties.

1.1.1 General Definition

A porous material is a solid that has pores throughout its body. The pores show a translational repetition in three dimensional ways, while regularity is not required. One way to think about a porous material is to consider it as a material with gas-solid interfaces as the most distinguishable characteristic, which indicates classical colloid and interface science, i.e. the creation of interfaces due to nucleation phenomena, which can be applicable to the nucleation of pores, decreasing interface, and the stabilization of interfaces, is of fundamental importance to the formation of porous materials[1].

Many porous materials are metastable. The metastability is due to the rigid character of void-surrounding network, which is covalently cross-linked in most cases. However, it should be noticed that most of the porous materials reported in the literature may not be stable by thermodynamic means. As soon as the activation energy barrier is overcome, a porous material starts to break down to the most thermodynamically stable state. For porous silica, for instance, as the temperature is raised and the melting point is approached, primary particles in the network begin to fuse and the associated phase separation would result in a nonporous silica phase.

Control over interface energy and metastabilization of nanodimensional holes

are of particular importance as nanoporous structured materials are synthesized. The range of pore size from 0.6 nm to 1,000 nm can be regarded as nanoporous someone.

Additionally, when the pores happen to be filled with guest phases, these materials may still be referred to as porous as long as it is possible to remove the phases[2].

1.1.2 Classification

1.1.2.1 IUPAC Definition

According to the International Union of Pure and Applied Chemistry (IUPAC) definition, nano- porous materials are classified into three groups[3, 4], : microporous materials (pore size < 2 nm), mesoporous materials (pore size : $2 - 50$ nm) and macroporous materials (pore size > 50 nm).

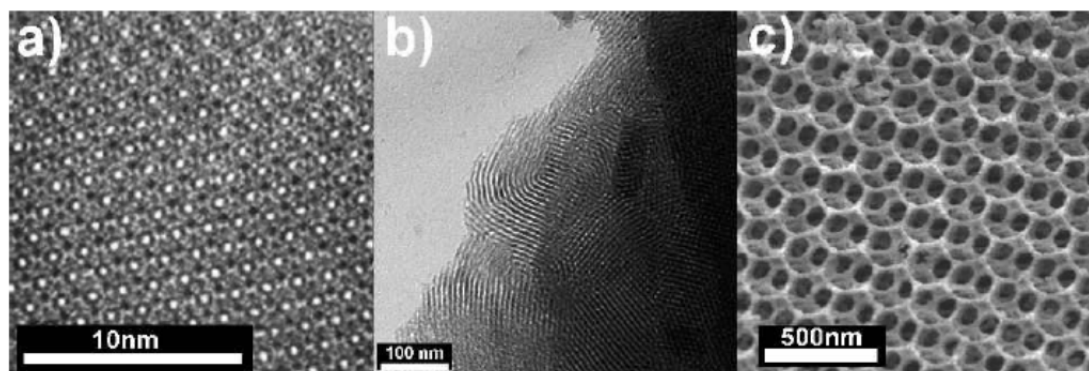


Figure 1-1 : Three different types of nanoporous silica materials; (a) A microporous material, (b) A mesoporous material, (c) A macroporous material[2].

A comparison of these different pore system is given in Figure 1-1, However, where ordered pore systems are shown. Microporous, mesoporous, or macroporous materials might have random systems of pores[2, 5-8]. In many cases, a material has more than one pore system. For instance, many microporous materials have many additional

meso- or macroporosity caused by random grain packing; many mesoporous materials have an additional macroporosity related to random grain packing, or an additional microporosity in the continuous network; and a number of macroporous materials can have additional meso- and microporosity[2].

Many microporous materials have many additional meso- or macroporosity caused by random grain packing; many mesoporous materials have an additional macroporosity related to random grain packing, or an additional microporosity in the continuous network; and a number of macroporous materials can have additional meso- and microporosity[2].

1.1.2.2 Network Materials

Network materials have a function to host pores and can be divide into two categories according to their compositions; (1) inorganic materials and (2) organic materials. Inorganic materials usually have higher structural and thermal stability and stiffness. They can be classified to :

- a. Inorganic oxide-type materials, e.g. porous silica, porous titania, and porous zirconia.
- b. Nanoporous carbon materials, activate carbons and carbon nanotubes.
- c. Binary compounds such as sulfides, nitrides, phosphate,...,etc, among which AlPO_4 is probably one of the well known ones
- d. Single element materials such as nanoporous silicon with luminescent properties[9].

There are a few examples of nanoporous organic materials, such as

polymers[10], which are prepared by various templating methods.

1.1.3 Gas Adsorption Analysis

Gas sorption analysis is a well applied to decide and classify porous materials according to their pore size distributions, surface areas, and pore volumes[3, 4, 11, 12].

In a typical sorption experiment, the adsorption amount of gas such as nitrogen, krypton, and carbon dioxide is measured as a function of relative pressures p/p_0 (<1) at a constant temperature, where p and p_0 are the equilibrium vapor pressures of the condensate liquid in the pores and the bulk liquid, respectively. The interaction between the pore walls and the adsorbate is based on physisorption by Van Der Waals Interaction and leads to the formation of adsorbate layers at low p/p_0 . The macroscopic laws of classical thermodynamics predict that the confinement effect of pores with radii on the nanometer scale results in gas condensation inside the pores at p smaller than p_0 .

In a gas adsorption analysis, the adsorbed volume is plotted in respect with p/p_0 , and this called “*sorption isotherm*”. At a low p/p_0 , gas adsorption in micropores takes place first through a process of volume filling rather than capillary condensation[11, 13]. The profile of the isotherm is distinguished by different pore sizes, based on the classification by IUPAC. The isotherms of microporous materials are characterized by a steep increase of the isotherm at low p/p_0 , ending up in a plateau at the increased p/p_0 domain. In a mesoporous material, with the increasing p/p_0 , a liquid-like adsorbate film of proportionate thickness $t(p/p_0)$ is formed on the pore walls. At a certain p/p_0 , capillary condensation takes place, filling the mesopores with liquid, which is reflected in the isotherm as a rapid increase in the adsorbed amount. A comparison of sorption

isotherm with different pore sizes is shown in Figure 1-2.

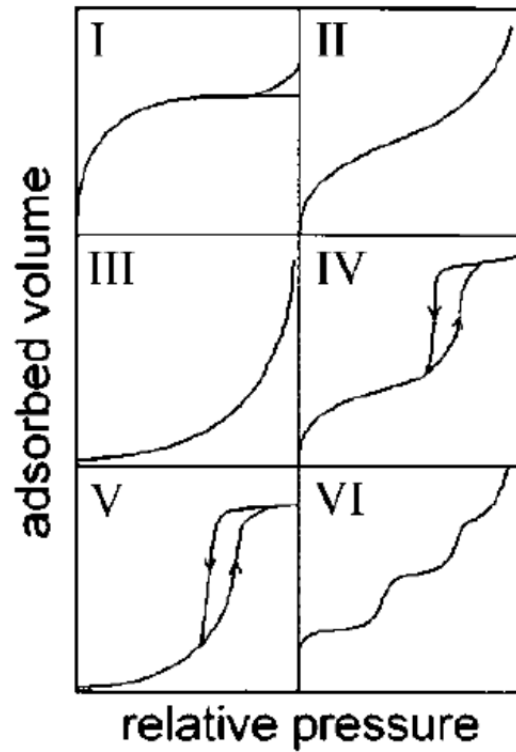


Figure 1-2 : Sorption isotherms of microporous materials (I), mesoporous materials (V), and macroporous materials (III, IV)[2].

The correlation between the vapor pressure and the pore size is given by the Kelvin equation[2] :

$$\ln(p/p_0) = \frac{2\gamma V_L}{RT r_m}$$

where r_m = the mean radius of pores, $\gamma \cong$ the surface tension, $V_L \cong$ the molecular volume of the condensate.

That is, the isotherm of a microporous material show a steep increase at very low pressure and reach a flat plateau rapidly. The isotherm of a mesoporous material

is characterized by a capillary condensation step and a hysteresis, which might be induced by the force between molecules in the adsorbate layer. The isotherm of a macroporous material show a single or multiple adsorption steps near the pressure of the standard bulk condensed state, with the close to one.

The total pore volume (the porosity), is given by the cumulative uptake of adsorbate. Based on the classical interpretation of Cohan and Kelvin equation[14], the condensation of a liquid in a nano- porous material at a certain p/p_0 can be related to the corresponding mesopore size, thus also providing the information of a pore size distribution (PSD). Since the condensation starts at a specific relative pressure p/p_0 , where the walls are covered by a film of thickness $t(p/p_0)$ (t : thickness of the adsorbate film), in the modified Kelvin equation, $2/r_m$ is replaced by $f/(r - t(p/p_0))$, where r is the actual mesopore radius and f is the meniscus shape factor, which is 1 or 2 for the filling or emptying of the mesopore, respectively. This procedure represents the basis of the well-known “Barrett-Joyner-Halenda (BJH)” method, currently the most frequently used method to determine PSDs[15]. Moreover, the pore geometry significantly affects thermodynamic properties of confined fluids and their adsorption behavior[16, 17]. The confinement is stronger in spherical pores compared with cylindrical pores of the same diameter, which shift the capillary condensation to lower p/p_0 .

Another approach to calculate pore volumes and mesopores sizes is based on the Gurvich approach[13], in which the adsorbed volume $V_{0.4}$ at $p/p_0 \approx 0.4$ is used to determine the pore diameter by $D = 4V_{0.4}/S_{BET}$, where S_{BET} is the specific surface area obtained from the method developed by Brunauer, Emmet, and Teller (BET)[18]. The BET method is based on the assumption that multilayer formation takes place prior to

capillary condensation and that equilibrium states are reached at different rate constants for adsorption and desorption for the mono and multiple layers. The adsorbed amount n_a , p/p_0 , and the monolayer capacity n_m related to the BET equation, from which the specific surface area S_{BET} is calculated as $S_{\text{BET}} = n_m a_m N_A$, where a_m is the area of an adsorbate molecule and N_A is the Avogadro's number.

1.1.4 Synthesis of Nanoporous Materials

1.1.4.1 Templating Methods

Templating methods are one of the most successful ways to synthesize nanoporous materials[2], shown schematically in Figure 1-3.

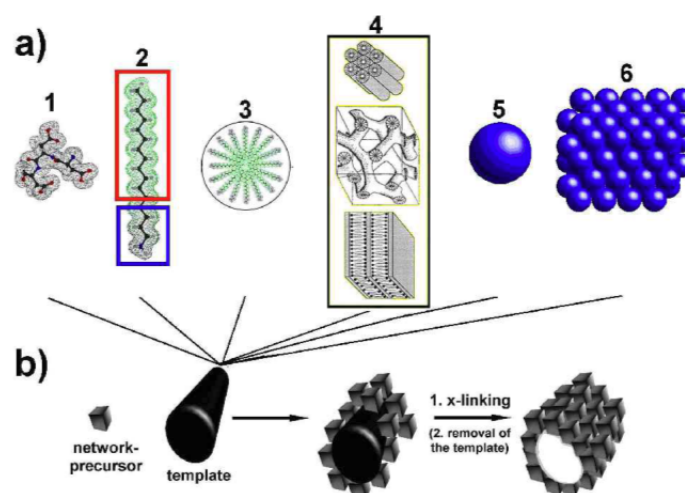


Figure 1-3 : Schematic illustration of the approach to obtain nanoporous materials by templating methods. (a) A range of applicable templates beginning with single molecules (1) or amphiphiles (2) assemblies of amphiphiles as micelles (3) or lyotropic phases (4) or polymeric spheres (5) or assemblies of spheres (6). These units are surrounded or bonded to the network precursor systems in the actual templating step (b). The created pore resembles the size, shape, and even functional characteristics of the template in an ideal case. Finally, the template is removed [2].

An organic (or sometimes inorganic) compound acts as a template, place holder which later becomes the void space, pores in nanoporous materials. The templating

methods can allow the control of not only pore size but also pore shape. At first, a target template structure must be provided (Figure 1-3a) and the template structure must be compatible with solvents involved in the bond formation process between network materials and template. The creation of porous materials always involve the formation of high surface areas with high interface energy, and the thermodynamic optimization of surface energy is required to prevent the porous materials from rearranging into more stable nonporous phases.

The template structure can have various sizes length scales. The smallest pores such as micropores can be obtained by their molecular templates (Figure 1-3a, (1)). The created pores have the shape and size similar to the template molecules. The mesopores whose pore size is the range between 2 nm and 50 nm can be obtained by the assemblies of template molecules. The assemblies of amphiphiles (Figure 1-3a, (3)) are often used because of their self-organizing properties and their capability for lowering interface energy. An amphiphilic molecule (Figure 1-3a, (2)) typically has one hydrophilic and one hydrophobic part, which has a tendency to lead to microphase separation[1]. The resulting template structures are micelles or ultimately of lyotropic phases with different symmetries such as lamellar, hexagonal, or gyroid, as depicted in Figure 1-3a, (3). The macropores whose pore size is above 50 nm can be obtained by various polymer/metal oxide spheres such as latex spheres, silica spheres or their assemblies or colloidal crystals (Figure 1-3a, (6)).

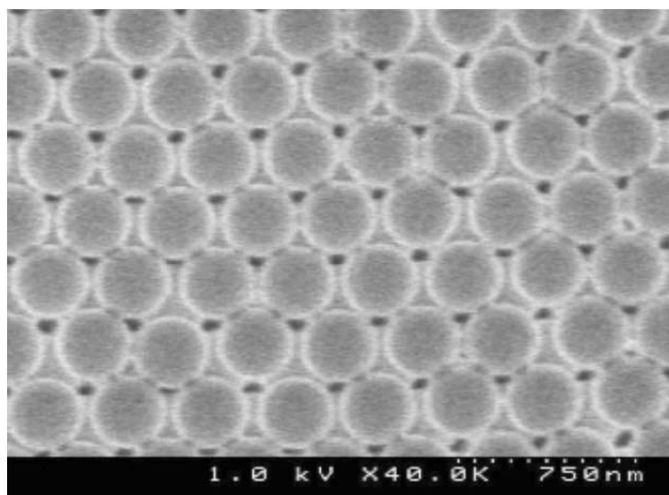


Figure 1-4 : SEM image of a macroporous material formed by a colloidal crystal of latex sphere[2].

Figure 1-4 Shows a colloidal crystal formed by negatively charged 280 nm latex spheres. As can be seen from this SEM image, the dense packing of 280 nm spheres can create regular voids with the size range around 70 nm.

1.1.4.2 Nanocasting Methods

The nanocasting pathways use hard templates to create ordered replicas, provide promising routes for the preparation of meso-structured materials with novel framework compositions[19]. When a hard template is used, the synthesis corresponds to a direct casting mechanism, where a relatively precise negative replica of the template is created[20]. The nanocasting pathway involves three main steps: i) the formation of the template; ii) the casting with target precursors, and iii) the removal of the template, as shown in Figure 1-5 Inorganic, ordered porous solids are often used as the nanoscale hard template in the first step. For instance, zeolite, alumina membranes, ordered mesoporous silica, ordered mesoporous carbon, or for somewhat larger

structure sizes, the assembly structure of colloidal spheres have been employed.

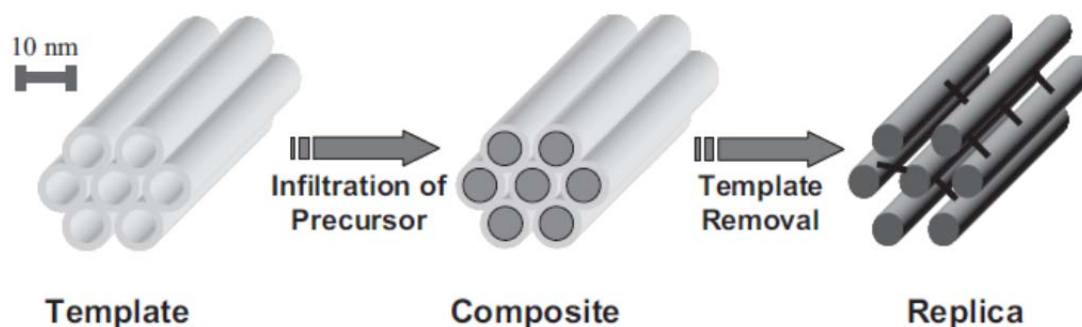


Figure 1-5 : Schematic illustration of the nanocasting pathway[21].

The pore structures of these parent materials can be translated to the solid structure of the generated porous materials, while the walls of the parent become the voids of the replica. In order to control the morphology and structural parameters of the replicas, templates with a controllable morphology and structure are desirable.

One of the most versatile hard templates is ordered mesoporous silica, since it can be prepared in shapes as diverse as noodle like, spherical, fibrous, rodlike, and even with chiral morphologies. Another requirement for the template is the ability to remove it without affecting the cast. Possible removal methods include leaching, melting, or combustion. The target material is usually not incorporated in the pore system of the template, but in the form of a precursor that subsequently has to be converted to the final material. The precursor needs to meet several requirements: As it enters the template structure, it must either be gaseous, highly soluble, or liquid at moderate conditions, so that it can be infiltrated into the voids of the template. Conversion to the desired composition should be simple and with as little volume

shrinkage as possible. Finally, it should not chemically react with the hard template. In addition, the templates should be easily and completely removed by chemical (leaching, combustion) or physical (thermal treatment) methods.

For example, monolithic mesoporous carbon with a bicontinuous cubic structure (*Ia3d* symmetry) was prepared by using mesoporous silica monoliths as the hard template[22]. This monolithic carbon shows a uniform pore size of 4.6

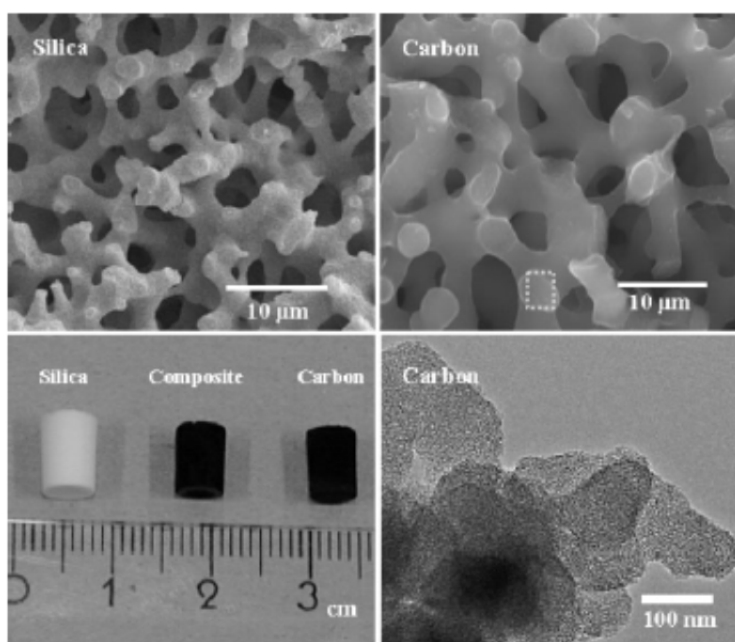


Figure 1-6 : SEM images (upper), Photograph (lower, left) and TEM image (lower, right) of silica and Carbon Monolithic[21].

nm, a surface area of 1,530 m²/g, and was described as a promising electrode for electrochemical double-layer capacitors. The difficulty in preparing such carbon monoliths is replated to the preparation of the noncracked silica monoliths templates. Owing to the stresses involved in the preparation, cracking of the structures can occur at different stages.

The most sensitive ones are the drying stage, due to capillary forces, and the

calcination stage, due to the temperature-induced stress and/or pressure inside the monoliths during the decomposition and combustion of the organic materials. Thus, the preparation of monolithic mesoporous carbon with an ordered mesostructure is still a great challenge. Inspired by the synthetic method proposed by Nakanishi[23], silica monoliths with a hierarchical structure containing macropores and mesopores can be prepared by adding poly(ethylene glycol) and/or hexadecyltrimethylammonium bromide as a porogen[24]. Regardless of the loading with the carbon precursor, the obtained carbon monolith is a positive replica of the silica monolith on the nanometer scale, and a negative replica on the nanometer scale, as shown in Figure 1-6. Combined volume and surface templating, together with the controlled synthesis of the starting silica monoliths used as the scaffold, provides a flexible means of pore-size control on several length scales simultaneously[25].

The synthesis of ordered macroporous colloidal crystals via the replication of ordered array structures of polystyrene or silica lattices has received much attention in physics, chemistry, and materials science. Such synthesis can also be considered and generalized as nanocasting processes. As seen from Figure 1-7, colloidal crystals are first formed by packing uniform spheres into 3D or 2D arrays. Then the interstitial space of the colloid crystals is filled with liquid precursor that is subsequently converted into a solid skeleton. Periodic porous solids with various compositions, including silicates and organosilicates, metal oxides, metals, metal chalcogenides, and carbon allotropes, have been prepared by nanocasting from colloidal crystals. The resulting materials could be interesting for various applications[26, 27].

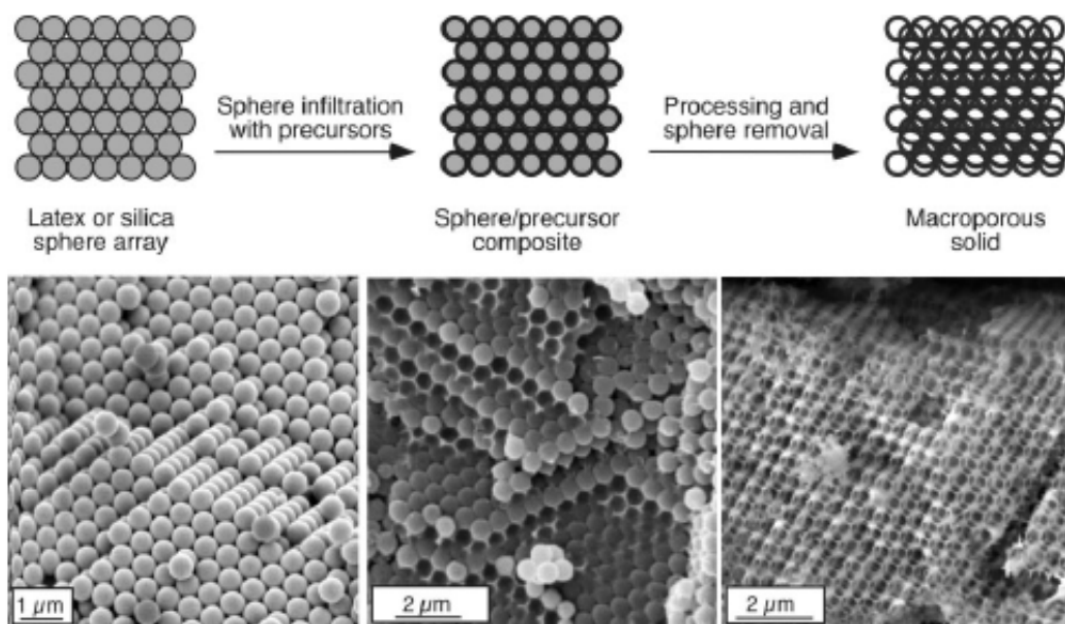


Figure 1-7 : General synthetic scheme for ordered macroporous solids and the corresponding SEM images for a polystyrene/silica system prepared with tetraethylorthosilicate[21].

1.2 Nanoporous Materials Functionalized (NMF) Liquids

For many decades, people have been actively investigating high-performance energy absorption materials, so as to develop lightweight and small-sized protective and damping devices, such as blast mitigation helmets, vehicle armors, car bumpers, etc. Recently, the high absorption efficiency of nanoporous materials functionalized (NMF) liquids has drawn considerable attention. In this section, nanoporous materials functionalized (NMF) liquids will be reviewed in terms of their energy absorption behaviors.

1.2.1 Definition

A nanoporous materials functionalized (NMF) liquid is a liquid suspension of

nanoporous particles with large nanopore surface area, ranging from 100 m²/g to 2,000 m²/g (Figure 1-8).



Figure 1-8 : The shape of NMF liquid

The Inner pore surfaces should be hydrophobic, i.e. the liquid phase must be non-wetting under ambient condition. A NMF liquid has a high energy absorption efficiency, $E = 5 \text{ J/g} \sim 100 \text{ J/g}$, much higher than that of many conventional protection materials such as composites, shape memory alloy, expanded polypropylene (EPP), expanded polystyrene (EPS), providing a promising way for the development of advanced protection devices and energy storage devices[28, 29] (Figure 1-9).

The NMF liquid in Figure 1-9 is a dispersive suspension in saturate sodium chloride solution of MCM-41(Mobile crystalline material) silica particles whose inner surface is modified with dimethyloctylsilyl group. Energy absorption behaviors of NMF liquids are controllable by using suitable nanoporous materials of optimized pore sizes, pore surface areas, pore surface wettability and various liquid phases. The

Pressure-volume curves in Figure 1-9 show the energy absorption performance.

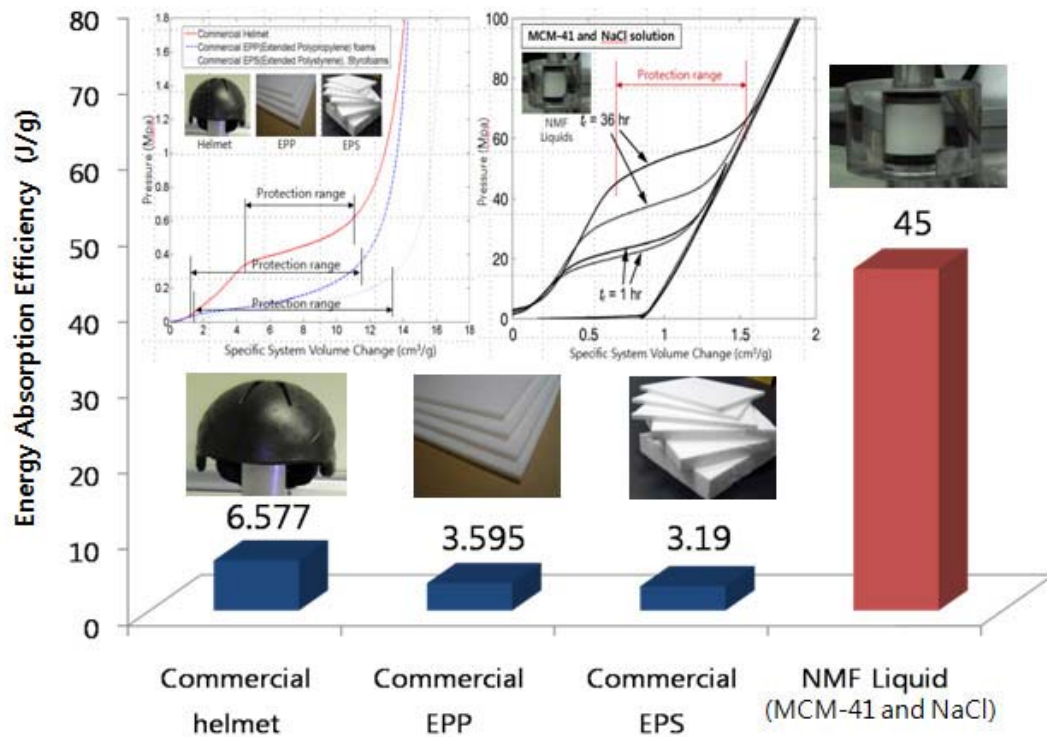


Figure 1-9 : A comparison of energy absorption efficiency in conventional protective materials and NMF Liquid

1.2.2 Energy Absorption Mechanism

An NMF liquid consists of nanoporous particles immersed in a liquid phase. The nanopore surfaces must be non-wettable to the hydrophilic liquid phase. In order to do it, the inner surface of nanopore should be kept hydrophobic.

When nanoporous particles is immersed in water under atmosphere pressure, the nanopores remain empty due to capillary effect and repulsion between the surface of nanopores and the liquid phase. Figure 1-10 is shown the illustration of nanopore in NMF liquid.

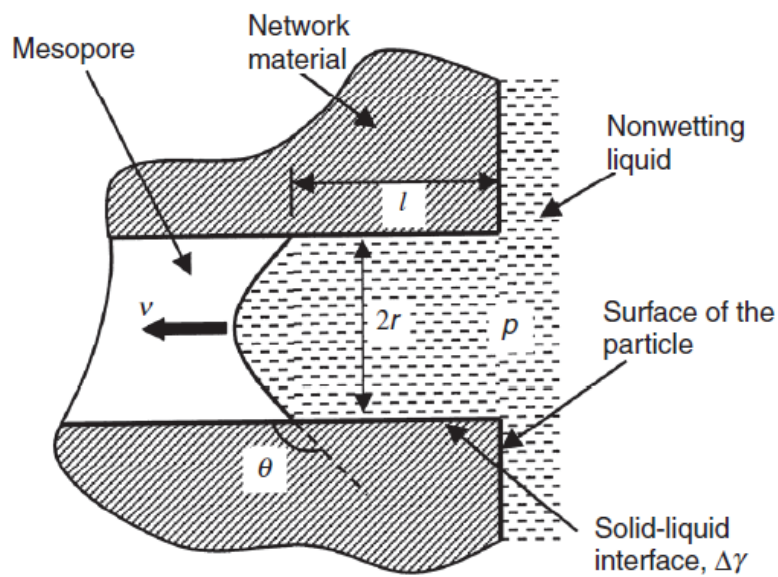


Figure 1-10 : A illustration of nanopore in NMF liquid[30]

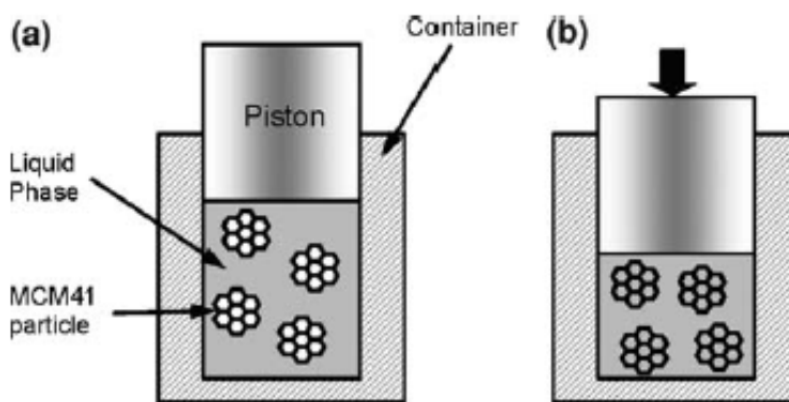


Figure 1-11 : NMF liquid behaviors; (a) prior to and (b) after the pressure-induced infiltration[31].

As an external pressure is applied, the system free energy in liquid phase would be rapidly increased and when the pressure reaches the critical value, the capillary effect can be overcome and liquid molecules can enter the nanopores. This critical pressure is called the infiltration pressure. Figure 1-11 shows the NMF liquid

behaviors; 1) below the infiltration pressure, 2) after the pressure-induced infiltration takes place[31]. During the pressure induced infiltration, mechanical work is converted to solid-liquid interfacial energy.

At the equilibrium state, the system free energy is given as $E = \Delta\gamma_{sol-liq} \cdot A$, where $\gamma_{sol-liq} = rP_{in}/2$, $\gamma_{sol-liq}$ = the interfacial tension, A is the nanopore surface area, r is the pore radius, and P_{in} is the infiltration pressure. In a number of NMF liquid systems, the confined liquid molecules would remain in the nanoenvironment when the external pressure is reduced, so hysteretic behaviors are observed during compression-decompression on the NMF liquids.

1.2.3 Energy Absorption Behaviors of NMF Liquids

Figure 1-12 shows the Quasi-Static behavior of a NMF liquid in which the hydrophobic mesoporous materials were dispersed in pure water and then sealed in a hydraulic device. The mesoporous materials in this system was Fluka 100 C₈ reversed phase mesoporous silica particles with an end-capped structure. The particle size was in the range of 15 – 35 μm , and the average pore size was 7.8 nm, with a standard deviation of 2.4 nm. The specific area was 287 m^2/g and The specific pore volume was 0.55 cm^3/g The surface coverage of carbon ranged from 10-12%.

The loading - unloading cycles were repeated until the P - ΔV curve reached the steady state, where the specific volume change ΔV is defined as the ratio of the volume change to the weight of the mesoporous silica particles. During loading, as the pressure increases, initially the system volume decreases nearly linearly (section OA at the 1st loading). In other words, the initial pressure is too low for water molecules to overcome the repulsion effect between the nanopore wall and the water molecules, so

the linear compression behavior of pure water and empty mesoporous silica particles is dominant. When the pressure (P) reaches the critical value (P_{in}), the repulsion effect between the surface of nanopores and water molecules is overcome and the water molecules can enter the nanopores until the pores are filled. That is, the pressure induced infiltration begins (section AB in the 1st cycle) and as a result the slope of the P - ΔV curve decreases considerably, forming a plateau region.

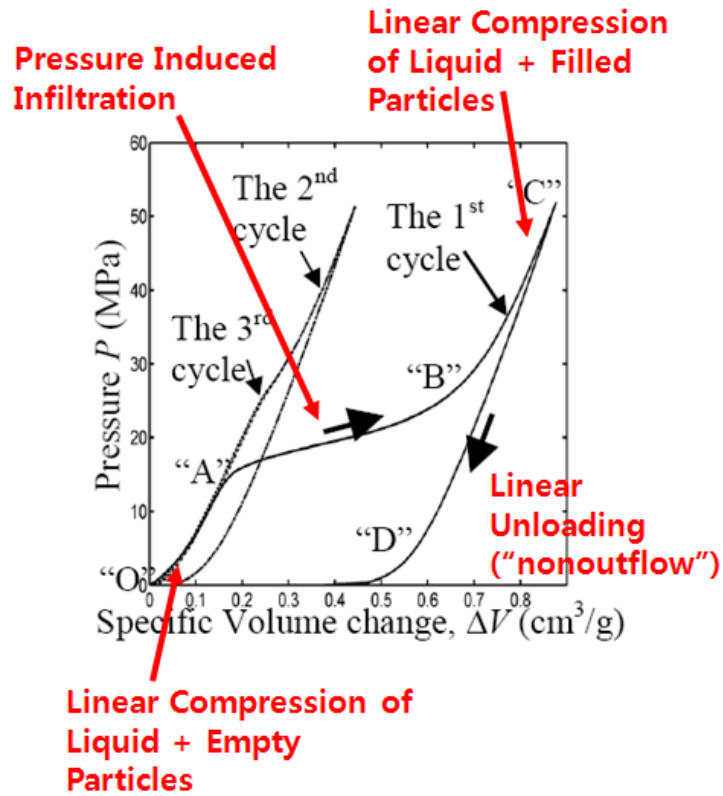


Figure 1-12 : Quasi-Static behaviors of NMF Liquid (hydrophobic mesoporous silica particles in pure water)[32].

In the 1st cycle, the infiltration pressure (P_{in}) is taken as the pressure at the middle point of the plateau region, where the effective pore volume of mesoporous silica particles is reduced. The specific volume change associated with the plateau is around 0.5 cm³/g, close to the specific pore volume of mesoporous silica particles.

When the pressure (P) is higher than the infiltration Pressure (P_{in}), as the pressure increases, the system volume decreases (section BC in the 1st loading cycle). To say that again, the linear compressible behavior of the filled mesoporous silica particles and water molecules is shown, because mesoporous silica particles have little pore volume to occupy water molecules. During unloading (section CD in the 1st cycle), the pressure decreases rapidly as the crosshead is moved back. We define the “outflow” pressure (= Defiltration Pressure), P_{out} ($=P_{de}$), somewhat arbitrarily as the pressure in the unloading section of the 1st cycle at which the slope decreases by 50%.

When P is higher than P_{out} , P - ΔV curve is quite linear, indicating that the outflow of the liquid in the nanopores is difficult. When P is lower than P_{out} , the slope of the P - ΔV curve is lowered; that is, the confined liquid starts to come out. However, until the pressure is reduced back to the atmosphere pressure, the compressed system volume isn't fully recovered, indicating that the defiltration of confined water molecules in nanopores is hard. In other words, there is still a significant portion of liquid confined in the nanoenvironment.

In the 2nd cycle and the 3rd cycle, initially as the pressure increases, the system is compressed with the bulk modulus quite close to that in the 1st cycle curve. The system seems slightly stiffer, probably due to the residual water molecules in the nanopores. The critical Pressure at which the pressure-induced infiltration takes place, however, is much higher than that in the 1st cycle curve and there is no infiltration plateau at P_{in} in the 1st cycle.

Another significant difference is that the specific volume change in the plateau is smaller than that in the 1st cycle, since the residual water molecules occupies most of

the porous space prior to the onset of the 2nd infiltration. In the 3rd cycle, there is no significant further change in P - ΔV curve comparing to the 2nd cycle.

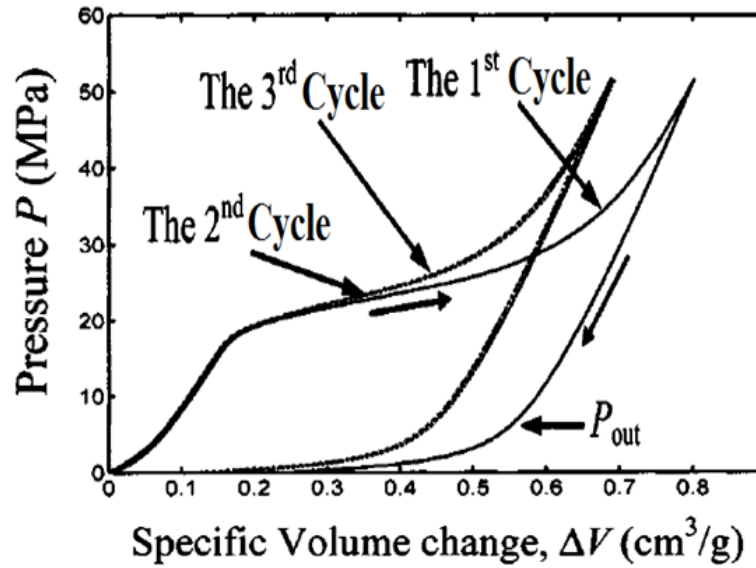


Figure 1-13 : Quasi-Static behaviors of NMF Liquid (hydrophobic mesoporous silica particles in 23.1 wt % NaCl solution)[32]

It is clear that the energy absorption behaviors of this NMF liquid particular consist of two parts: The reversible part is probably related to the liquid molecules in larger pores that can come out once the applied pressure is released; The irreversible part that remains in the nanopores even when the pressure is reduced to 0.

Figure 1-13 Shows energy absorption behaviors in Quasi-Static loading system when 23.1 wt% NaCl solution was used. When the 23.1 wt% NaCl solution was used as a liquid phase, P_{in} in the 1st cycle increases upto 26 MPa (in the pure water system, P_{in} is 21 MPa) and P_{out} also increases from 2.5 MPa (in pure water system) to 5.0 MPa.

Increased P_{in} is due to the increase of the repulsion effect between the surface of nanopores and liquid molecules.

2 ANION EFFECTS

2.1 Introduction

2.1.1 Background

As an electrolyte dissolves in a bulk water phase, cations and anions are separated by water molecules. Each solvated ion is usually surrounded by a number of water molecules[33]. The coordinate number is dependent on the ion size, ion charge, molar concentration, temperature, etc. As the electrolyte solution flows in a large channel, the ion behavior is quite homogeneous, which can be well described by the classic fluid mechanics[33]. At the solid-liquid interface, the ions in the inner layer, the Gouy–Chapman layer, are relatively immobile, and the ions in the outer layer, the Stern layer, are relatively mobile[34]. The net ion motion along the axial direction can lead to a stream current effect[35], which has been detected in nanochannels as small as 10–50 nm[36, 37].

As the channel size is smaller than a few nanometers, the continuum theory breaks down, not only because the surface to volume ratio is ultrahigh, but also because the molecular and ion configurations can be directly confined by the nanochannel wall[38]. The interaction among the solvent/solute molecules and ions with the nanochannel wall has a number of unique characteristics. Even when the nanochannel surface is nominally wettable, the nanochannel size must be much larger than the molecular/ion size, otherwise the infiltration can be difficult[39, 40].

As an ion is solvated, the size of the hydration shell surrounding it is typically in the range of a few to 10 Å. When an ion is in a nanochannel that is of the effective

diameter comparable with or smaller than this characteristic length, the solvated structure is distorted[41]. Configurations that would be energetically unfavorable in a bulk phase can be dominant, which significantly affects the system free energy[42]. Under this condition, the space may be insufficient for the layered structure that usually exists at a large surface,[43] which further changes the ion transport behaviors.

One of the fundamental questions that still remain unanswered is, in a nanochannel, what is the role of anions. At a large solid surface, the anion density in the Gouy–Chapman and the Stern layers tends to be low[44]. Therefore, the anion effect on the solid-liquid interfacial properties, such as the interfacial tension, is secondary. In a nanochannel, since anions can directly contact the solid atoms, a squeezing effect can be induced[45]. While a number of computer simulations have been conducted on ion transport behaviors[46], experimental data are still scarce.

2.1.2 Introduction to Zeolite Socony Mobil (ZSM)-5

Zeolite Socony Mobil – 5 (ZSM-5), is an aluminosilicate zeolite mineral, a member of the pentasil family of zeolites. Its chemical formula is $\text{Na}_n\text{Al}_n\text{Si}_{96-n}\text{O}_{192} \cdot 16\text{H}_2\text{O}$ ($0 < n < 27$). Patented by Mobil Oil Company in 1975, it is widely used in the petroleum industry as a heterogeneous catalyst for hydrocarbon isomerization reactions[47].

ZSM-5 is composed of several pentasil units linked together by oxygen bridges. A pentasil unit consists of eight five-membered rings. In these rings (Figure 2-1a), the vertices are Al or Si and an O atom is assumed to be bonded between the vertices (Figure 2-1c). The pentasil chains are interconnected by oxygen bridges and form corrugated sheets with 10-ring holes (Figure 2-1d). Like the pentasil units, each 10-

ring hole has Al or Si as vertices with an O bonded in between. Each corrugated sheet is connected by oxygen bridges, forming a structure with straight 10-ring channels running parallel to the corrugations and sinusoidal 10-ring channels perpendicular to the sheets (Figure 2-2)[47]. Adjacent layers are related by inversion points. The estimated pore size of a channel that is parallel with the corrugations is 5.4–5.6 Å [48].

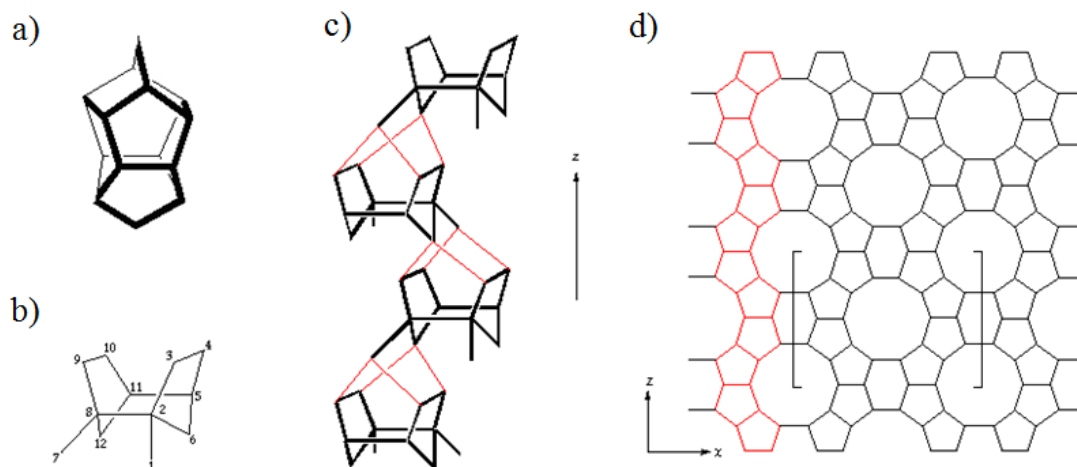


Figure 2-1 : Formation of ZSM-5 Zeolite (a) Pentasil unit b) Secondary building unit (SBU) in pentasil unit c) SBU linked chains d) Layer formed from linked chain)[49]

ZSM-5 catalyst was first synthesized by Argauer and Landolt in 1972[49]. It tends to be of a high silicon to aluminum ratio.

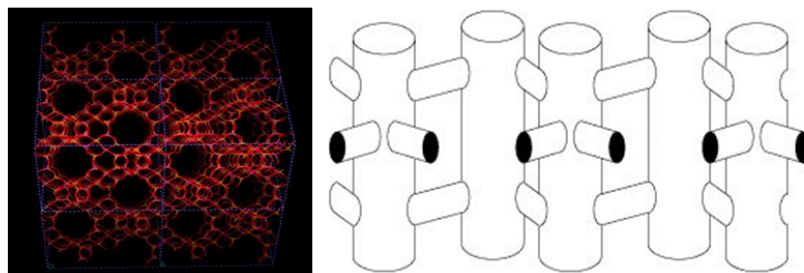


Figure 2-2 : Pore structure of ZSM-5[2]

2.2 Experimental

2.2.1 Chemicals

ZSM-5 Zeolite (CBV 8014; average pore size : 0.6 nm; Particle size : 10 – 50 μm) was obtained from Zeolyst international Co (Conshohocken, PA). Silicon tetrachloride (SiCl_4), Sodium chloride (NaCl), Sodium sulfate (Na_2SO_4), Sodium acetate ($\text{CH}_3\text{CO}_2\text{Na}$), Sodium phosphate (Na_3PO_4), Aceton were obtained from Sigma-Aldrich Chemical Co. (St. Louis, MO)

2.2.2 Materials Preparation

2.2.2.1 The treatment of ZSM-5

The treatment of ZSM-5 follows the following steps :

- a. About 2 g of ZSM-5 was dried in vacuum oven at 120 °C for 6 h.
- b. The dehydrated ZSM-5 immediately was placed in a tube furnace.
- c. Silicon tetrachloride vapor flew through the materials at 400 °C for 2.5 h.
- d. After furnace cooling, ZSM-5 was rinsed in acetone and warm water repeatedly.
- e. The material was transferred to a quartz tube furnace and exposed to an air flow with saturated water steam at 140 °C for 8 h. The steam flow rate was maintained at 25 ml/min.
- f. After air cooling, the material was calcined in air at 550 °C for 2 h.

2.2.2.2 Electrolytes with 0.5 M sodium concentration

Electrolytes with 0.5 M sodium ion concentration were prepared following these

Steps :

- a. Add sodium salt into 100 mL Volumetric flask.
- b. Distilled water was added into the volumetric flask until the 100 mL.
- c. The solution was stirred vigorously until the salt was fully dissolved.

Table 2-1 : Electrolytes composition with 0.5 M sodium ion concentration

Sodium Salt	Chemical Formula	Molecular Weight	Amount (g)	Concentration (M, Na ⁺ Salt)	Concentration (M, electrolyte)
Sodium Chloride	NaCl	58.44	2.922	0.5	0.5
Sodium Acetate	NaC ₂ H ₃ O ₂	82.03	4.102	0.5	0.5
Sodium Sulphate	Na ₂ SO ₄	142.04	3.551	0.5	0.25
Sodium phosphate	Na ₃ PO ₄	163.94	2.732	0.5	0.17

2.2.2.3 Electrolytes with 2 M sodium concentration

Electrolytes with 2 M sodium ion concentration were prepared following these

Steps :

- a. Add sodium salt into 100 mL Volumetric flask (Table 2-2).
- b. Distilled water was added into the volumetric flask until the 100 mL.
- c. The solution was stirred vigorously until the salt was fully dissolved.

Table 2-2 : Electrolytes composition with 2 M sodium ion concentration

Sodium Salt	Chemical Formula	Molecular Weight	Amount (g)	Concentration (M, Na ⁺ Salt)	Concentration (M, electrolyte)
Sodium Chloride	NaCl	58.44	11.688	2	2
Sodium Acetate	NaC ₂ H ₃ O ₂	82.03	16.406	2	2
Sodium Sulphate	Na ₂ SO ₄	142.04	14.204	2	1
Sodium phosphate	Na ₃ PO ₄	163.94	10.929	2	0.67

2.2.2.4 Testing cell

The testing cell was prepared by sealing 0.3 of the surface treated ZSM-5 zeolite (Figure 2-3) and 3.5 g of electrolyte solution in a hardened steel cylinder which consists of a hardened steel body and two pistons, equipped with reinforced O-rings. The cross-sectional area of the piston was 286.52 mm².

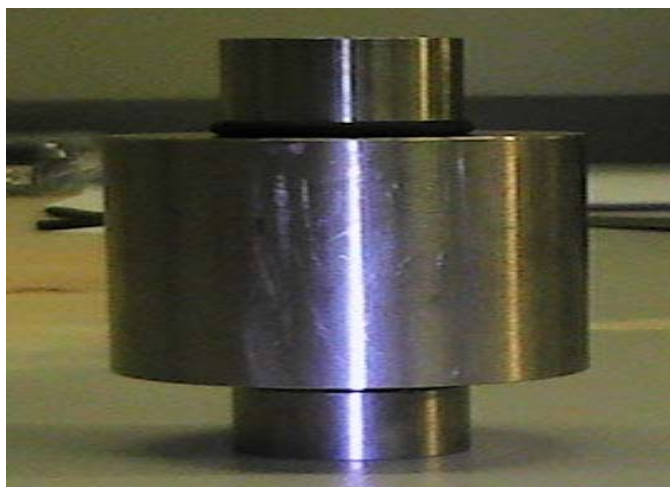


Figure 2-3 : Hardened steel testing cell

2.3 Results and Discussion

The liquid phase in the testing cell was compressed by a type-5580 Instron machine (Figure 2-4). When the piston load was sufficiently high, as will be discussed shortly, the pressure induced infiltration would take place and the infiltration plateau in sorption isotherm curve was measured. The piston was stopped once the infiltration was completed. The piston speed was kept at 1 mm/min. Reference experiments were performed by using distilled water. Typical sorption isotherm curves are shown in Figure 2-5 and Figure 2-6. The dashed line in Figure 2-5 shows the transport behavior of pressurized water molecules.



Figure 2-4 : Type 5580 Instron Machine

Because the treated ZSM-5 sample is highly hydrophobic, the nanopores remain empty when the zeolite crystals are immersed in water. As an external pressure, P , is applied on the liquid phase, the average molecular distance in the liquid phase is reduced, and, thus, the system free energy, E , increases. The increase in E is balanced

by the mechanical work done by the piston.

If the value of P is sufficiently high, the repelling effect of nanopore wall can be overcome, and water molecules start to enter the nanopores. On the one hand, because the zeolite crystals are much stiffer than the liquid phase, the nanopore wall can be regarded as rigid. Under this condition, the influence of the external pressure field inside the nanopores is negligible. Thus, when the liquid phase is confined, the work done by P is released, which can be assessed as $NP(\pi r^2 d)$, where r is the effective nanopore radius, d is the infiltration depth, and N is the number of nanopores.

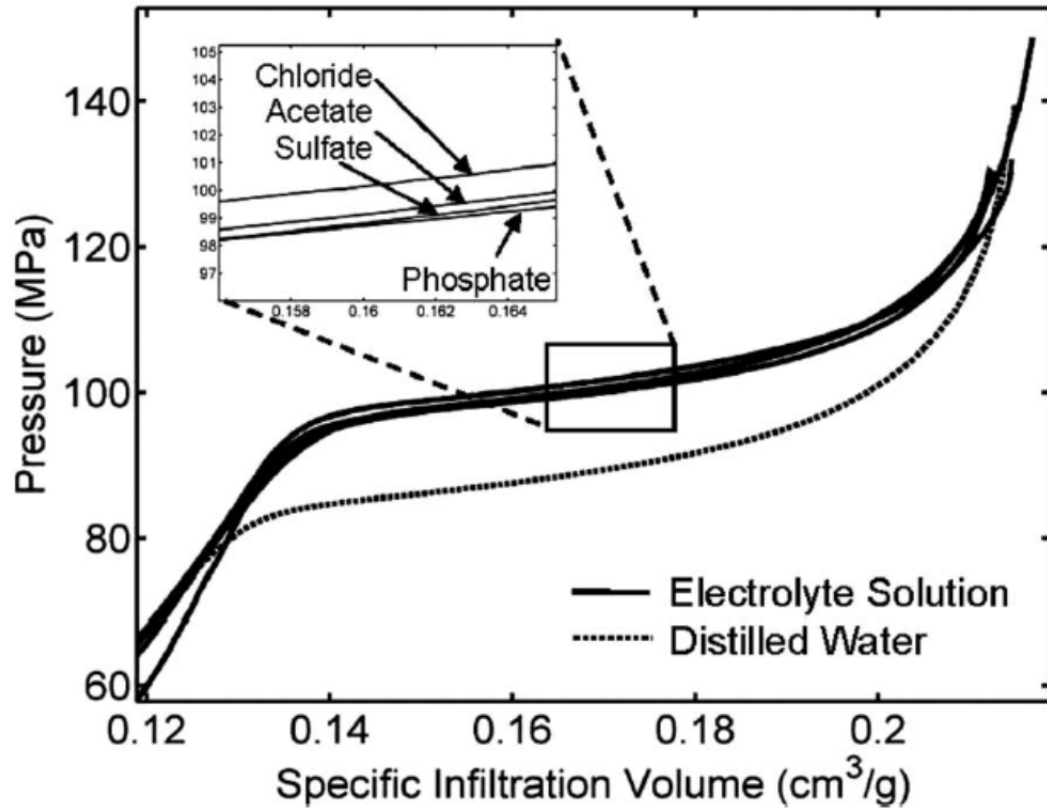


Figure 2-5 : Typical sorption isotherm curves when the cation concentration is 0.5 M

On the other hand, as the hydrophobic nanopore surface is exposed to the liquid phase, the system free energy increases by $N\gamma(2\pi r)d$, where γ is the effective solid-liquid

interfacial tension. At the equilibrium condition, $P_i = 2 \gamma / r$, with P_i indicating the critical pressure at which the ion transport starts.

When P reaches P_i , water molecules keep infiltrating into the nanoporous space with a relatively small pressure increment, and, hence, an infiltration plateau is formed in the sorption isotherm curve.

The infiltration plateau ends when the nanopores are filled. The pressure increase during the infiltration process is probably associated with the column resistance that water molecules must overcome to slide against the nanopore surface[50].

From Figure 2-5, it can be seen that for the reference system, P_i is about 81 MPa. The effective interfacial tension is $\gamma = P_i r / 2 = 12.15 \text{ mJ/m}^2$, where r is taken as 3 Å (Table 2-3).

Table 2-3 : Ion transport pressure (P_i) and effective interfacial tension (γ) when sodium ion concentration is 0.5 M

Anion	Ion transport Pressure (P_i , MPa)	Effective interfacial tension (γ , mJ/m ²)
Distilled water	81	12.15
Chloride (Cl ⁻)	99.3	14.89
Acetate (CH ₃ CO ₂ ⁻)	98.5	14.78
Sulfate (SO ₄ ²⁻)	98.3	14.77
Phosphate (PO ₄ ³⁻)	98.3	14.74

With the addition of electrolyte, the main characteristics of sorption isotherm curves are remained. The critical pressure, P_i , however, becomes much higher. When the sodium cation concentration C_0 is 0.5M, as shown in Figure 2-5, P_i is around 98 MPa. Correspondingly, the effective interfacial tension γ increases to 14.7 mJ/m², higher than that of pure water by nearly 21 %. Clearly, with the solvated ions, the repelling effect of nanopore walls is more pronounced, which fits with the prediction of

classic theory that the surface tension of an electrolyte solution is higher than that of water. The rearrangement of ion configuration near the solid surface demands additional external work. Thus, with the electrolyte, the system free energy rises.

As the ion concentration increases, the difference in ion transport pressures of different electrolytes becomes evident (Figure 2-6).

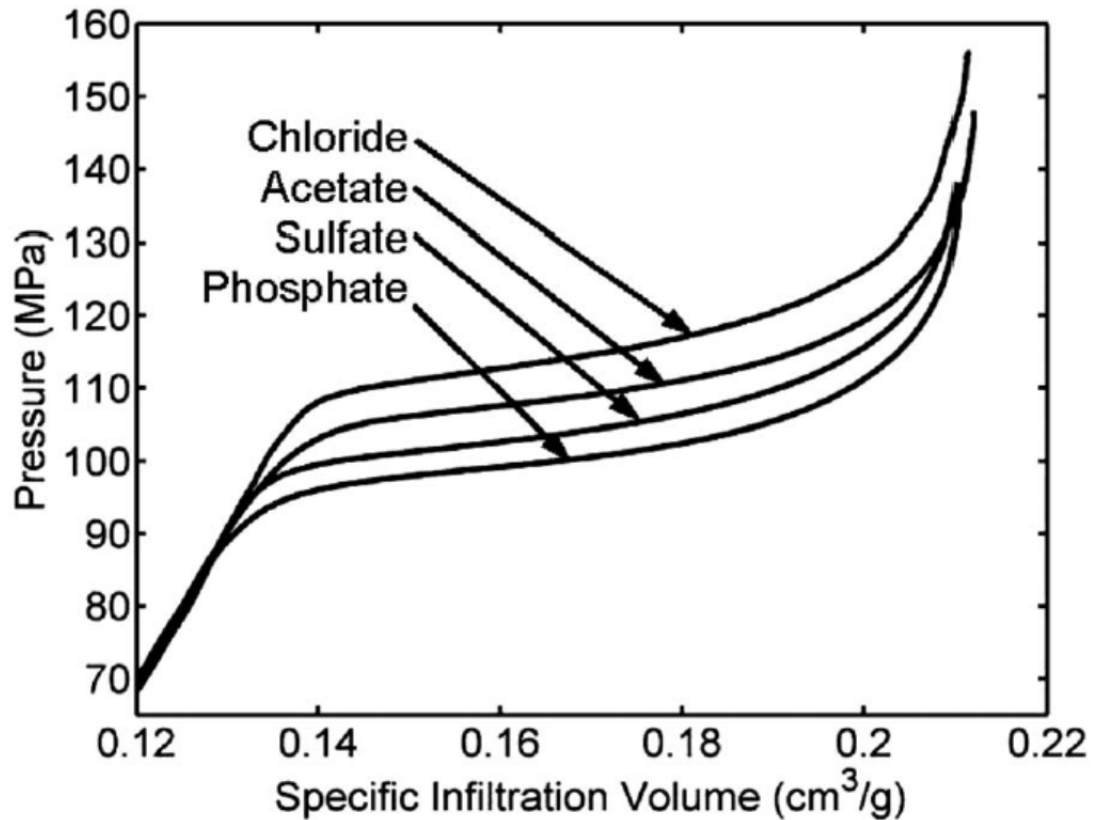


Figure 2-6 : Typical sorption isotherm curves when the cation concentration is 2 M

It is interesting that when $C_0 = 0.5$ M, the influence of the type of anion on γ is negligible, as shown in Figure 2-7. When the anion changes from phosphate to chloride, P_i increases slightly from 98.3 to 99.3 MPa, close to the tolerance of the testing system. The effective interfacial tension varies from 14.74 mJ/m² to 14.89 mJ/m² by only 1.02% (Table 2-3).

In the sodium phosphate based system, the increase in ion concentration does not considerably affect P_i . In all the other three systems, P_i largely increases.

In the sodium sulfate based system, the ion transport pressure increases by 4 MPa; correspondingly, the effective interfacial tension varies by 0.6 mJ/m².

In the sodium acetate based system, the ion transport pressure increases by 8 Mpa, which implies that the effective interfacial tension rises by 1.2 mJ/m².

The largest increase in P_i occurs in the sodium chloride based system, which is 15 MPa. The corresponding variation in effective interfacial tension is 2.2 mJ/m².

Clearly, there must be an abrupt change in configuration of confined anions When the cation concentration increases from 0.5 M to 2 M (Table 2-4).

Table 2-4 : Ion transport pressure (P_i) and effective interfacial tension (γ) when sodium ion concentration is 2 M

Anion	Ion transport Pressure (P_i , MPa)	Effective interfacial tension (γ , mJ/m ²)
Distilled water	81	12.15
Chloride (Cl ⁻)	114.3	17.09
Acetate (CH ₃ CO ₂ ⁻)	106.5	15.98
Sulfate (SO ₄ ²⁻)	102.3	15.37
Phosphate (PO ₄ ³⁻)	98.3	14.74

When the ion concentration is relatively low, since the solid surface tends to adsorb cations, the anions would be repelled to the central part of a nanopore. Note that the cation ion diffusion and adsorption process can be fundamentally different from that at a large solid surface. The cations cannot be fully solvated since the characteristic van der Waals size of a fully solvated structure is comparable with the effective nanopore diameter. Thus, high-energy configurations that are “stretched” along the axial direction can be dominant, and the ion transport rate can be either

increased or decreased, depending on the energy barrier offered by the solid atoms.

As the anions move toward the interior, they are somewhat shielded by the cations and water molecules. As a result, when their concentration and ion charges vary, there is little variation in ion transport pressure, which reflects the system free energy variation rate.

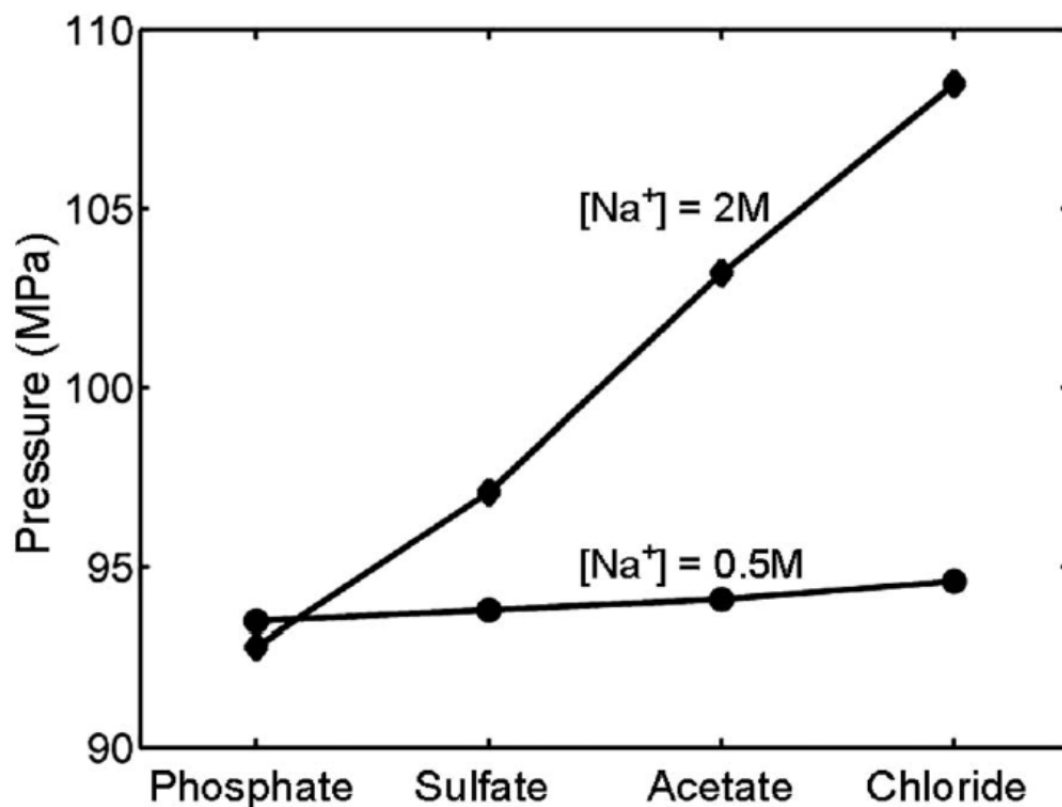


Figure 2-7 : The ion transport pressure of various electrolyte solution with different concentration

When the ion concentration is relatively high, the inner space in the nanopore becomes insufficient for all the anions.

In the ZSM-5 testing sample, effective nanopore size is around 0.6 nm. If the thickness of the liquid molecular layer immediate adjacent to the solid atoms is 0.25 nm,

the cross-sectional length scale of the inner space is only 1 Å. If the number of anions is increased, a portion of them would direct contact the solid atoms, and their influence on the solid-liquid interfacial tension, i.e., the ion transport pressure, would be much more pronounced (Figure 2-7).

Sodium phosphate is of the lowest anion concentration. Even when the cation concentration is 2 M, most of the confined anions, whose concentration 0.67 M is only slightly higher than 0.5 M, can still be separated from the solid atoms. Hence, the ion transport pressure is similar with that of the low ion concentration system.

In the sodium sulfate solution, the anion concentration is 1 M. As a certain portion of anions are in direct contact with the solid phase, they increase the system free energy. When the anion species is changed to acetate, the anion charge is decreased to 1 but the concentration is increased to 2 M. The system free energy increases more evidently.

Figure 2-7 also indicates that the anion size is another important factor that affects the ion transport pressure. While the cation ion concentrations and the anion concentrations of the sodium chloride solution are the same with that of the sodium acetate solution, the value of P_i of the former is higher. A major difference between the two systems is the anion size. Since chlorine anions are smaller than acetate anions, it is easier for the former to diffuse away from the central part of a nanopore and approach the solid atoms. Consequently, more anions are involved in the high-potential configurations, leading to the increase in system free energy.

2.4 Concluding Remarks

In an experimental study on transport of pressurized electrolyte solutions in a

ZSM-5 zeolite, it is noticed that when the anion concentration is relatively low, its influence on ion transport pressure is negligible; when the anion concentration is relatively high, its effect becomes significant. The ion size also has a pronounced influence on the system free energy. These phenomena can be attributed to the confined ion structures in nanopores.

Chapter 2, in part, is a reprint of the material as it appears in Effects of anion concentration on ion-transport pressure in nanopore. Kim, Taewan; Lu, Weiyi; Han, Aijie; Punyamurtula, Venkata K.; Chen, Xi; Qiao, Yu, *Applied Physics Letters*, vol 94, 013105, pp 1-3, 2009. The dissertation/thesis author was the primary investigator and author of this paper.

3 EFFECTS OF SURFACE GROUP LENGTH

3.1 Introduction

3.1.1 Background

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[51]. If the tube or pore size is relatively small, the liquid molecules tend to have a chainlike structure[52].

At a finite temperature, liquid molecules can rapidly transport across a short nanotube[53]. If the tube is long or the pore is deep, an external mechanical, thermal, or electric field can greatly promote the molecular motion[32]. If the inner surface of a macroscopic channel is nonwetable, 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[54]. 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[39].

Once the liquid molecules are confined inside a nanopore, they may or may not defiltrate when the external pressure is removed[55], 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[56]. For nanoporous

materials, a few researchers argued that gas nanophase and pore texture play critical roles[57]. 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[58].

3.1.2 Mobile Crystalline Material – 41 (MCM-41)

MCM-41 (Mobile Crystalline Material No. 41) is a silicate obtained through the templating mechanism, and the name was given to a series of mesoporous materials that were first synthesized by Mobil's researchers in 1992 [59-61]. MCM-41 and MCM-48 (Mobile Crystalline Material No. 48) are two of the most popular mesoporous molecular sieves[62].

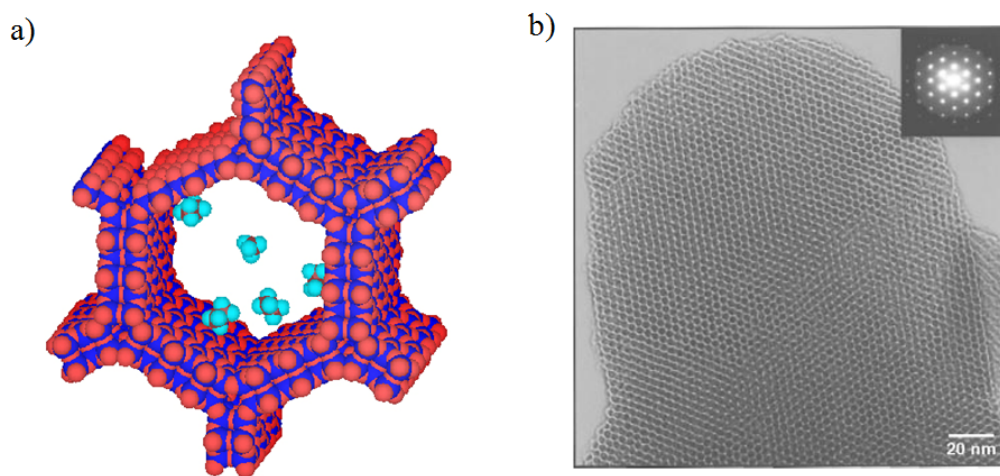


Figure 3-1 : a) Illustration of MCM-41 by ball model (Red ball : oxygen atoms, blue ball : Si atoms), b) TEM image of MCM-41[63]

These materials also possess large surface area, which can be up to more than 1000 m²/g (Figure 3-1). MCM-41 and MCM-48 have been employed as catalysts for various chemical reactions, as supports for drug delivery systems, and as adsorbents in waste[62, 64].

3.2 Experimental

3.2.1 Chemicals

Sodium Silicate (Na₂O₃Si, M.W. 122.06 g/mol), cetyltrimethyl ammonium bromide (C₁₉H₄₂BrN, M.W. 364.45 g/mol), sodium hydroxide (NaOH, M.W. 39.99 g/mol), ammonium hydroxide (NH₄OH, M.W. 35.04 g/mol), acetic acid (C₂H₂O₂, M.W. 60.05 g/mol), sodium chloride (NaCl, F.W. 58.44 g/mol), toluene (C₇H₈, M.W. 92.14 g/mol), chloro(dimethyl)octylsilane (C₁₀H₂₃SiCl, M.W. 206.83 g/mol), chlorotrimethyl silane (C₃H₉SiCl, M.W. 108.64 g/mol), ethanol (C₂H₅OH, 46.07 g/mol), pyridine (C₅H₅N, M.W. 79.1 g/mol) were purchased from the Sigma-Aldrich Chemical Co. (St. Louis, MO).

3.2.2 Materials Preparation

3.2.2.1 Synthesis of MCM-41[64]

MCM-41 was synthesized through the following steps:

- a. 12.20 g (0.04) mole of sodium silicate, 36.45 g (0.1 mol) of cetyltrimethyl ammonium bromide, 4 g (0.11 mol) of sodium hydroxide, 1.05 g (0.03 mol) of ammonium hydroxide and 360 g (20 mol) of H₂O were added to a 1L round bottom flask.

- b. The mixture was stirred vigorously for 1 h, and then its pH value was kept at 10 by adding acetic acid.
- c. 15 % sodium chloride solution was added to the mixture.
- d. The mixture was vigorously stirred for 3 min, until the solution was clear. Then further stirred for 3 min.
- e. The mixture was thermally treated in an autoclave at 95 °C for 72 h.
- f. The mixture was filtered by an aspirator and then dried in vacuum oven at 80 °C for 12 h.
- g. The dried powder was calcined at 550 °C for 6 h
- h. The MCM-41 particles were obtained. The average pore size was 2.6 nm, according to Barret–Joyner–Halenda (BJH) analysis, and the specific surface area was 1,050 m²/g (Figure 3-2 and Figure 3-3).

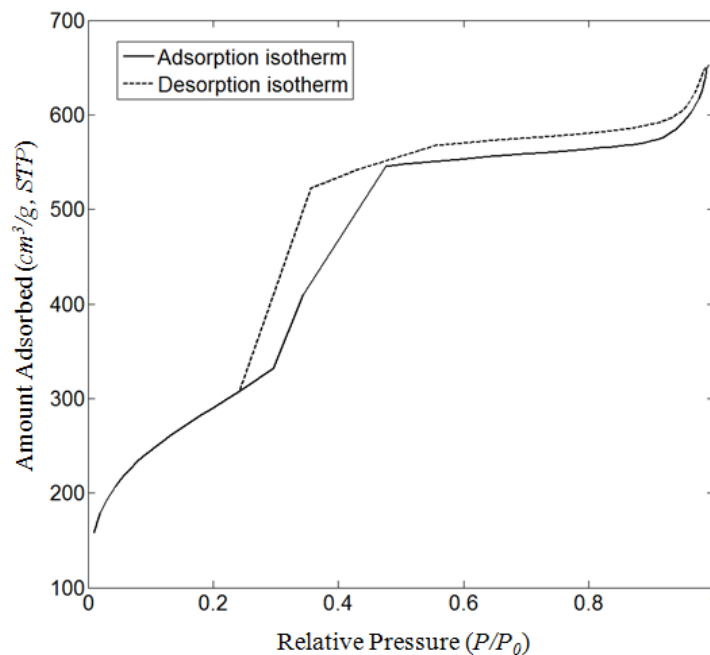


Figure 3-2 : The N₂ sorption isotherm curve at 77 K on MCM-41

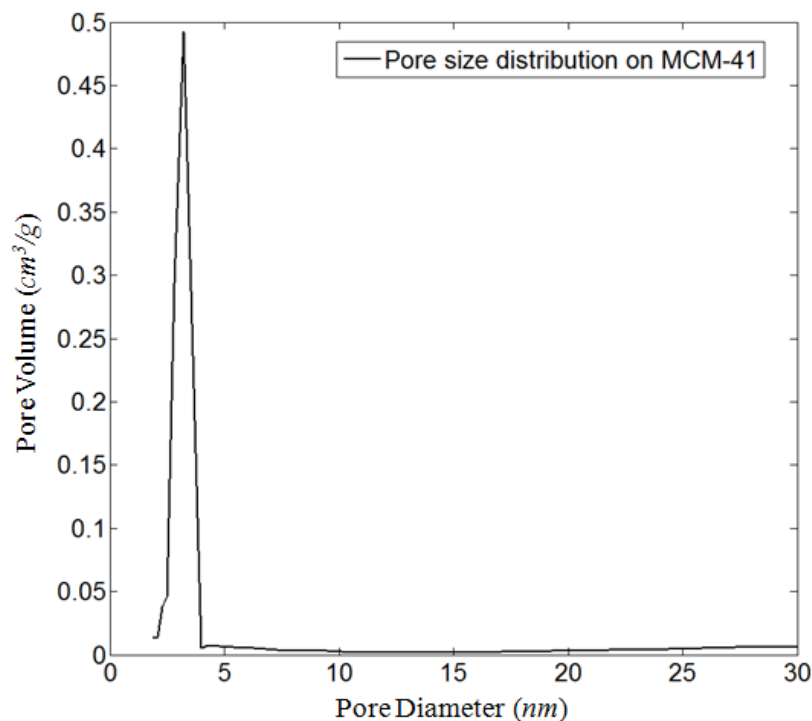


Figure 3-3 : The Pore size distribution on MCM-41

3.2.2.2 Surface modification of MCM-41 (Figure 3-4)

The synthesized MCM-41 was modified as the following:

- a. 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 and refluxed at 80 °C for 3 h, with vigorous stirring.
- b. The mixture was cooled down to the room temperature.
- c. 1 mL of chloro(dimethyl)octylsilane or chlorotrimethylsilane (for C₈ or C₁ treatment, respectively) and 0.1 mL of pyridine (the catalyst) were added to the dispersive MCM-41 mixture.
- d. The mixture was reflux at 95 °C for 5 h and then quenched.

- e. The mixture was filtered by an aspirator and then the surface modified MCM-41 was washed with dry toluene and ethanol for several times
- f. C_1 or C_8 Surface modified MCM-41 was dried in vacuum oven at 50 °C for 24 h.

During the surface modification, hydroxyl sites were deactivated and C_8 or C_1 groups were grafted on the nanopore surfaces[65]. The MCM-41 modified by C_8 groups was end capped by C_1 groups for three times.

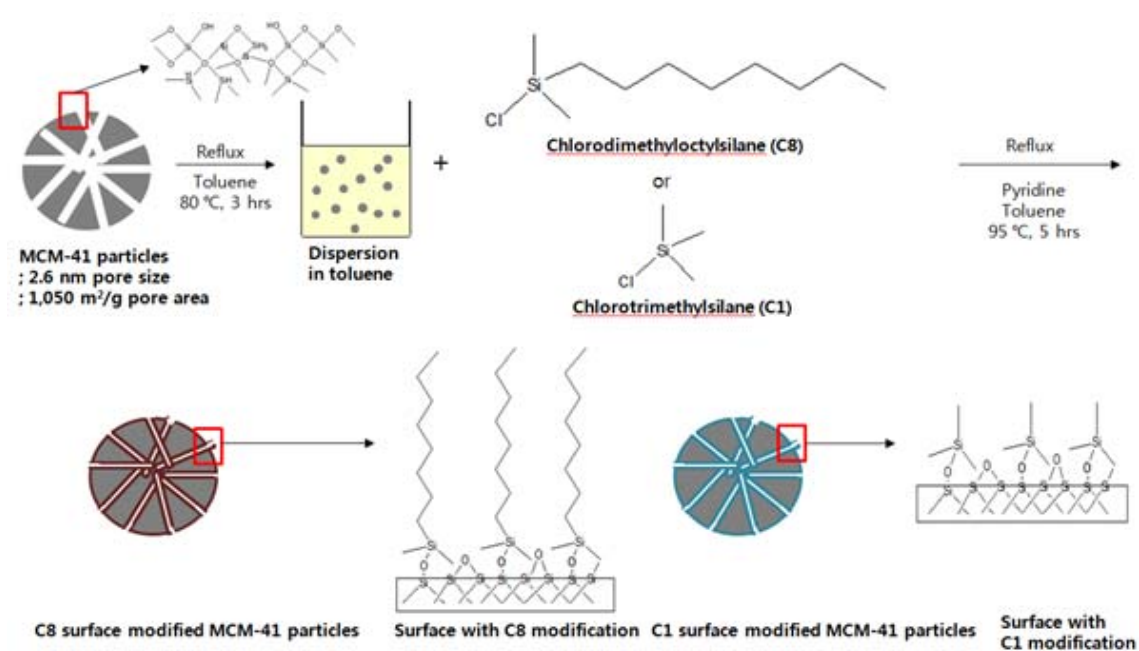


Figure 3-4 : Schematic illustration C_1 , C_8 surface modification on MCM-41

3.2.2.3 Testing cell

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 two steel pistons, equipped by a reinforce O-ring (Figure 2-3). The cross-sectional area of the piston was 286.52 mm².

The sodium chloride was added to amplify the surface group effect and to

promote defiltration[32]. By using a 5580-type Instron machine (Figure 2-4), the piston was compressed into the cylinder at the rate of 0.5 mm/min, applying a quasi-hydrostatic 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.

3.3 Results and Discussion

Since C_8 groups are hydrophobic, the modified nanopore inner surfaces are nonwetttable 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 (Figure 3-5).

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 (Figure 3-5).

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[66].

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 first loading. Eventually, when the pressure reaches 48 MPa, most of the nanoporous space is occupied and the infiltration plateau ends.

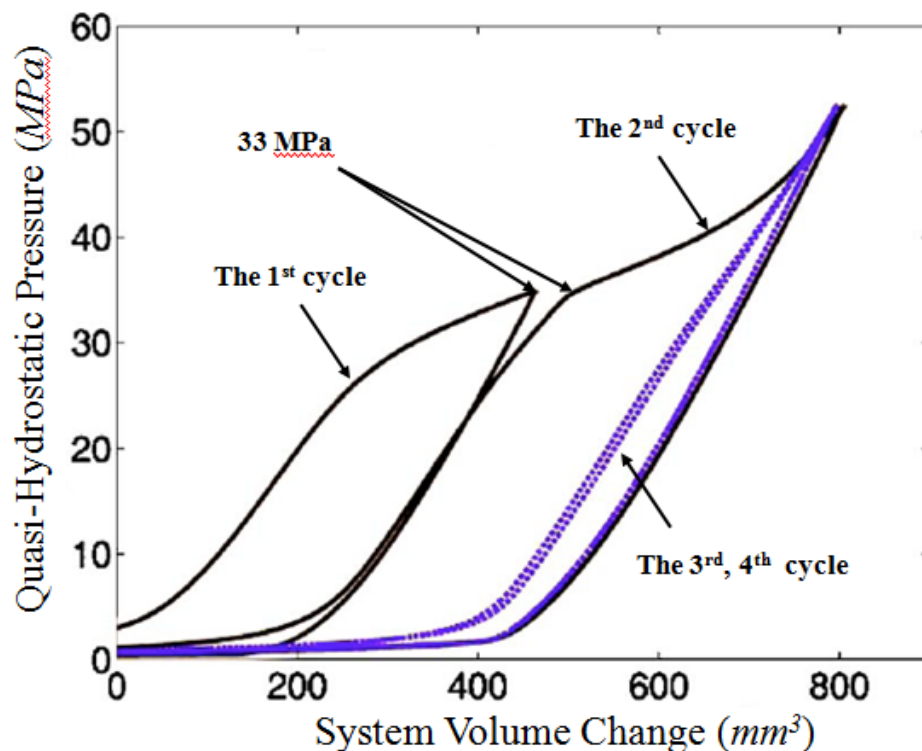


Figure 3-5 : Typical liquid intrusion curves of the MCM-41 modified by C₈ chains

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 (Figure 3-5).

The loading path of the MCM-41 modified by C₁ groups is of similar characteristics (Figure 3-6). 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.

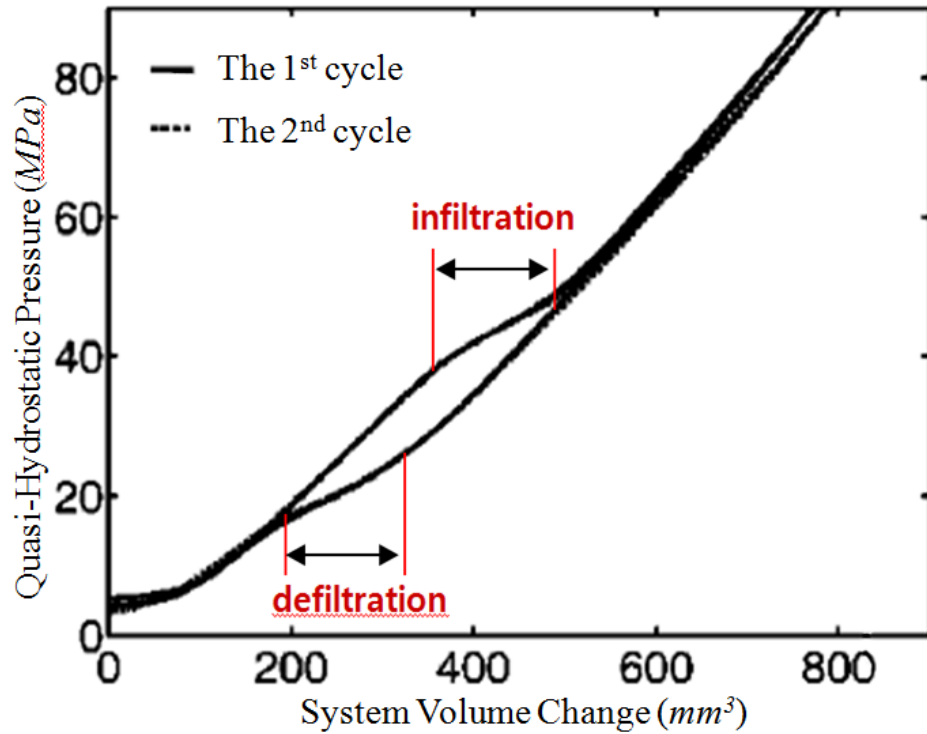


Figure 3-6 : Typical liquid intrusion curves of the MCM-41 modified by C_1 chains

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 C_1 and C_8 groups are similar (Figure 3-4). 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 C_1 and C_8 chains are the same, causing similar degrees of hydrophobicity. The major difference is the chain length. The length of a C_1 group, $OSi(CH_3)_3$, is only about 0.3 nm, while the length of a C_8 group, $OSi(CH_3)_2(CH_2)_7CH_3$, is much longer (1.1 nm). Thus, the effective nanopore size of the MCM-41 modified by C_1 groups is nearly 2 nm, and that of the MCM-41 modified by C_8 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[67]. 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 Figure 3-7 and Figure 3-8, 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.

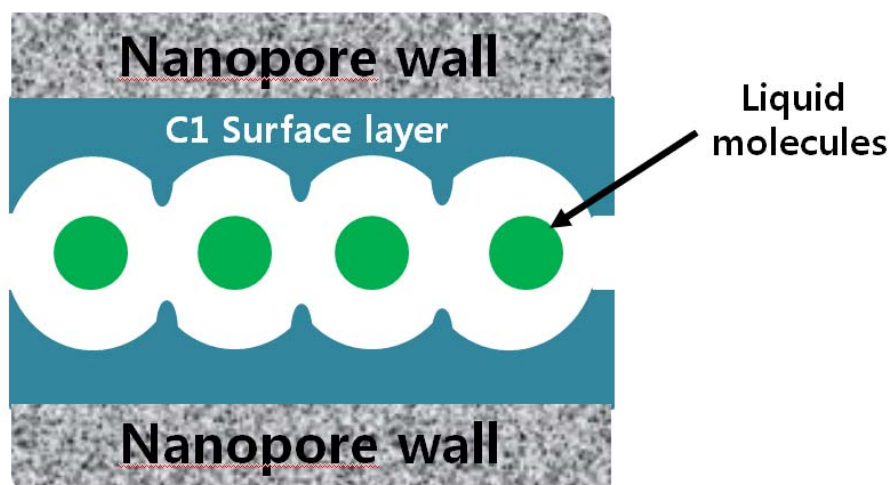


Figure 3-7 : Illustration of confined liquids in nanopore; C₁ modified inner surface in MCM-41

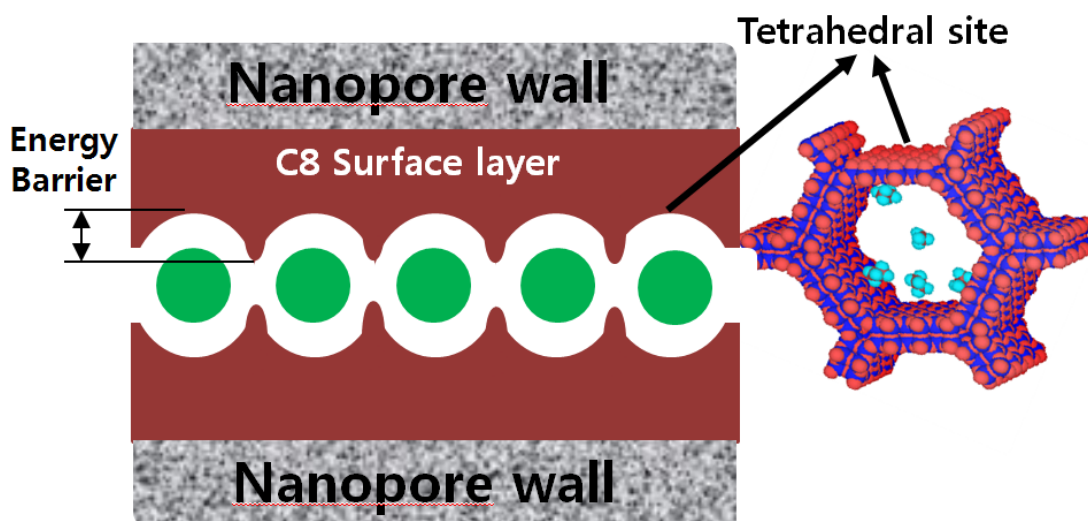


Figure 3-8 : Illustration of confined liquids in nanopore; C₈ modified inner surface in MCM-41

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[67].

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.

3.4 Concluding Remarks

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 chainlike 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 indispensable factor that must be taken into account for studies of unloading behaviors.

Chapter 3, in part, is a reprint of the material as it appears in Effects of surface-group length on liquid defiltration in a MCM-41. Kim, Taewan; Han, Aijie; Qiao, Yu, *Journal of Applied Physics*, vol 104, 034304, pp 1-3, 2008. The dissertation/thesis author was the primary investigator and author of this paper.

4 ELECTRIC FIELD EFFECTS

4.1 Introduction

4.1.1 Background

At the nanometer scale, surface phenomena become dominant, primarily due to the ultralarge surface to volume ratio[68]. Surface processes that are negligible at macroscopic level can be greatly amplified, which is one of the key reasons why nanomaterials became an active area of research in the past couple of decades.

For instance, the excess solid liquid interfacial tension, $\Delta\gamma = \gamma_{sl} - (\gamma_s + \gamma_l)$, is typically at the level of a few 10^2 mJ/m² [43], much smaller than the surface free energy of a solid material, with γ_{sl} being the solid-liquid interfacial tension and γ_s and γ_l the surface tensions of solid and liquid, respectively. However, if liquid-solid contact and separation can be achieved in a nanoporous material, because the specific surface area (A) is $10^2 - 10^3$ m²/g [2], the associated energy change can be 10–100 J/g [69], causing a considerable temperature variation[70].

As discussed in previous chapters, the surface properties of a nanomaterial often need to be modified to meet the functional requirements. A powerful method is to perform surface grafting treatment. With a coating layer, the surface properties can be entirely changed. The commonly used surface groups include silyl materials, which can react with the hydroxyl sites at a solid surface and form relatively strong bonds[71]. Before the treatment, the hydroxyl sites make the surface quite polar and, thus, hydrophilic[72, 73]. After the treatment, the silyl groups are nonpolar and the surface tends to be hydrophobic. Similar concept can be extended to other surface reactions,

so that the surface properties can be adjusted in broader spectra[74].

Conventional surface treatment techniques lead to fixed surface morphologies. Once the surface groups are grafted, their configurations would not change, except that in a harsh environment they may degrade. For instance, if the temperature is higher than a critical level, surface chains can decompose and the surface treatment effects are reduced[75]. As an external thermal or electric field is applied, the effective surface tension can vary due to the well known thermo-wetting and/or electro-wetting phenomena[76-78]. However, these changes are relatively weak. In a changing working environment, it is often desirable that the surface properties can be adjusted in broad ranges.

One method is to use surface chains of charged end groups. The chains should be relatively long and flexible, and their configurations are influenced by surface charges[79]. Previously, studies on controllable surface chains were focused on outer surfaces of particles and fibers [80], compared with which controlling inner surfaces of nanoporous materials was relatively uninvestigated.

4.1.2 Black Pearl – 2000 (BP2000)

Black Pearl 2000 (BP 2000) is a highly porous and conducting nanoporous carbon from Cabot Co. Ltd. According to the gas absorption analysis, the nanopore size distribution is bimodal, which shows a substantial amount of macropores and micropores and a gap in the mesopore region (Figure 4-1). The lower peak is at 1–2 nm, and the higher peak is at about 54 nm (Figure 4-1). The specific nanopore surface area is nearly 1200 m² /g and the porosity is around 70%. The TEM image shows that the primary particles are highly agglomerated (Figure 4-2)[81].

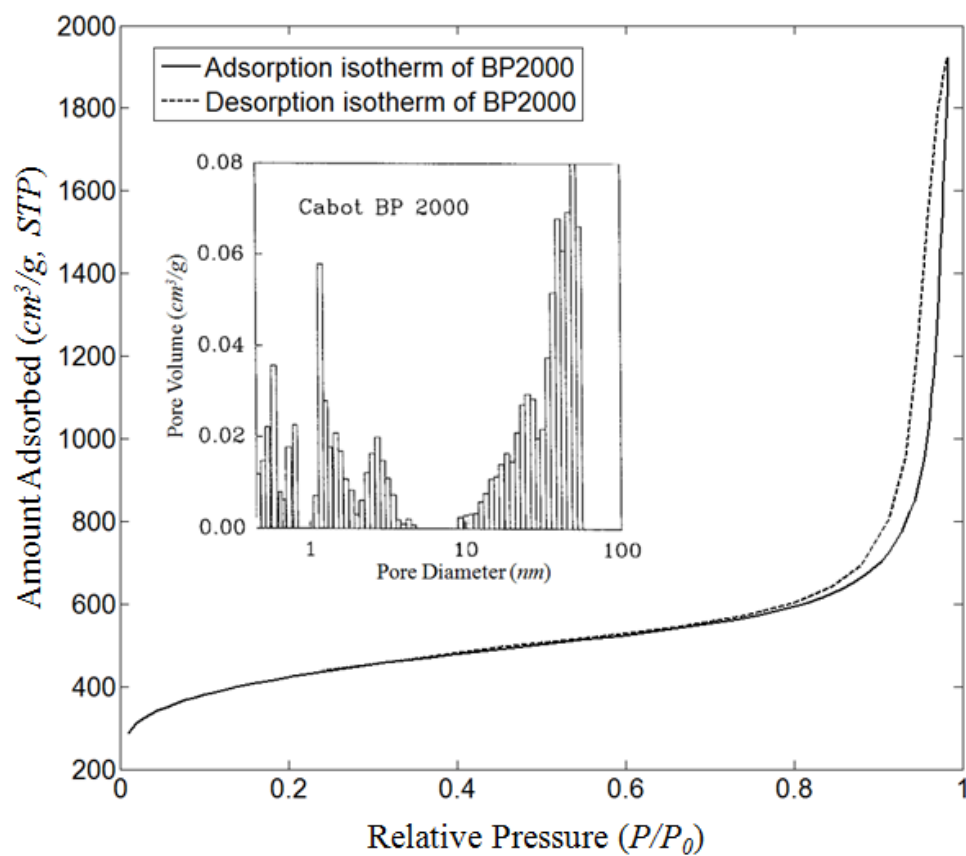


Figure 4-1 : The N₂ sorption isotherm curve at 77 K of BP-2000. The inset shows the pore size distribution[82]

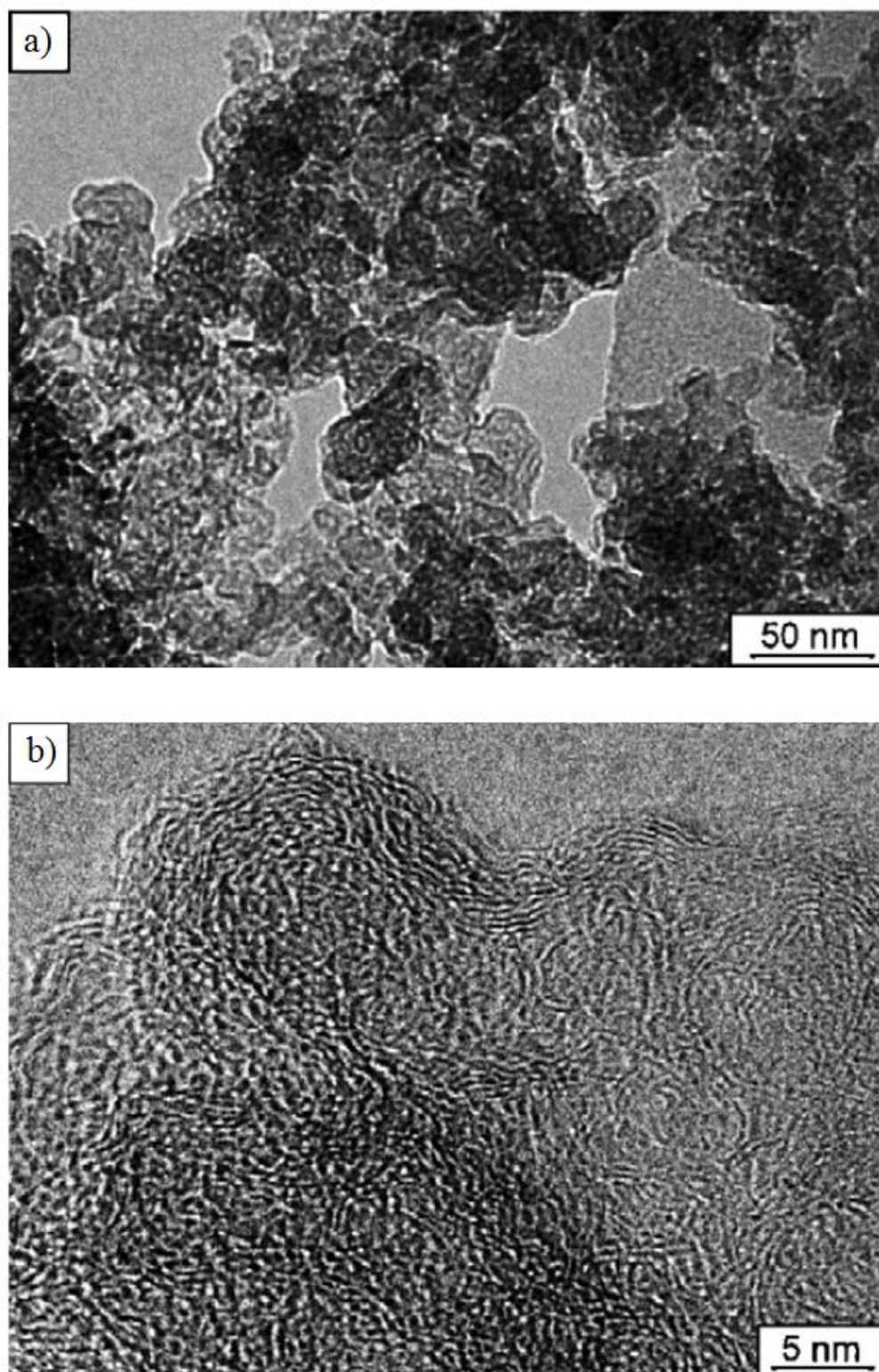


Figure 4-2 : TEM (a), HR-TEM (b) image of BP 2000 [81]

4.2 Experimental

4.2.1 Chemical

Black Pearl 2000 (BP 2000) powder was obtained from the CABOT Co. (Alpharetta, GA). Teflon membrane was purchase from Whatman Inc. (Piscataway, NJ). Gold foil, acetylene black, acetic acid ($C_2H_4O_2$, M.W. 60.05 g/mol), toluene (C_7H_8 , M.W. 92.14 g/mol), chlorotrimethyl silane (C_3H_9SiCl , M.W. 108.64 g/mol), ethanol (C_2H_5OH , 46.07 g/mol), pyridine (C_5H_5N , M.W. 79.1 g/mol), 16-mercaptohexanoic acid ($HS(CH_2)_{15}CO_2H$, M.W. 288.49 g/mol), polyvinylidene fluoride ($((CH_2CF_2)_n$, $M_w = 275,000$), lithium chloride ($LiCl$, M.W. 42.39 g/mol), acetone (CH_3COCH_3 , M.W. 58.08 g/mol) were purchased from the Sigma-Aldrich Chemical Co. (St. Louis, MO).

4.2.2 Materials Preparation

4.2.2.1 Heat treatment of BP 2000

Heat treatment of BP 2000 was performed as the following:

- a. 2 g of BP 2000 was heated at 450 °C in nitrogen for 12 h, and then cooled down to room temperature.
- b. The heat treated BP 2000 was washed with acetone and warm water for several times
- c. The washed BP 2000 was filtered by an aspirator, and then dried in vacuum oven condition at 80 °C for 10 hr.

4.2.2.2 Surface modification of BP 2000 with Chlorotrimethyl Silane[83]

Surface modification of BP 2000 was performed as the following:

- a. 40 mL of dry toluene was added to a 3 neck round-bottom flask and refluxed at 80 °C for 3 h while being stirred.
- b. The mixture was cooled down to the room temperature.
- c. 1.0 mL of chlorotrimethylsilane was added into the flask in nitrogen purge.
- d. 0.870 g of BP 2000 powders were added into flask in nitrogen purge.
- e. 0.1 mL of pyridine was dropped in when the mixture was stirred.
- f. The mixture was first stirred at 10 rpm at room temperature for 10 min in N₂, and then refluxed at 100 rpm at 90 °C for 2 h in N₂.
- g. After the treatment, the mixture was quenched in ethanol to the room temperature.
- h. The mixture was filtered by an aspirator and the C₁ surface modified BP 2000 was washed with dry toluene, acetone and warm water repeatedly.
- i. The C₁ surface modified BP 2000 was dried in vacuum oven at 120 °C for 12 h (Figure 4-3).

After the C₁ surface modification, a monolayer of silyl groups were grafted at the nanopore surfaces. The surface density of silyl groups was relatively high while there were still hydroxyl sites available for further surface modification[84].

4.2.2.3 Surface modification with 16-mercaptohexanoic acid

A chain of 16-mercaptohexanoic acid (MHA, SH(CH₂)₁₅CO₂H)) has 15 trans carbon-carbon bonds, which is relatively flexible and nonpolar (hydrophobic). Once it

reacted with the hydroxyl sites at the carbon surface, the other end was capped by a negatively charged carboxylate (CO_2H) group, which was hydrophilic.

The grafting was performed as the following:

- 40 mL of dry toluene was added to a 3 neck round-bottom flask.
- 2.0 mL of MHA and 0.5 g of BP 2000 powders were added into the flask in nitrogen purge.
- The mixture was refluxed at 100 rpm at 95 °C for 36 h and then cooled down to room temperature.
- The mixture was filtered by an aspirator and filtered. The MHA surface modified BP 2000 was washed with acetone and distilled water repeatedly.
- The surface modified BP 2000 was dried in air.

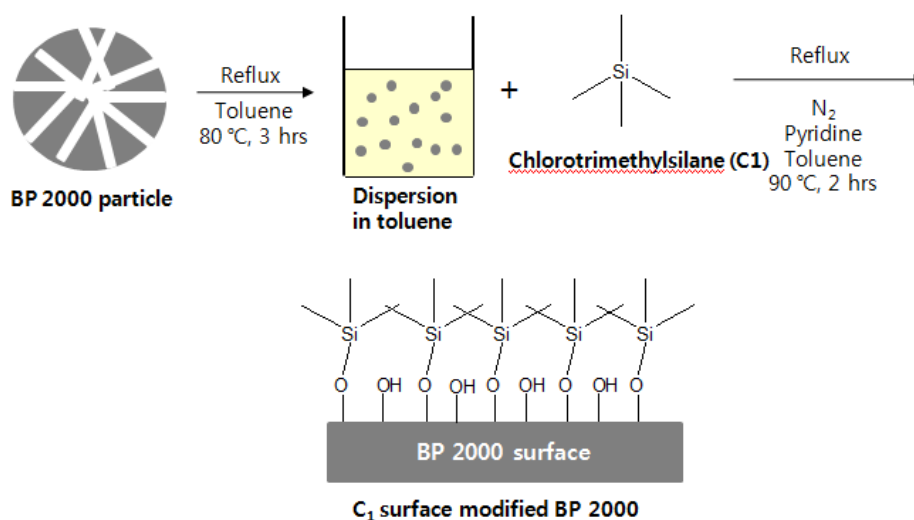


Figure 4-3 : Schematic of surface modification of BP 2000 with chlorotrimethylsilane

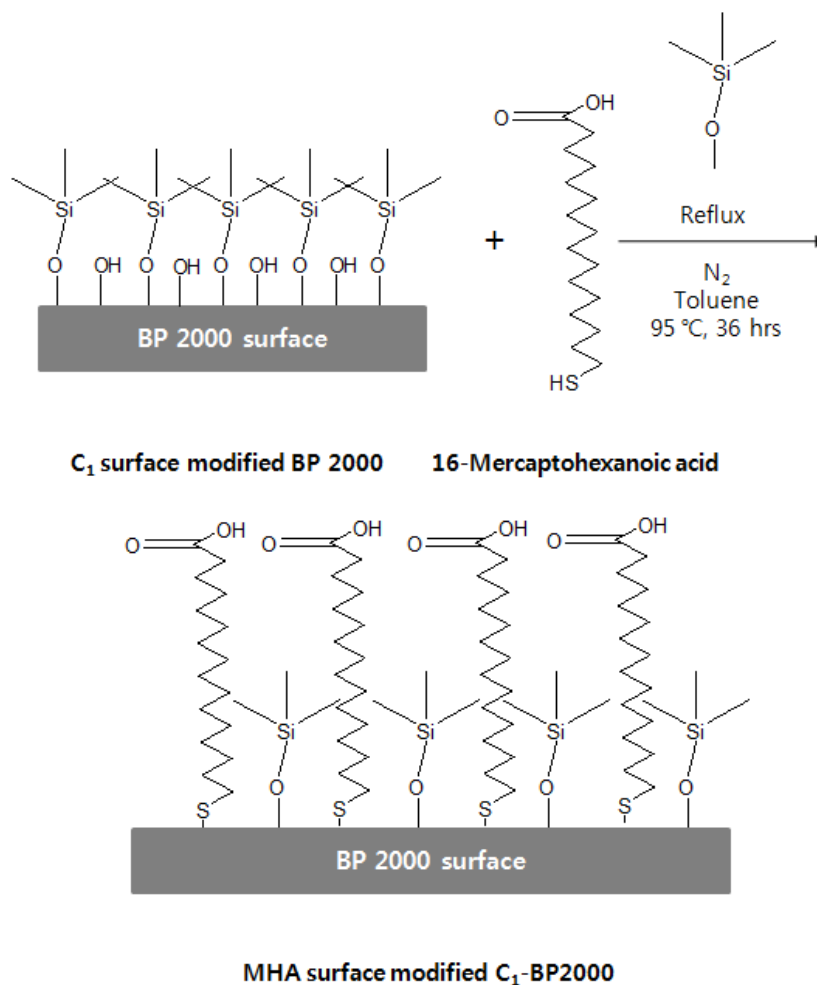


Figure 4-4 : Schematic illustration of surface modification of C1-BP2000 with MHA

4.2.2.4 Testing cell

The preparation of the testing cell followed the following steps:

- a. 8 g of surface treated BP2000 powders, 1 g of acetylene black (AB) and 1 g of Polyvinylidene fluoride (PVDF) were added to an agate mortar.
- b. The mixture was ground and mixed with pestle homogeneously for 30 min; the AB and PVDF particles were solid and, therefore, did not affect the porosity.

- c. The mixture was compressed at 8 MPa into thin disks, with the diameter of 12.7 mm and the thickness of about 0.2 mm; the carbon disk was conductive, with the resistivity of about $20 \mu\Omega\text{m}$.
- d. A multilayer electrode was produced by repeatedly folding a gold foil. The carbon disks were inserted in between the gold layers, as depicted in Figure 4-5. Between two adjacent gold layers, two carbon disks were separated by another gold layer. The outer gold layers were connected together, forming the counterelectrode; The carbon disks and the counterelectrode were insulated by porous teflon membranes, and the membrane thickness was $50 \mu\text{m}$.
- e. The system was immersed in a 15% aqueous solution of lithium chloride (LiCl) and sealed in a steel cylinder; the electrode was insulated from the testing cell by a Teflon tape.

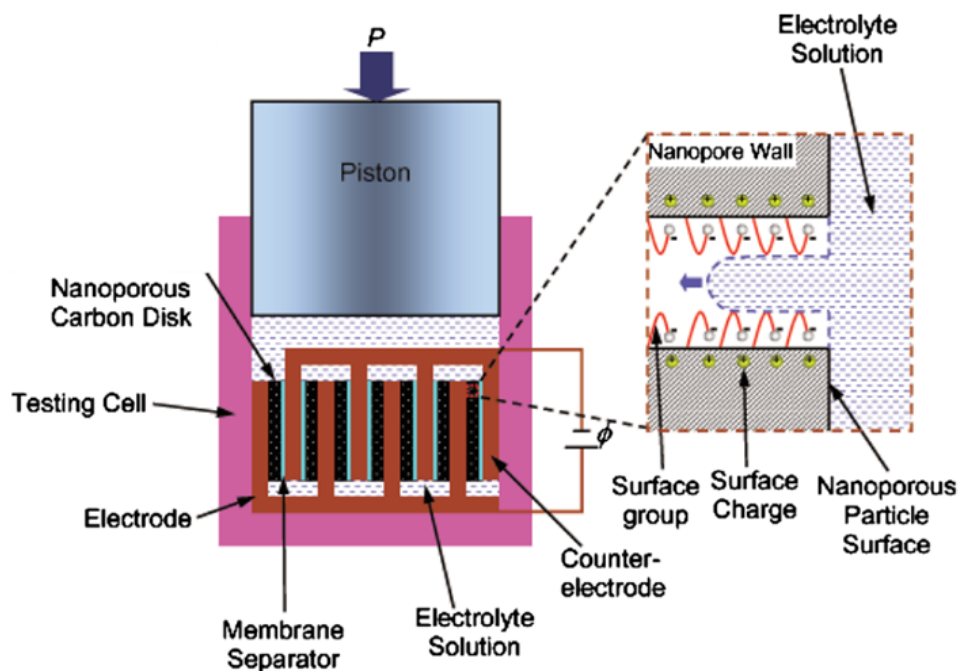


Figure 4-5 : Schematic of experimental set up

4.3 Results and Discussion

A constant voltage, ϕ , was applied by a dc power supply between the electrode and the counterelectrode. The applied voltage was 0.48 V, 0V, or 0.48 V. The degree of hydrophobicity of the nanopore surfaces was measured by intruding the LiCl solution into the nanopores. The pressure was applied by a type 5580 Instron machine through a piston, at a constant rate of 0.5 mm/min (Figure 2-4).

As the pressure was increased to 14 MPa, the piston was moved out at the rate of - 0.5 mm/min. Typical sorption isotherm curves at different voltages are compared in Figure 4-6. According to the gas absorption analysis, the nanopore size distribution is bimodal. The lower peak is at 1–2 nm, and the higher peak is at about 54 nm. The specific nanopore surface area is nearly 1,200 m²/g. The porosity is around 70%.

In the C₁ surface modification, the nanopore walls are covered by hydrophobic trimethylsilyl groups; in the second surface modification step, the grafted surface groups are MHA chains. As depicted in the inset in Figure 4-5, if the MHA chains are bent, the hydrophobic chains are exposed to the liquid phase. If the MHA chains are straight, the charged carboxylate end groups would attract water molecules and oppositely charged ions.

The dashed line in Figure 4-6 shows that the overall effect of the two types of surface groups makes the nanopore walls effectively hydrophobic. Thus, when the applied pressure P is relatively low, the liquid phase cannot enter the nanopores.

When P is reached to about 3.5 MPa, the repelling effect of the nanopore wall is overcome. Associated with the liquid infiltration, the system volume decreases rapidly as the pressure is increased.

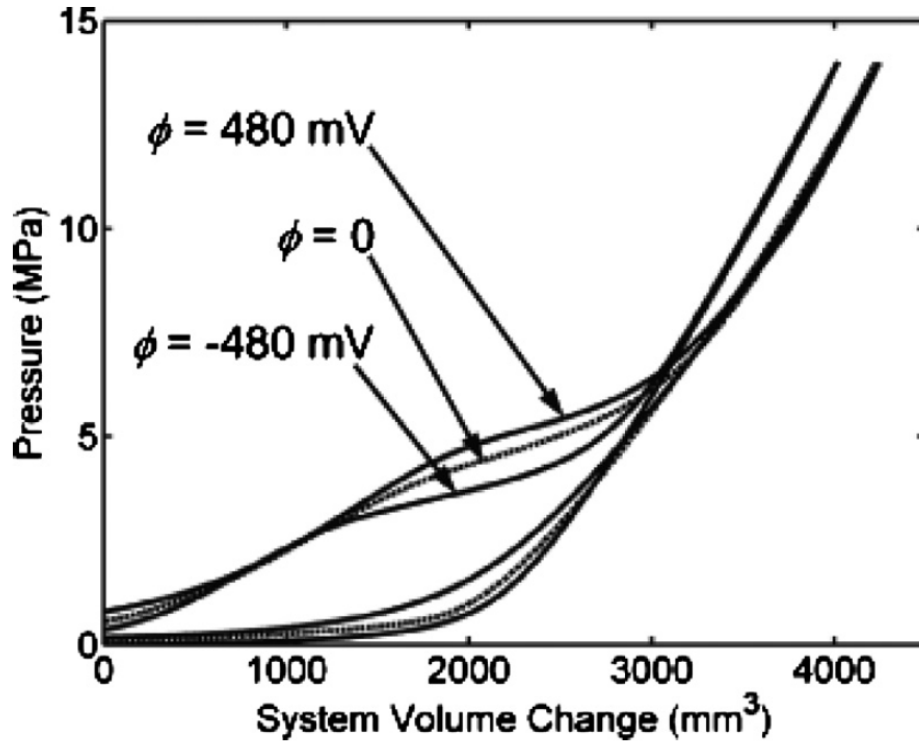


Figure 4-6 : Typical sorption isotherm curves according to the different applied voltage

According to the classic Laplace–Young equation, the infiltration pressure P_{in} can be related to the interfacial tension $\Delta\gamma$ as $P_{in} = 4 \Delta\gamma/D$, where D is the effective nanopore size.

Hence, the infiltration pressure of the small nanopores (1–2 nm) should be higher than that of the large nanopores (50–60 nm) by more than an order of magnitude, and the sorption isotherm curve may contain two distinct infiltration plateaus. Such two-staged structure, however, is not observed in the current pressure range, suggesting that the smallest nanopores are not involved in the infiltration process.

The slope of the infiltration plateau reflects the variation in nanopore size, as shown in Figure 4-7.

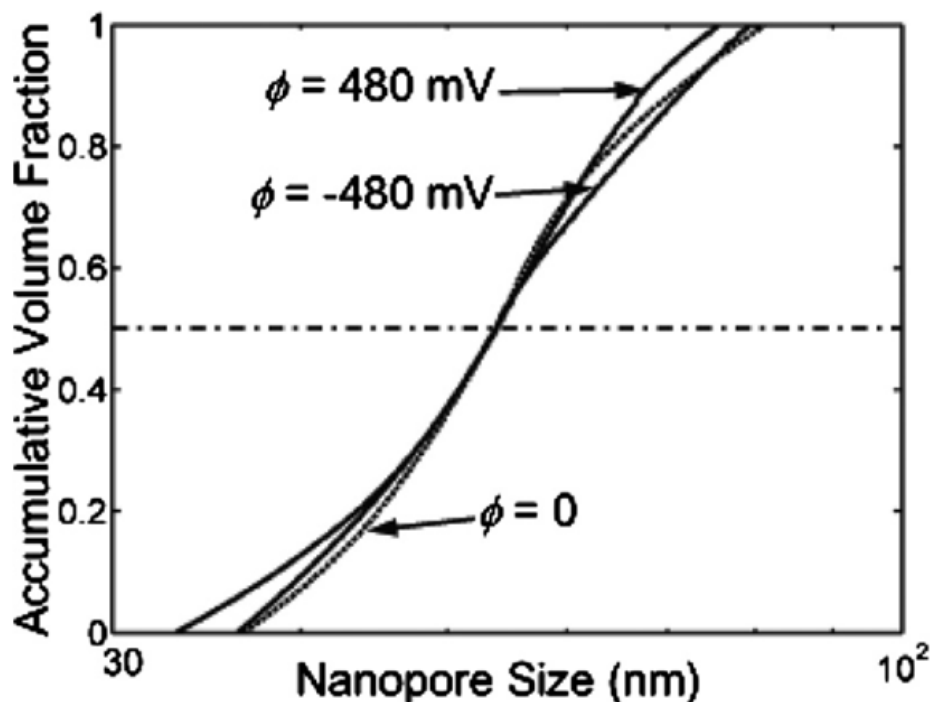


Figure 4-7 : The calculated accumulative nanopore volume distribution curve

The value of excess interfacial tension, $\Delta\gamma$, is set as 51.3 mJ/m^2 (Table 4-1), such that the nanopore size at 50 % infiltration volume fits with the higher peak of the gas absorption analysis result (54 nm). This value is comparable with but higher than the effective interfacial tension of trimethylsilyl treated surfaces[84], suggesting that the MHA groups increase the degree of hydrophobicity.

Once a voltage is applied, positive surface charges tend to attract the negatively charged carboxylate groups of MHA chains; and, thus, they are fully bent. Under this condition, the hydrophilic components are “shielded” by the hydrophobic components.

The testing data in Figure 4-6 indicate that the infiltration pressure increases considerably. Through a similar analysis of the pore size distribution, the effective interfacial tension can be determined as 59.4 mJ/m^2 , higher than that of uncharged

system by nearly 15 % (Table 4-1).

Table 4-1 : Infiltration pressure (P_{in}) and interfacial tension ($\Delta\gamma$) according to the applied voltage

applied voltage (ϕ)	Infiltration Pressure (P_{in})	Interfacial tension ($\Delta\gamma$)	Pore size at 50% infiltration volume (nm)
+ 480 mV	4.4 MPa	59.4 mJ/m ²	54
0 mV	3.8 MPa	51.3 mJ/m ²	54
- 480 mV	3.0 MPa	40.5 mJ/m ²	54

The increase in P_{in} is quite uniform in the entire infiltration plateau, indicating that the surface charge effects are independent of the nanopore size.

It also implies that, without the external electric field, the MHA chains are only partly straight; otherwise the attraction electric force would not cause detectable variation in surface property.

When the direction of the applied voltage is reversed, the surface charges become negative, which tend to repel the like-charged carboxylate groups. Hence, the MHA chains become straight, and the hydrophilic components are exposed to the confined liquid, leading to the decrease in effective interfacial tension.

From the nanopore size distribution analysis (Figure 4-7), it is calculated that the effective value of $\Delta\gamma$ is lowered to 40.5 mJ/m², about 21% smaller than that of the uncharged system (Table 4-1).

Clearly, the carboxylate groups can no longer be shielded. The negative charge effect is more pronounced than the positive charge effect, which may be attributed to the initial partly bent configuration of the MHA groups. Similar to the positively charged system, the variation in infiltration pressure is uniform.

4.4 Concluding Remarks

Through a two-stepped surface modification procedure, the inner surfaces of a nanoporous carbon can be modified by trimethylsilyl group and MHA.

Initially, the surface groups are partly bent, and the nanopore walls are hydrophobic. The surface properties can be controlled by an electric field, as the negatively charged carboxylate groups are repelled or attracted by the surface charges. Thus, the surface wettability can be controlled electrically.

Chapter 4, in part, is a reprint of the material as it appears in Electrically controlled hydrophobicity in a surface modified nanoporous carbon. Kim, Taewan; Lu, Weiyi; Lim, Hyuck; Han, Aijie; Qiao, Yu, *Applied Physics Letters*, vol 98, 053106, pp 1-3, 2011. The dissertation/thesis author was the primary investigator and author of this paper.

5 SURFACE MODIFICATION EFFECTS

5.1 Introduction

When nanoporous particles with hydrophobic inner and outer surface are dispersed in water, the liquid molecule cannot enter the nanopores. When an external pressure is applied, the system free energy increases. When the pressure reaches to a certain critical value (P_{in}), the capillary effect would be overcome. The value of P_{in} is highly dependent on the degree of hydrophobicity of the nanopore inner surfaces, which is influenced by a number of factors.

Controlling the infiltration/defiltration behaviors is one of the most important tasks of NMF liquid development, so as to meet various functional requirements.

We investigated the Daisogel SP300-5 (Daiso Co., Japan) nanoporous silica. It has a large surface area, a sharp particle size distribution, and a relatively uniform pore size distribution.

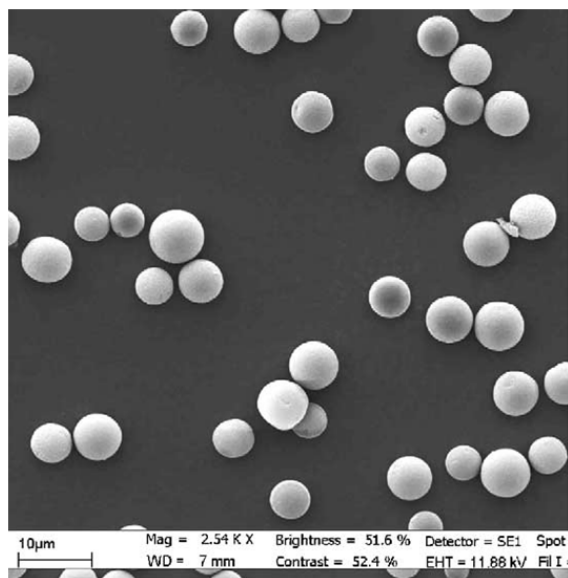


Figure 5-1 : The SEM image of daisogel SP300-5 [85]

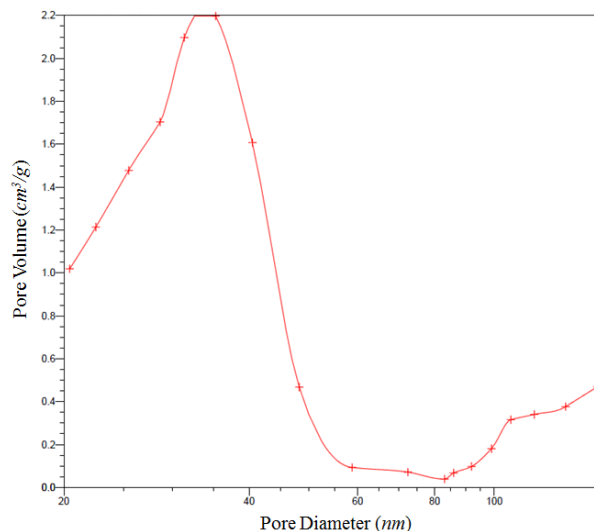


Figure 5-2 : The pore size distribution of daisogel SP300-5

Its average particle size is about 5 μm (Figure 5-1)[85], the average pore size of 30 nm, and the specific pore volume of 0.9 cm^3/g (Figure 5-2).

5.2 Experimental

Daisogel SP300-5 (SiO_2 , M.W. 60.08 g/mol) was obtained from Daiso Co., LTD (Japan). Lithium chloride (LiCl , M.W. 42.39 g/mol), toluene (C_7H_8 , M.W. 92.14 g/mol), chlorotrimethyl silane ($\text{C}_3\text{H}_9\text{SiCl}$, M.W. 108.64 g/mol, C_1 reagent), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 46.07 g/mol), pyridine ($\text{C}_5\text{H}_5\text{N}$, M.W. 79.1 g/mol) were purchased from the Sigma-Aldrich Chemical Co. (St. Louis, MO).

The Daisogel silica was surface treated as the following:

- a. 3 g of daisogel SP300-5 was first vacuum dried at 100 $^\circ\text{C}$ for 12 h and then immersed in 100 ml of dry toluene and refluxed at 80 $^\circ\text{C}$ for 6 h.
- b. The mixture was cooled down to room temperature.

- c. 30 mL of chloro(dimethyl)octylsilane (C_1) and 3 mL of pyridine were injected into the dispersive mixture.
- d. The mixture was reflux at 95 °C for a certain period of time, and then quenched in ethanol to room temperature. The treatment time was either 24 h, 48 h, or 96 h.
- e. The mixture was filtered by an aspirator and washed with dry toluene and ethanol repeatedly.
- f. The C_1 -surface treated daisogel SP300-5 was dried in vacuum at 80 °C for 24 h.

During the surface modification, the hydroxyl groups on the nanopore walls reacted with the C_1 reagent. As a result, C_1 surface groups were grafted to the nanopore surfaces[70].

The testing cell was prepared by sealing 0.3 g of the C_1 -surface modified daisogel SP300-5 and 3.5 g of 46 wt% aqueous lithium chloride (LiCl) solution in a stainless steel cylinder. The cross-sectional area of the stainless steel cylinder is 286.52 mm². Tests were performed in a type 5580 instron machine, with the loading rate of 1 mm/min.

5.3 Results and discussion

Before surface treatment, daisogel SP300-5 silica is hydrophilic, and, thus, can be soaked up by the liquid phase spontaneously. Thus, when an external pressure is applied, no further infiltration would occur, as shown in Figure 5-3.

When the inner surfaces of daisogel SP300-5 are modified by chlorotrimethylsilane ($OSi(CH_3)_3$), a monolayer of silane groups is formed and the pore surfaces become effectively nonwetttable. Figure 5-3 shows that the energy absorption

behaviors of the NMF liquids are dependent of the treatment time, t .

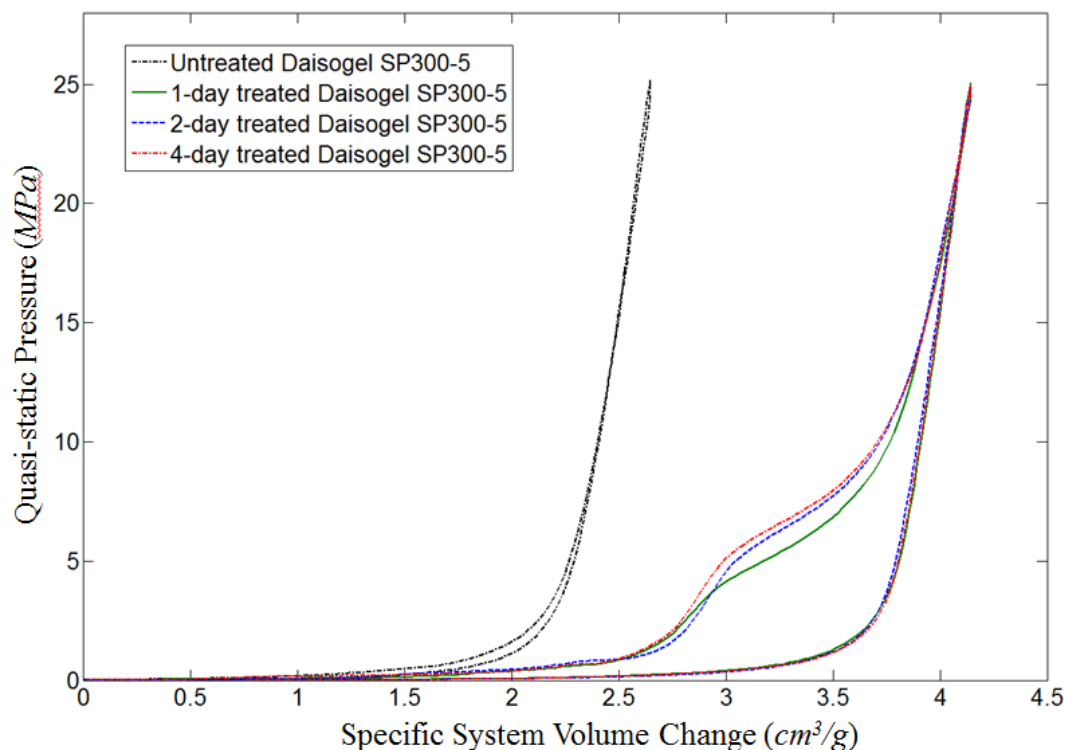


Figure 5-3 : Typical sorption isotherm curves of daisogel SP300-5

The surface treatment time increases from 1 day to 4 days, the pore volume distribution curve is almost the same, indicating that the accessible pore volume is not dependent on the silane group density. Regardless of the difference in treatment time, for all the surface modified daisogel SP300-5 silicas, the width of the infiltration plateau, which reflects the specific volume of the nanopores that are filled by the confined liquid, is about $0.83 \text{ cm}^3/\text{g}$, slightly smaller than the BJH measurement result ($0.9 \text{ cm}^3/\text{g}$).

Clearly, It is difficult for the gas/water molecules to enter the space between adjacent silane groups, and, thus they tend to stay in the interior of the nanopores, so that the silane groups behave as a “dense” coating layer.

The treatment time has a pronounced influence on the infiltration pressure. As

shown in Figure 5-3, only when a sufficiently high pressure is applied, the capillary effect can be overcome. After being surface treated for 1 day, the daisogel SP300-5 silica becomes quite hydrophobic and the infiltration pressure is 6.1 MPa. In this chapter, the infiltration pressure, P_{in} , is defined as the pressure at the middle point of the infiltration plateau, using $P_{in} = 4\Delta\gamma / D$, the excess solid–liquid interfacial tension ($\Delta\gamma$) can be assessed as $\Delta\gamma = P_{in} \times D / 4 = 45.75 \text{ mJ/m}^2$, with D being set to 30 nm. As the surface modification reaction time increases, more chlorotrimethylsilane molecules react with the nanopores, and the number density of hydrophobic surface groups becomes larger. Consequently, the repulsive force between the confined liquid molecules and the nanopore wall increases, which result in a increased P_{in} and $\Delta\gamma$. When the surface modification reaction time rises to 2 days, P_{in} increases to 7 MPa and the effective $\Delta\gamma$ is 52.5 mJ/m^2 .

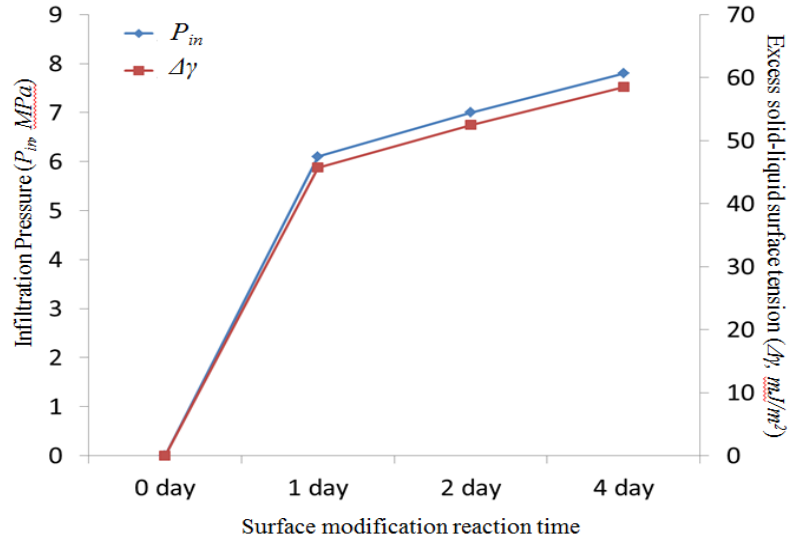


Figure 5-4 : The infiltration pressure (P_{in}) and The excess solid-liquid surface tension ($\Delta\gamma$) as functions of the surface modification time

As the surface modification time increases to 4 days, P_{in} rises to 7.8 MPa and the effective $\Delta\gamma$ becomes 58.5 mJ/m².

Figure 5-4 is shown that the infiltration pressure (P_{in}), the excess solid-liquid interfacial tension ($\Delta\gamma$) and surface modification time relationship is quite linear.

5.4 Concluding Remarks

The infiltration pressure (P_{in}) and the excess solid-liquid interfacial tension ($\Delta\gamma$) considerably increase with surface treatment time, which indicate that the enhanced hydrophobicity in nanopore wall can dominate the infiltration pressure (P_{in}) and the excess solid-liquid interfacial tension ($\Delta\gamma$).

6 PARTICLE SIZE EFFECTS

6.1 Introduction

In the previous chapters, the pore structure effects on nanofluidic behaviors are discussed in detail. Another major factor of the NMF liquid system design is the size of nanoporous particles, which will be the focus of this chapter.

A variety of C₈ surface modified Daiso silica gels were investigated. As shown in Table 6-1, the materials have the same average pore size, but different particle sizes, ranging from 10 μm and 100 μm .

Table 6-1 : Daiso silicas under investigation

Part No.	Pore volume (cm ³ /g)	Average Particle size (μm)	Average Pore size (nm)	Surface functional group	Carbon (wt%)
SP1000-20	0.9	20	100	Octyl group (C ₈)	1.3
SP1000-40/60	0.9	50	100	Octyl group (C ₈)	1.3
IR1000-60/230	0.9	100	100	Octyl group (C ₈)	1.3

6.2 Experimental

6.2.1 Raw Materials

Daisogel SP1000-20, Daisogel SP1000-40/60 and Daisogel IR1000-60/230 were obtained from Daiso Co., Ltd (Osaka, Japan). Ethanol (C₂H₅OH, 46.07 g/mol), pyridine (C₅H₅N, M.W. 79.1 g/mol), lithium chloride (LiCl, M.W. 42.39 g/mol), toluene (C₇H₈, M.W. 92.14 g/mol), chloro(dimethyl)octylsilane (C₁₀H₂₃SiCl, M.W. 206.83 g/mol) were purchased from the Sigma-Aldrich Chemical Co. (St. Louis, MO)

6.2.2 Materials Preparation

6.2.2.1 Surface modification of silica gels

The carbon content of the as-received silica gels was relatively low, compared with small-pore-sized silica gels, where the carbon content was typically ~ 10 %. In order to increase the degree of hydrophobicity, a surface treatment was conducted as the following:

- a. 1 g of silica gel particles was vacuum dried at 100 °C for 2 h and then immersed in 40 ml of dry toluene and refluxed at 80 °C for 3 h.
- b. The mixture was cooled down to room temperature.
- c. 1 mL of chloro(dimethyl)octylsilane (C_8) and 0.1 mL of pyridine (the catalyst) were dropped into the dispersive porous silica suspension.
- d. The mixture was reflux at 95 °C for 1 day and quenched in ethanol to room temperature.
- e. The reaction was filtered by an aspirator and the surface modified silica gel was washed with dry toluene and ethanol repeatedly.
- f. The C_8 Surface modified silica gel particles were dried in vacuum oven at 50 °C for 24 h.

6.2.2.2 Testing procedure

About 0.1 g of surface treated silica gel powders and 3.5 g of 46 wt% lithium chloride solution were sealed by two stainless steel pistons, equipped by reinforced O-rings (Figure 2-3). The cross-sectional area of the piston was 286.52 mm².

Lithium chloride was employed since it is neutral and has relatively small cation

and anion sizes. As the liquid phase was ionized, its molecular structure was changed. Around cations, water molecules form hydration shells, while anions are often unsolvated.

The energy absorption behaviors of the surface treated silica gels were measured by a type 5580 Instron machine. The loading rate was 5 mm/min and the peak pressure was 6.63 MPa

6.3 Results and Discussion

Figure 6-1 shows the sorption isotherm curves of NMF liquids based on various silica gels. The major difference between them is the particle size, which are 20 μm , 50 μm and 100 μm .

At the beginning stage, the quasi-static pressure cannot overcome the capillary effect of the nanopores. Thus, as the pressure is applied, the system volume variation is relatively small. When pressure reaches the critical value of infiltration (P_{in}), the increase in effective solid-liquid interfacial tension ($\Delta\gamma$) in nanopores can be balanced by the release of compression energy, and, thus the pressure-induced infiltration takes place.

The rapid system volume decrease associated with the liquid infiltration causes the formation of an infiltration plateau.

For self-comparison purpose, in the following discussion the critical infiltration pressure (P_{in}) is taken as the pressure at the middle point of the infiltration plateau.

Eventually, when the nanopores are fully occupied by the confined liquid, the infiltration process ends.

During unloading, a defiltration plateau is observed in the sorption isotherm curve of every silica gel under investigation.

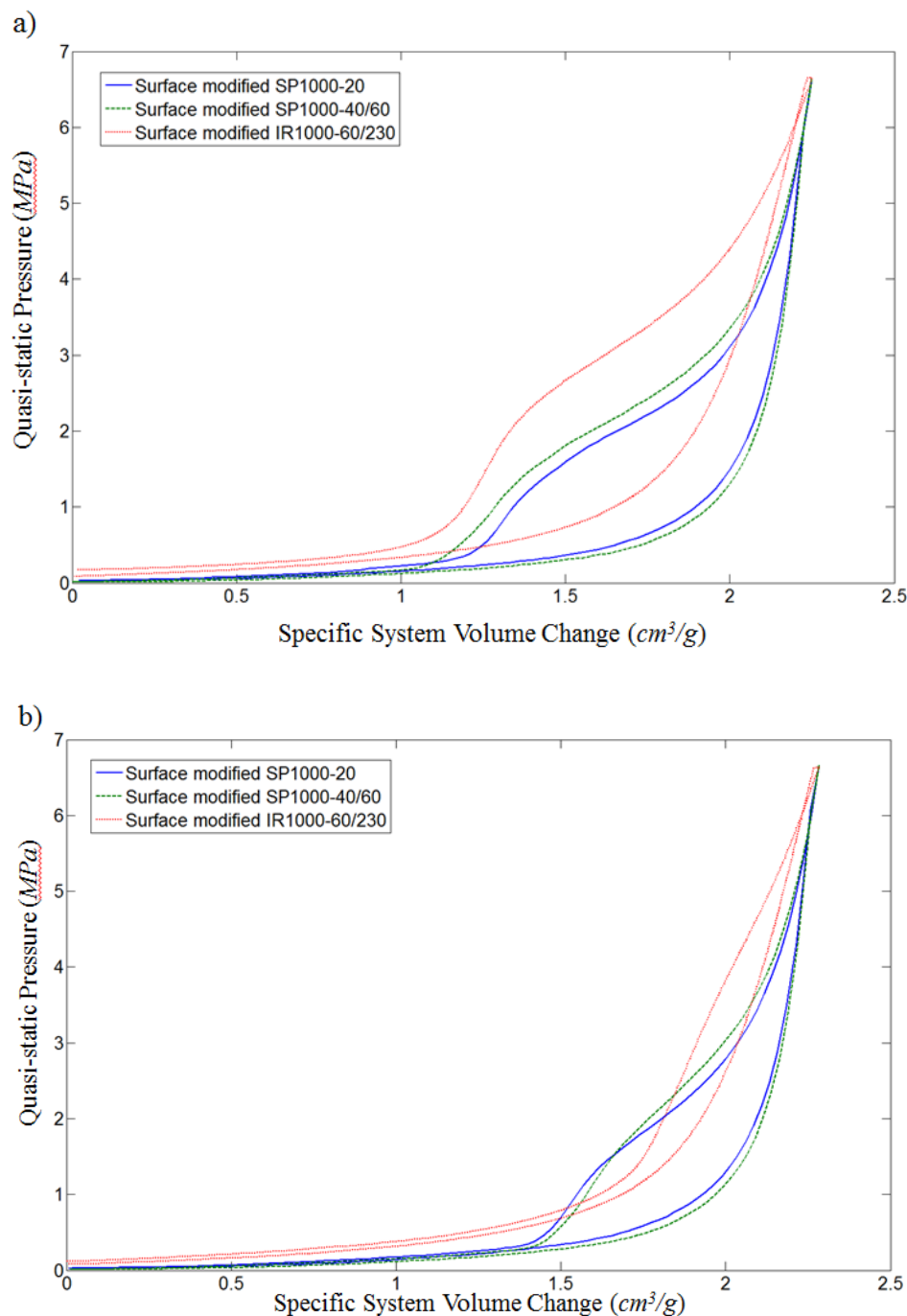


Figure 6-1 : The sorption isotherm curves of NMF liquids based on C8 surface modified silica gels for (a) the 1st loading and for (b) the 2nd loading

However, the width of defiltration plateau is somewhat shorter than the infiltration plateau; that is the system volume does not fully recover after a full loading-

unloading cycle, as a portion of the confined liquid remains in the nanopores.

When the liquid phase is introduced in the nanopores under the infiltration pressure (P_{in}), the work done by external loading can be assessed as $NP(\pi r^2 d)$, where r is the effective nanopore size, d is the effective infiltration depth, and N is the number of nanopores. As the hydrophobic nanopore surface is exposed to the liquid, the system free energy would increase by $N\Delta\gamma(2\pi r)d$. At the equilibrium condition, $\Delta\gamma = 2r/P_{in}$. Thus, the value of $\Delta\gamma$ can be calculated based on the measured. P_{in} is 2.48 MPa for the silica gel with the 20 μm particle size, $P_{in} \approx 2.48$ MPa, and the effective interfacial tension 62 mJ/m^2 , if r is taken as 50 nm. As the particle size is increased, P_{in} becomes higher. With the same pore volume and pore diameter, as the particle size increases to 50 μm , $P_{in} \approx 2.76$ MPa and $\Delta\gamma = 69 \text{ mJ/m}^2$; as the particle size is 100 μm , $P_{in} \approx 3.5$ MPa and $\Delta\gamma = 88 \text{ mJ/m}^2$. It is remarkable that as the particle size (r) (and also the infiltration depth (d)) increase, the value $\Delta\gamma$ rises somewhat linearly.

This must be attributed to the column resistance offered by the nanopore wall to the confined liquid, the details of which are still under investigation (Figure 6-2).

The effective energy absorption efficiency (E^*) of a NMF liquids can be assessed as $E^* = \Delta\gamma \cdot A$, where A is the specific surface area, as shown in Figure 6-3

It can be seen that increasing the particle size has a beneficial effect on E^* .

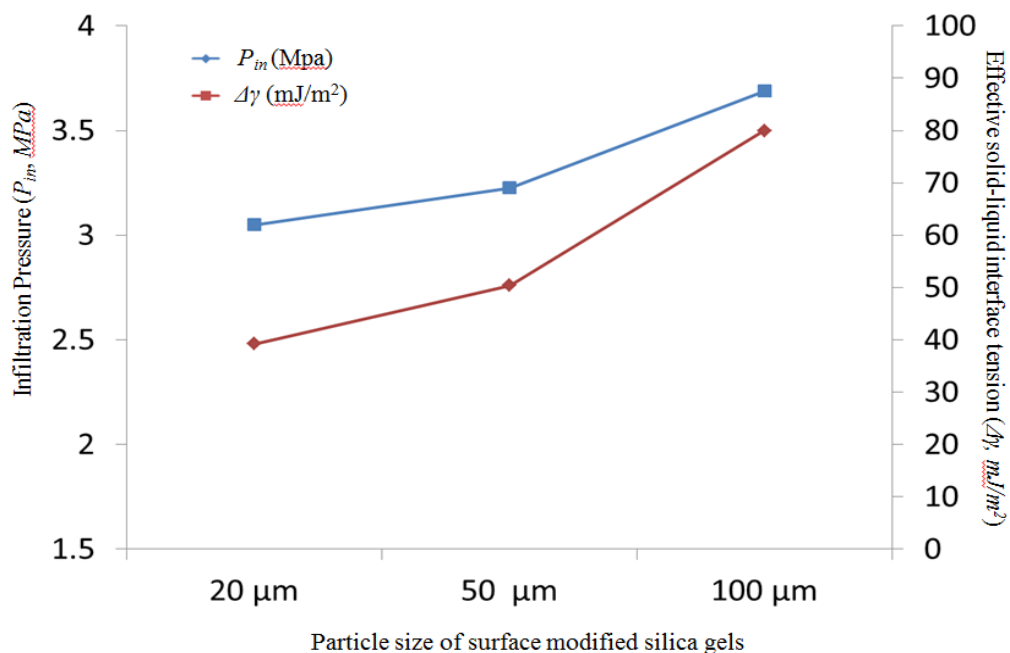


Figure 6-2 : The infiltration pressure (P_{in}) and the effective interface tension ($\Delta\gamma$) as functions of the particle size

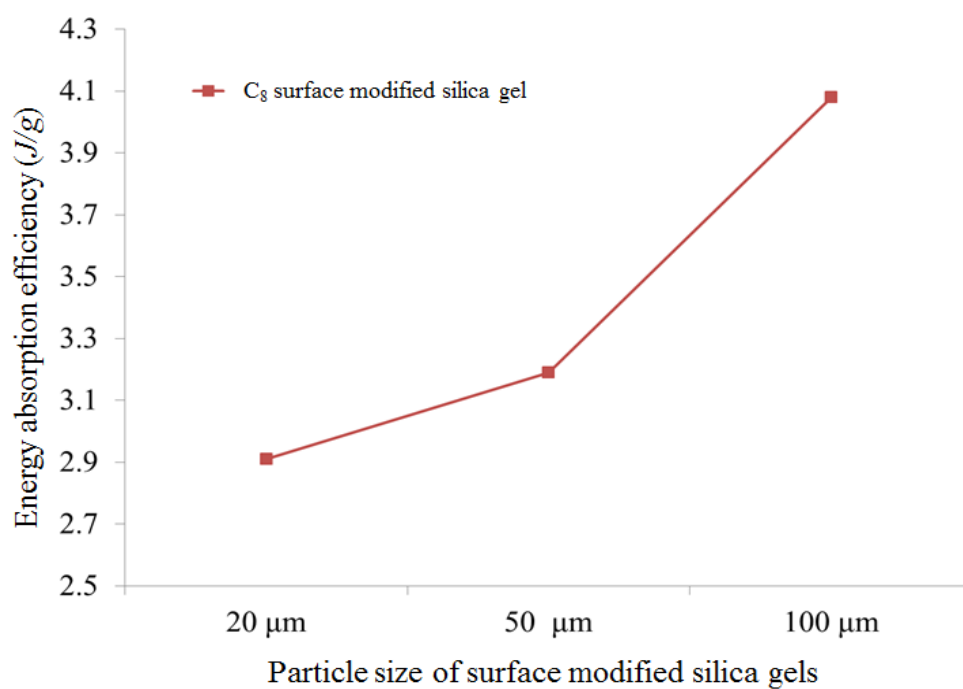


Figure 6-3 : Energy absorption efficiency (E^*) of NMF liquids as functions of the particle size

6.4 Concluding Remarks

As the particle size of silica gels increases, with the same surface modification process, pore size, and pore volume. The infiltration pressure would increase significantly, indicating that, with a larger infiltration depth, the effective interface tension and the energy absorption efficiency tend to be higher. Such a particle size effect is contradictory to the prediction of conventional interface theory for large surfaces, which much be related to the unique solid-liquid interaction characteristics in the continuing nanoenvironment, e.g. the column resistance.

7 REPEATABLE ENERGY ABSORPTION BEHAVIORS UNDER CYCLIC LOADING

7.1 Introduction

As discussed previously, with an appropriate pore structure, liquid phase, and surface properties, a NMF liquid can work repeatedly for multiple loading-unloading cycles. Therefore, they are potentially useful for damping applications. However, in previous experiments, usually we only tested the system performance in the first 2 – 4 cycles, due to the limitations on testing machine. In order to understand long-term behaviors of NMF liquids, fatigue-type experiments must be carried out.

In our current study, zeolite y (ZY) and hexagonal mesoporous silica (HMS) are employed to develop NMF samples

Hexagonal mesoporous silica (HMS) has well-defined structure (e.g. Figure 7-1), somewhat similar with the structure of MCM-41, but with a smaller domain size, which enables the formation of textural pores along with framework pores[86].

The average pore size of HMS under investigation is about 5.0 nm. The specific pore surface area is 1,032 m²/g and the specific pore volume is 1.68 cm³/g (Figure 7-2 and Figure 7-3)

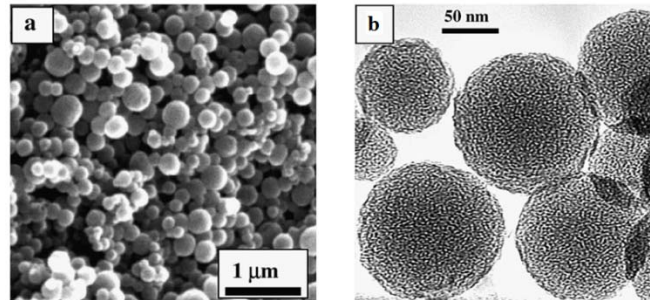


Figure 7-1 : (a) SEM and (b) TEM images of HMS sample [86]

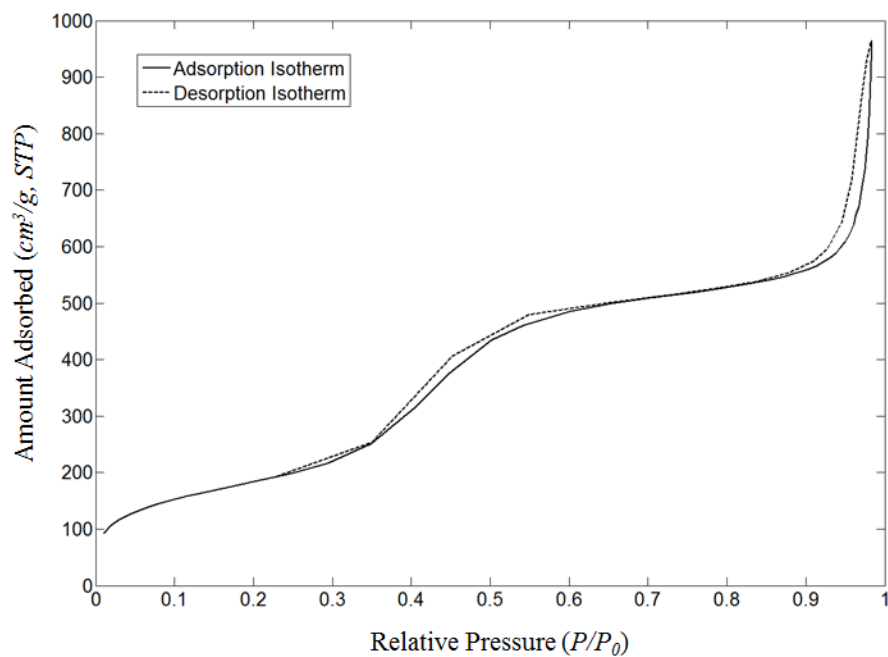


Figure 7-2 : The N₂ sorption isotherm at 77 K of the HMS

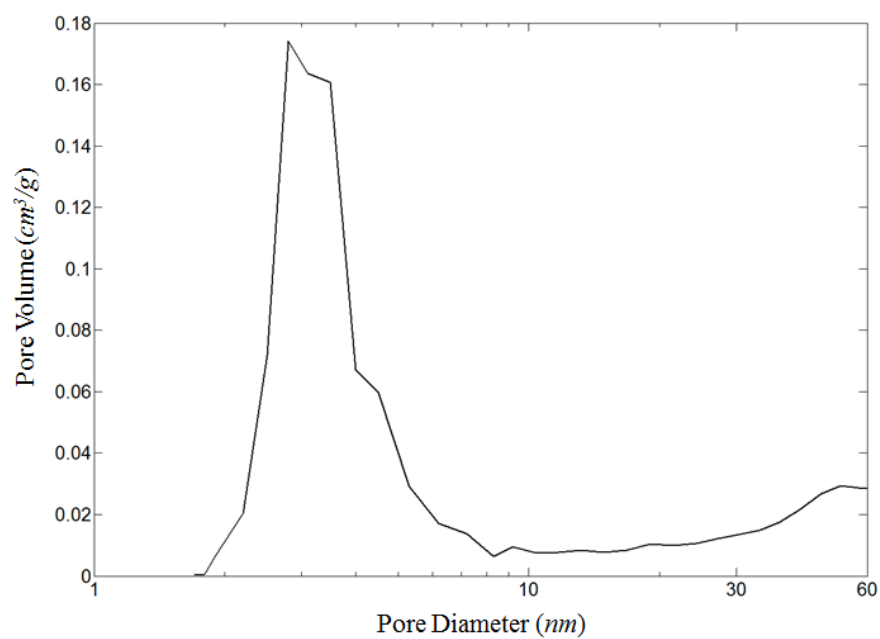


Figure 7-3 : The pore size distribution of the HMS

7.2 Experimental

7.2.1 Chemicals

Zeolite Y (CBV901) was obtained Zeolyst International Co. (Chicago, IL). Hexagonal Mesoporous Silica (HMS, SiO₂, M.W. 60.08 g/mol) was obtained from the Sigma-Aldrich Chemical Co. (St. Louis, MO). Ethylene diamine tetraacetic acid (EDTA, M.W. 292.24 g/mol), lithium chloride (LiCl, M.W. 42.39 g/mol), potassium chloride (KCl, M.W. 74.55 g/mol), toluene (C₇H₈, M.W. 92.14 g/mol), chlorotrimethyl silane (C₃H₉SiCl, M.W. 108.64 g/mol), ethanol (C₂H₅OH, 46.07 g/mol), pyridine (C₅H₅N, M.W. 79.1 g/mol) were obtained from the Sigma-Aldrich Chemical Co. (St. Louis, MO).

7.2.2 Materials Preparation

The ZY sample was treated as the following:

- a. 5 g of zeolite Y (CBV901 from Zeolyst) was added to 100 mL aluminum crucible and dried at 120 °C for 10 h.
- b. The aluminum crucible was placed in a tube furnace (Figure 7-4).
- c. Temperature was raised and kept at 400 °C for 0.5 h in a flow carrying saturated silicon tetrachloride. The material was then cooled down to room temperature.
- d. The heat treated ZY was washed with distilled water and dried at 120 °C for 10 h.
- e. The dried ZY was added into the aluminum crucible and placed into a tube furnace.

- f. The furnace temperature was raised and remained at 500 °C for 1 h, and then decreased gradually to room temperature.
- g. The heat treated ZY treated in saturated stream flow at 650 °C in a tube furnace for 48 h.
- h. 100 mL of 7.5 wt % ethylenediaminetetraacetic acid (EDTA) aqueous solution and the treated ZY were added to a 250 mL of 3-neck round-bottomed flask and the mixture was refluxed at 120 °C for 12 h.
- g. The mixture was filtered by an aspirator and the treated ZY was washed with water and ethanol repeatedly.
- h. The ZY was dried in vacuum at 80 °C for 12 h.



Figure 7-4 : The photo of tube furnace

The HMS was surface modified as the following:

- a. 3 g of hexagonal mesoporous silica (HMS) was vacuum dried at 100 °C for 2 h and then immersed in 40 ml of dry toluene and refluxed at 80 °C for 3 h.
- b. The mixture was cooled down to room temperature.
- c. 30 mL of chlorotrimethylsilane (C₁) and 3 mL of pyridine (the catalyst) were added into the dispersive HMS suspension.
- d. The mixture was reflux at 95 °C for 5 hrs and then quenched in ethanol to room temperature.
- e. The mixture was filtered by an aspirator and the C₁ surface modified HMS was washed with dry toluene and ethanol repeatedly.
- f. The C₁ Surface modified HMS was dried in vacuum at 50 °C for 24 h.

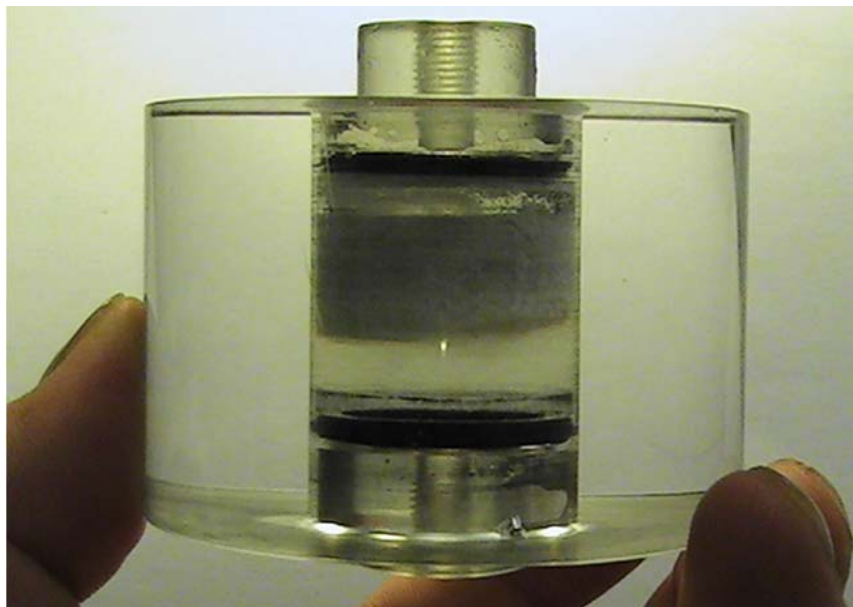


Figure 7-5 : The PMMA testing cell

The fatigue-type testing cell was prepared by sealing 0.3 g of heat treated ZY or HMS and 3.5 g of 26 wt % aqueous solution of potassium chloride (KCl) (for ZY) in a PMMA cylinder. Or 3.5 g of 46 wt % aqueous solution of lithium chloride (LiCl) (for

Figure 7-6 : The mechanical drawing of the fatigue testing machine.

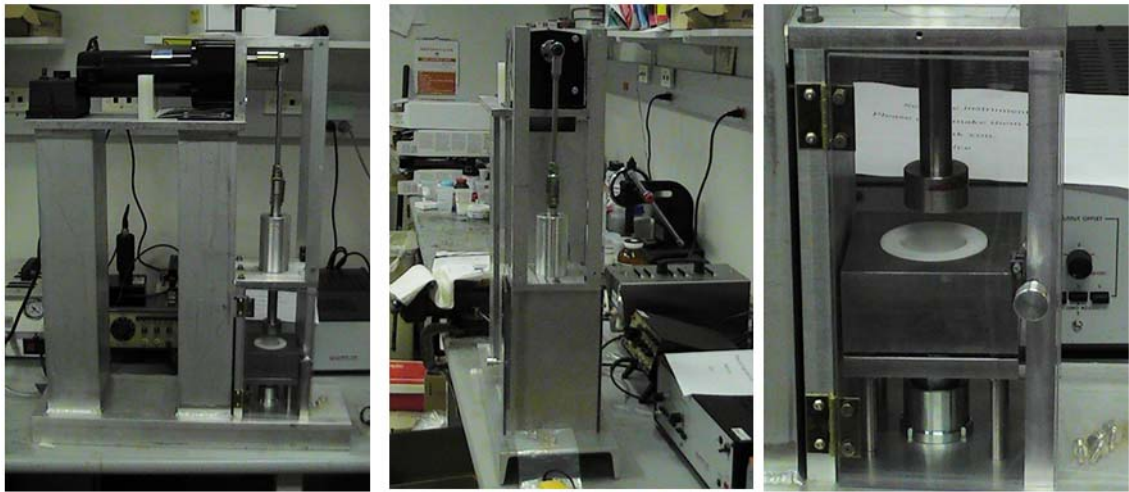


Figure 7-7 : The photos of the fatigue testing machine

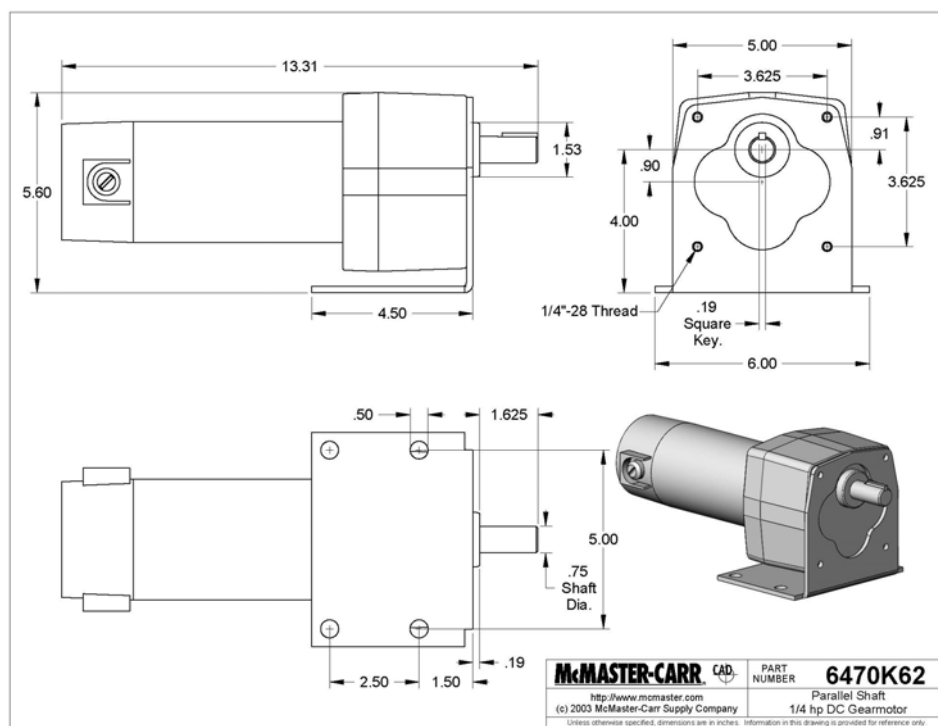


Figure 7-8 : The drawing of the DC gear

The machine consisted of a DC gear motor, a flying wheel, a connecting rod and,

a linear type bearing can be employed.

The quasi-static material behaviors were measured by a type 5580 Instron machine after the ZY or HMS sample was fatigue-tested for a certain loading cycles (Figure 2-4). The loading rate was 3 mm per min.

7.3 Results and Discussion

Figure 7-10 shows the energy absorption behavior of ZY in 26 wt% potassium chloride solution.

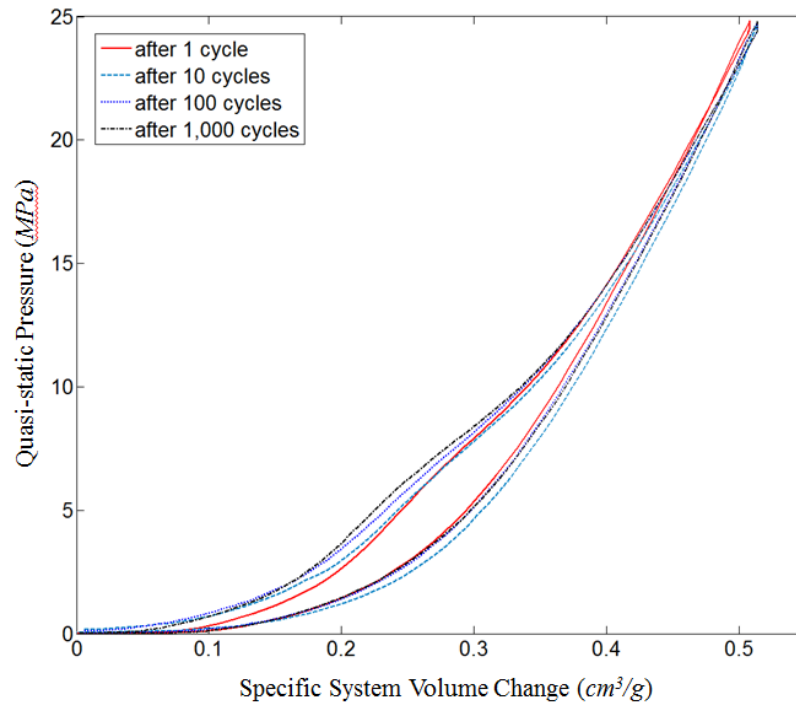


Figure 7-10 : Energy absorption behaviors of ZY

The Heat treated ZY is quite hydrophobic[87]. Therefore, under ambient pressure when the ZY is immersed in the potassium chloride solution, the liquid cannot enter the nanopores. When an external pressure is applied by the upper piston, the liquid can be intruded into the nanopores.

The widths of infiltration and defiltration plateaus for each cycle are the same, as they should be. However, as the number of fatigue loading cycle increases, the infiltration pressure rises, indicating that the effective interfacial tension becomes higher, probably due to the ion exchange between the confined liquid and the nanopore walls. That is, as the defect sites in the nanoporous phase are deactivated, the nanopore surfaces tend to be more non-polar.

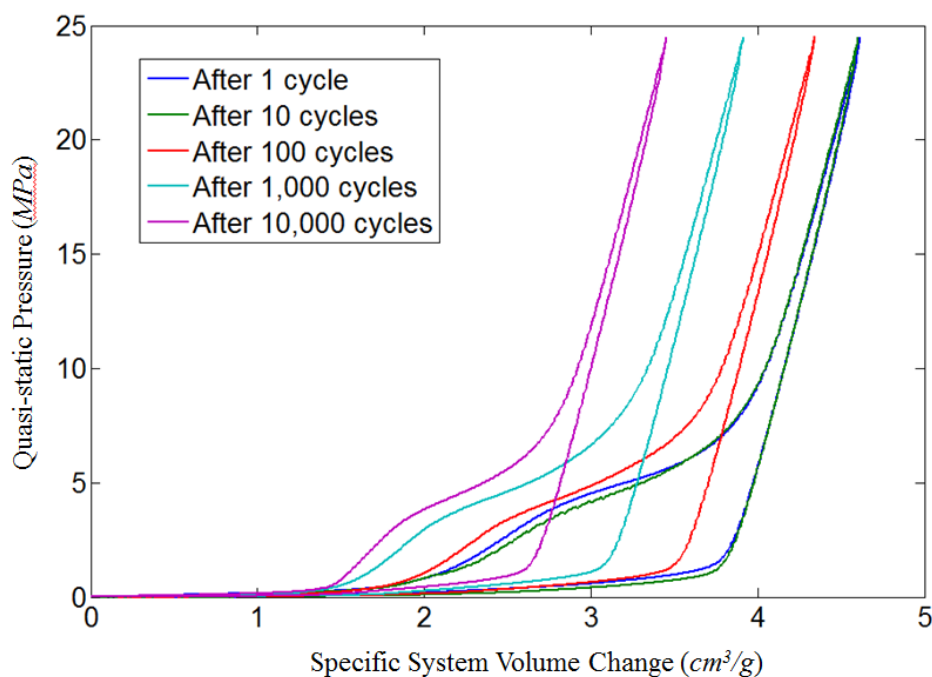


Figure 7-11 : The energy absorption behaviors of surface modified HMS

Figure 7-11 shows the HMS behaviors, as the number of fatigue loading cycle is increased, while the infiltration pressure remains unchanged, the width of infiltration plateau decreased significantly.

In the first 1,000 cycles, the reduction in infiltration plateau width is somewhat negligible. After 10,000 cycles, the effective nanopore volume decreases by 25 %.

Clearly, as the loading cycles continues, a portion of the grafted C_1 groups are deactivated, so that the confined liquid does not come out during unloading . This observation fits with the leachy phenomena reported previously.

7.4 Concluding Remarks

For heat treated ZY, as the number of fatigue loading cycle increases, the infiltration pressure also increase, indicating that the effective interfacial tension becomes higher. That is, the nanopore surfaces tend to be more non-polar.

For C_1 surface modified HMS, as the number of fatigue loading cycle is increased, while the infiltration pressure remains unchanged, the width of infiltration plateau decreased significantly. That is, a portion of the grafted C_1 group are out of working, which cause the defiltration to be difficult.

8 NOVEL SYNTHETIC METHODS OF NANOPOROUS SILICA WITH CONTROLLABLE PORE STRUCTURES

8.1 Introduction

8.1.1 Background

The ultra-high surface areas of nanoporous materials enable a large number of applications, which has opened new research fields. In order to apply them in a broader range of industrial fields, the materials cost should be minimized.

Moreover for specified functional requirements, the pore surface area, the pore size, the surface properties and the pore structure must be controlled appropriately.

In this chapter, a powerful synthetic method of nanoporous silica will be investigated, which leads to a relatively low material cost as well as controllable surface area, pore size, pore structure, and surface properties.

8.1.2 Porous glass

Porous silica glass has many applications such as desalination membranes[88], membranes for mixed gas separation, enzyme immobilization matrix, and catalyst support[89]. It is a unique material, with interconnecting pores of small diameters of 4 nm, large pore volume. Its processing was first studied by Corning Glass Co. in early 1930th [90]. According to its composition and synthetic method, the material can have a narrow pore distribution, a high thermal resistance, high chemical durability, high bio-stability, high compressive strength, and high compatibility with various surface modification processes[90]

8.2 Experimental

8.2.1 Chemicals

Silica (SiO_2 , M.W. 60.08 g/mol), boric trioxide anhydride (B_2O_3 , M.W. 69.62 g/mol), sodium oxide (Na_2O M.W. 61.98 g/mol), sodium hydroxide (NaOH , M.W. 39.99 g/mol), hydrochloric acid (HCl , M.W. 36.46 g/mol), lithium chloride (LiCl , M.W. 42.39 g/mol), toluene (C_7H_8 , M.W. 92.14 g/mol), chloro(dimethyl)octylsilane ($\text{C}_{10}\text{H}_{23}\text{SiCl}$, M.W. 206.83 g/mol), chlorotrimethyl silane ($\text{C}_3\text{H}_9\text{SiCl}$, M.W. 108.64 g/mol), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 46.07 g/mol), pyridine ($\text{C}_5\text{H}_5\text{N}$, M.W. 79.1 g/mol) were obtained from the Sigma-Aldrich Chemical Co. (St. Louis, MO).

8.2.2 Materials Preparation

8.2.2.1 Nanoporous silica

The synthetic procedure of the nanoporous silica is:

- a. 30g of silica (SiO_2), 9.85g of boric trioxide (B_2O_3) and 3g of sodium oxide (Na_2O) were added to an agate mortar.
- b. The powders mixture was ground and mixed with a pestle in the agate mortar for 1 h.
- c. The mixture was added into a 100 mL Pt crucible.
- d. The Pt crucible was placed in a box type furnace, at the temperature of 1,550 °C for 5 h.
- e. The Pt crucible was taken out by a pair of steel forceps and was placed on a firebrick at room temperature.
- f. The Pt crucible was air cooled to room temperature.

- g. The Pt crucible was placed back to the box type furnace.
- h. The temperature was increased with a rate of 3 °C/min to 720 °C, and was kept at 720 °C for 24 h.
- i. The Pt crucible was taken out and air cooled.
- j. The phase separated glass was fractured and ground by a pestle in an agate mortar for 30 min.
- k. 100 mL of 3N HCl and the phase separated glass powders were added into a 2 – neck round bottom flask with a reflux condenser, and were refluxed at 95 °C for 24 h.
- l. The mixtures were cooled down to room temperature and then filtrated by an aspirator and washing repeatedly with distilled water.
- m. Dry the powders at 120 °C for 24 hrs.
- n. 50 mL of 0.5 N NaOH solution and 2 g of the acid leached silica powders were added in a 100 mL beaker and stirred for 5 h at room temperature, followed by filtration by an aspirator and then washed with distilled water several times.
- o. Dry the powders at 120 °C for 24 hrs.
- p. The base etched porous silica powders were placed into the Pt Crucible in the box type furnace and then temperature was increased to 720 °C at a rate of 5 °C /min
- q. The temperature was kept at 720 °C for 2 h and the materials was then air cooled to room temperature.

8.2.2.2 Surface modification of nanoporous silica

The surface modification procedure is:

- g. 1 g of acid etched / base etched silica was first vacuum dried at 100 °C for 2 h and then immediately immersed in 40 ml of dry toluene and refluxed at 80 °C for 3 hrs with vigorous stirring.
- h. The mixture was cooled down to the room temperature.
- i. 1 mL of chloro(dimethyl)octylsilane (C_8 treatment) and 0.1 mL of pyridine were added to the dispersive mixture.
- j. The mixture was reflux at 95 °C for 5 h and then quenched in ethanol to room temperature.
- k. The mixture was filtered by an aspirator and washed with dry toluene and ethanol repeatedly.
- l. The C_8 Surface modified nanoporous silica was dried in vacuum at 50 °C for 24 h.
- m. The nanoporous silica powder modified by C_8 groups was end capped by C_1 groups for three times, filtered, washed and dried.

8.2.2.3 Pressure induced infiltration test

0.1 g of the C_8 treated, C_1 endcapped acid etched and base etched nanoporous silica and 3.5 g of 46 wt% lithium chloride solution were sealed in a stainless steel testing cell, which had a stainless steel cylinder and two pistons, sealed by reinforce O-rings (Figure 2-3). The cross-sectional area of the pistons was 286.52 mm². The lithium chloride was added to amplify the surface treatment effect.

By using a 5580-type Instron machine (Figure 2-4), the upper piston was compressed into the cylinder at the rate of 0.3 mm/min, applying a quasi-hydrostatic pressure on the liquid phase. After reaching 6.6 MPa, the piston was moved back at the same speed. Similar loading-unloading cycles were repeated for multiple times.

8.3 Results and Discussion

The nanoporous glass mainly contains SiO_2 , Na_2O , B_2O_3 , Al_2O_3 as well as other oxide materials. The glass phase can be separated into a SiO_2 rich phase and a B_2O_3 - Na_2O rich phase at ambient condition. In the phase separated glass, the amount of silica-rich phase is larger, and it forms the framework. The sodium-boron oxide phase forms nanochannels.

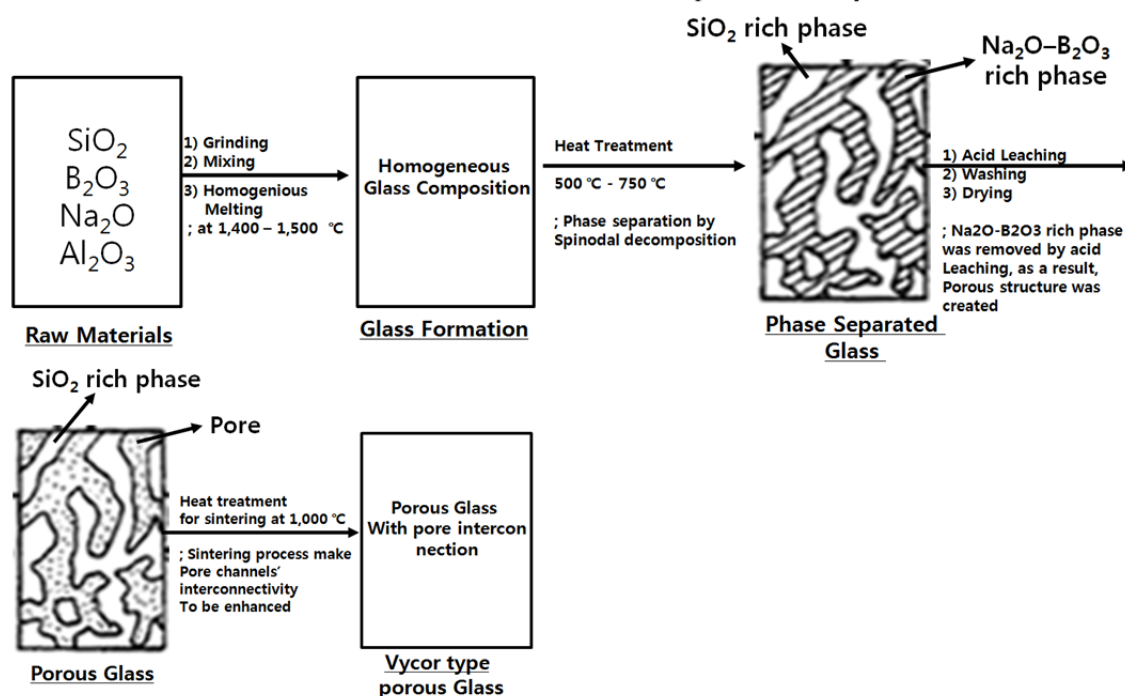


Figure 8-1 : General synthetic procedure of VICOR® porous glass by phase separation method[90]

Figure 8-1 depicts the general procedure of phase separation methods. In

Figure 8-1, after glass phase is formed, additional heat treatment at 500 °C – 750 °C induces phase separation. The glass phase can be separated to the SiO₂ rich phase and the B₂O₃-Na₂O rich phase by spinodal decomposition.

The B₂O₃-Na₂O rich phase can be dissolved in an acid solution. Thus, a porous structure can be created by leaching the nano-channel shaped B₂O₃-Na₂O rich phase with an acid [90] (Figure 8-2a). Note that in the phase diagram of SiO₂-B₂O₃-Na₂O[91], the separated SiO₂ rich phase contains a small amount of B₂O₃-Na₂O, and the B₂O₃-Na₂O rich phase contains a few percent of SiO₂[90].

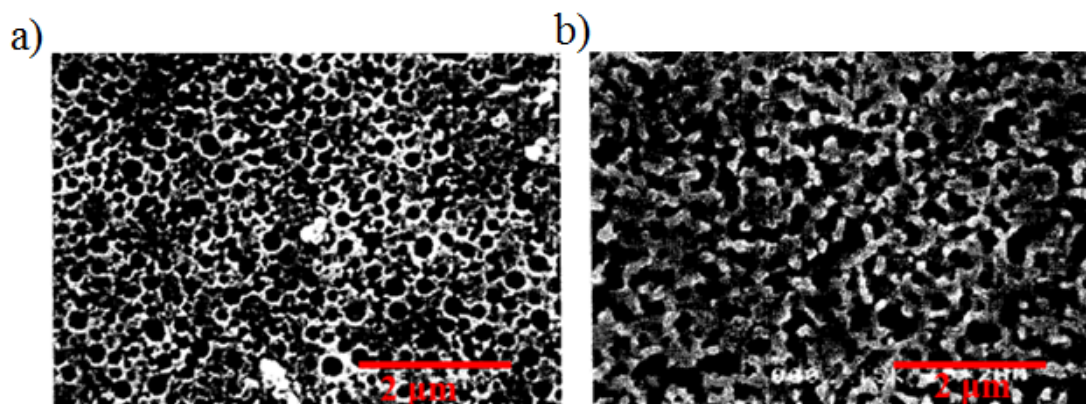


Figure 8-2 : Typical structures by phase separation (a) isolated structure after the removal of B₂O₃-Na₂O rich phase , b) Interconnecting structure after removal of remained SiO₂ colloid)[90]

During the acid leaching process, SiO₂ in the B₂O₃-Na₂O phase remained as colloids, which leads to the formation of a fine structure containing pores. The residual SiO₂ colloids in the pores should be removed to enhance the interconnectivity and to increase the pore size (Figure 8-2b)[90].

Immersing phase separated glass in a base solution is the most effective way to remove the SiO₂ colloids in the pores[90]. The pore size distribution before and after

the base treatment is shown in Figure 8-3.

The pore structure can be controlled by adjusting the thermal treatment temperature and time. A higher temperature and a longer time would result in a larger average pore size[90].

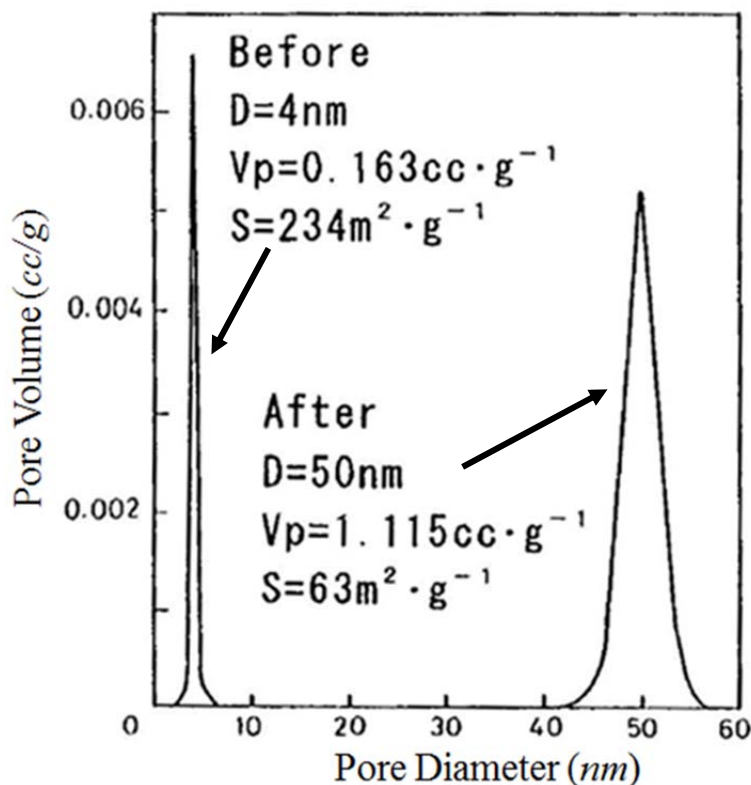


Figure 8-3 : The pore size distributions before and after the base treatment[90]

The synthesis process of the nanoporous glass is cost efficient, controllable, and over the pore size and a relatively simple (compare to the templating or nanocasting methods[2, 21])

Figure 8-4 is shows our synthesis procedure of nanoporous silica, inspired by the above discussion.

Transparent and homogeneous glass melt that contained SiO_2 , B_2O_3 , Na_2O was

obtained at 1,550 °C. In order to produce nanoporous powders with uniform pores, the homogeneity of the glass melt was critical. Air quenching was employed to prevent the phase separation of B_2O_3 , and Na_2O phase [92].

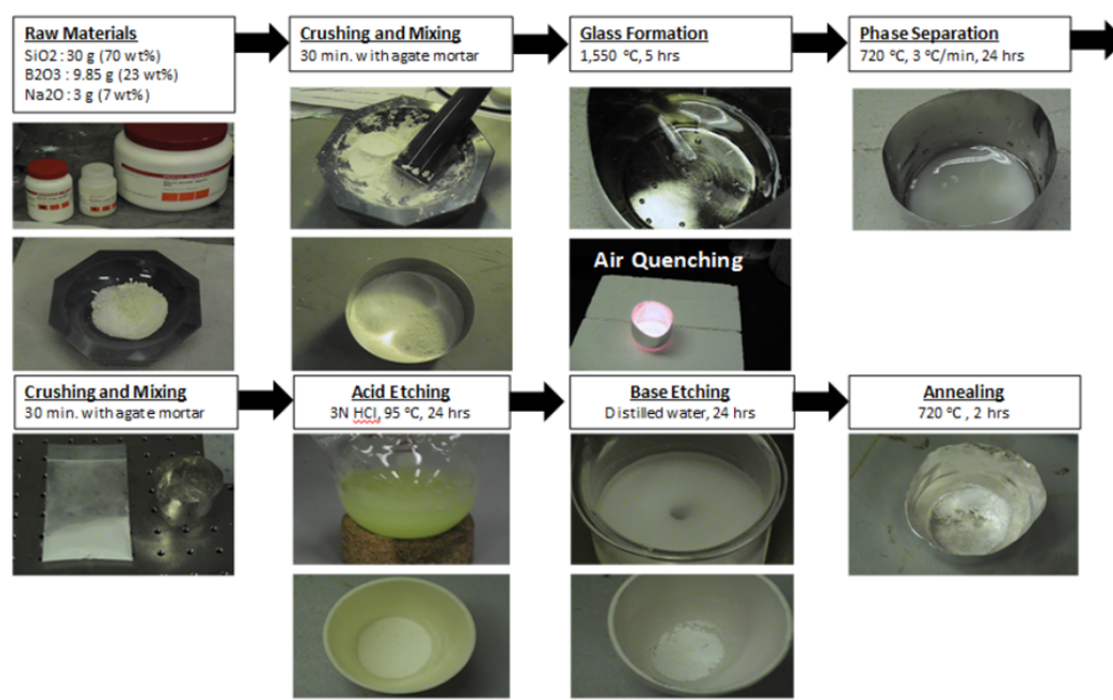


Figure 8-4 : The synthesis process of the nanoporous silica

Figure 8-4 shows that the glass melt was no longer transparent and the color changed to turbid after phase separation at 720 °C, which may be related to the inhomogeneity of nano/micro-structure. That is, grain boundaries between different phases and nanochannel shaped B_2O_3 - Na_2O phase were formed.

The B_2O_3 - Na_2O phase can be removed by an acid and as a result, nanoporous SiO_2 had a narrow pore size distribution. The average pore size was 4.5 nm and the pore volume was $0.079 \text{ cm}^3/\text{g}$ (Figure 8-5 and Figure 8-6).

The relatively small pore volume was caused by colloidal SiO_2 particles in the

pores, which also reduced the interconnectivity.

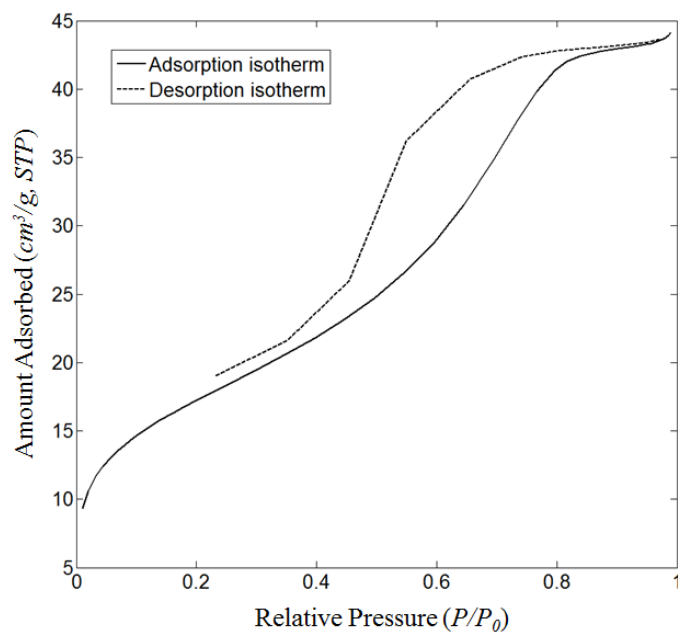


Figure 8-5 : N_2 sorption isotherm at 77 K on the nanoporous SiO_2 after refluxing at 95 °C for 24 h with 3N HCl

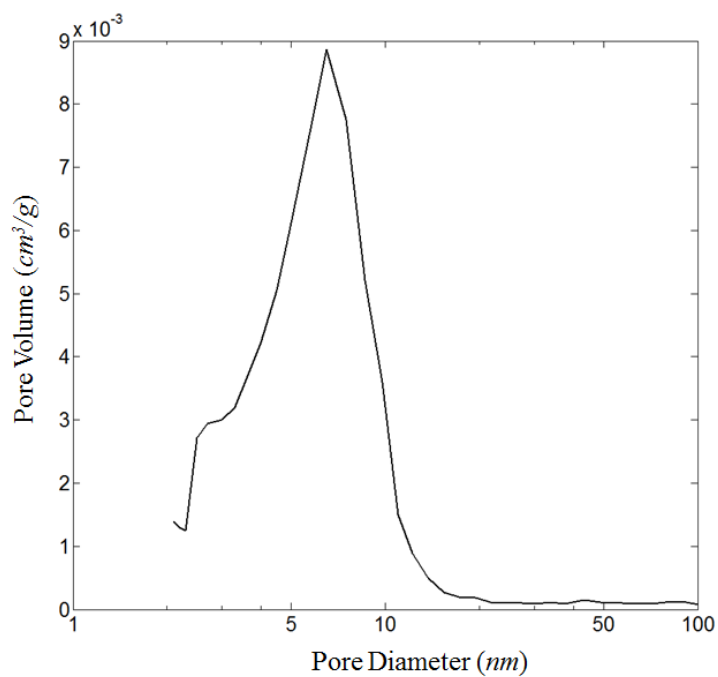


Figure 8-6 : The pore size distribution of the nanoporous SiO_2 after refluxing at 95 °C for 24 h with 3N HCl

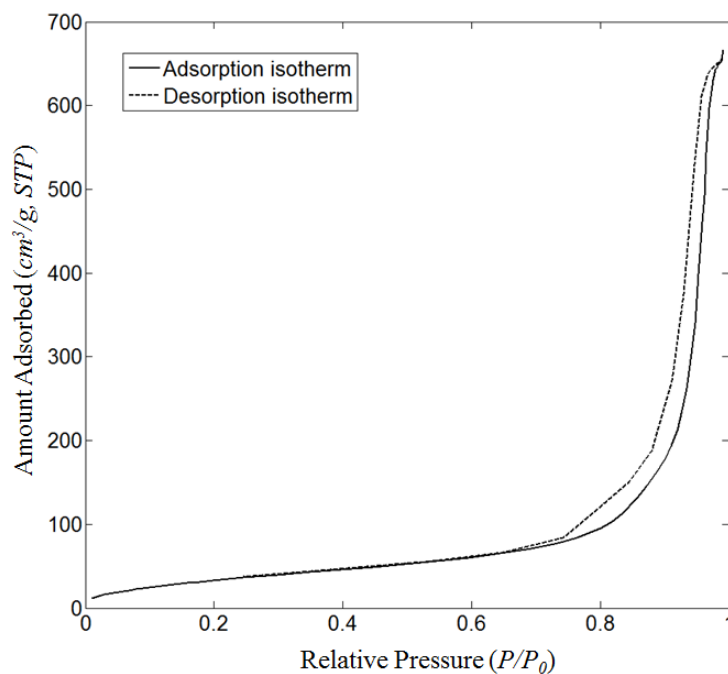


Figure 8-7 : N_2 sorption isotherm at 77 K of the nanoporous SiO_2 after stirring at 25 °C for 5 h in 0.5 N NaOH

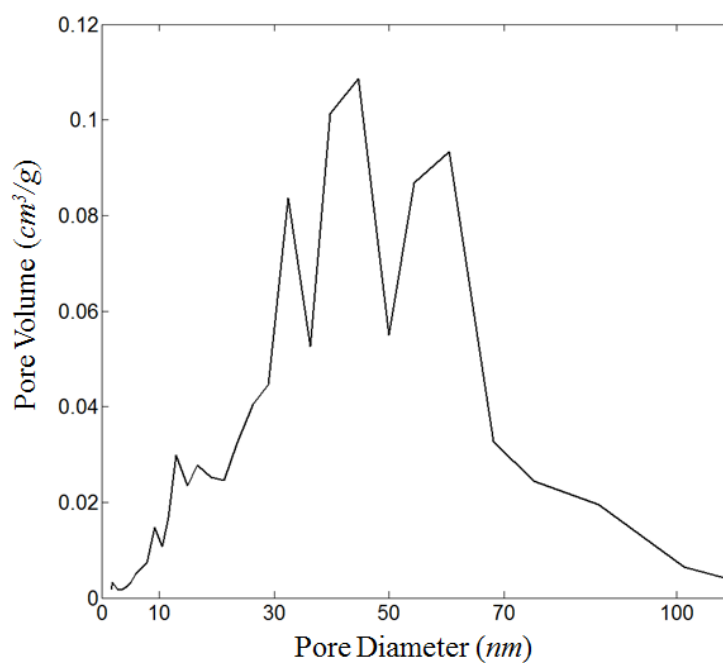


Figure 8-8 : The pore size distribution of the nanoporous SiO_2 after stirring at 25 °C for 5 h in 0.5 N NaOH

A base can dissolve the colloidal SiO₂ particles in the nanochannels, enlarging the pore volume and enhancing the interconnectivity.

Figure 8-7 and Figure 8-8 shows the pore size distribution after the base treatment. After the base treatment, the mesoporous SiO₂ had an average pore size of 24.3 nm and the pore volume was 1.02 cm³/g (Figure 8-8).

In order to increase the degree of hydrophobicity of nanopore walls, surface modification with chlorodimethyloctyl silane (C₈) and end-capping with chlorotrimethyl silane (C₁) was performed. A 46 wt% lithium chloride solution was used as the promotor to enhance the performance of NMF liquid. The C₁ end-capping and, C₈ surface modification procedure was similar as Figure 3-4.

During the surface treatment process, chlorodimethyloctyl silane molecules react with the hydroxyl sites at the silica inner surfaces and form a monolayer of dimethyloctylsilyl groups. As the polar hydroxyl sites are deactivated by the nonpolar surface groups, the nanopore walls become hydrophobic, and this effect can be amplified by adding electrolytes in the liquid phase. Figure 8-9 shows the typical energy absorption behavior of a nanoporous glass based NMF liquid. In the low pressure range, no infiltration can be detected. When the pressure is relatively high and the liquid starts to enter the nanopores, the system volume decreases rapidly, leading to the formation of the infiltration plateau. When the nanopores are filled, the infiltration plateau ends.

Upon unloading, the defiltration of confined liquid is apparently difficult. The defiltration of confined liquid is highly dependent on the structure of nanochannels, the effective pore size, and the surface properties[29].

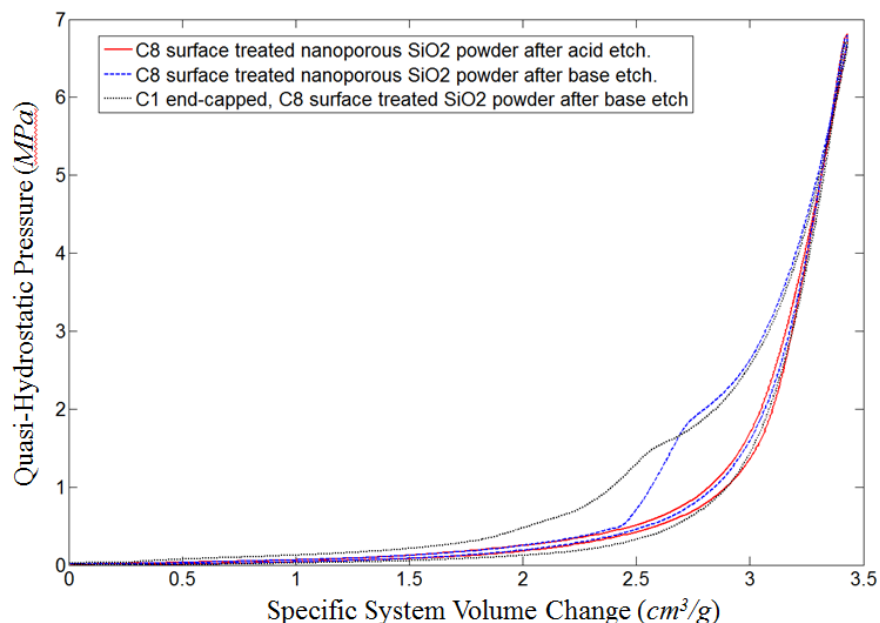


Figure 8-9 : Energy absorption behaviors of NMF liquids based on the surface treated synthetic nanoporous SiO₂. The liquid phase is saturated aqueous solution of LiCl

Figure 8-9 also shows that the removal of colloidal SiO₂ particle in nanochannels resulted in an infiltration plateau at a relatively low pressure and C₁ end-capping can enhance the performance of NMF liquid.

In the pressure range of the current study, there is no infiltration plateau for the synthetic nanoporous SiO₂ samples immediately after the acid etching process. That is, colloidal SiO₂ particles in nanopores significantly suppress liquid infiltration. After base etching, the specific system energy absorption efficiency is increased by nearly 25 %, which is further increased by about 12% by C₁-endcapping (Figure 8-10).

In the 2nd loading-unloading loop, the infiltration plateau of C₁-end capped, C₈ surface treated nanoporous silica powder is not detected (Figure 8-11).

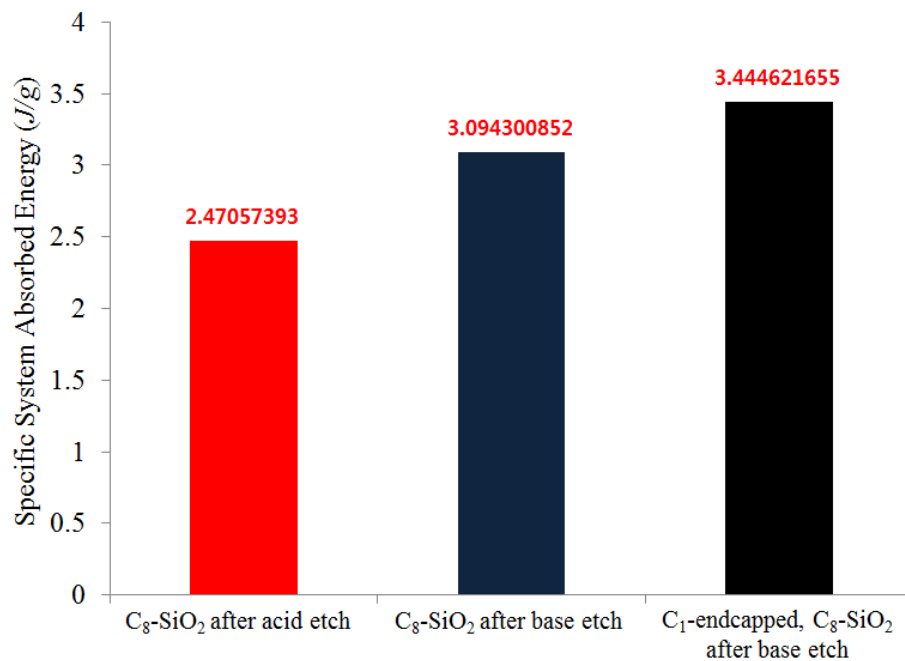


Figure 8-10 : The specific energy absorption efficiency

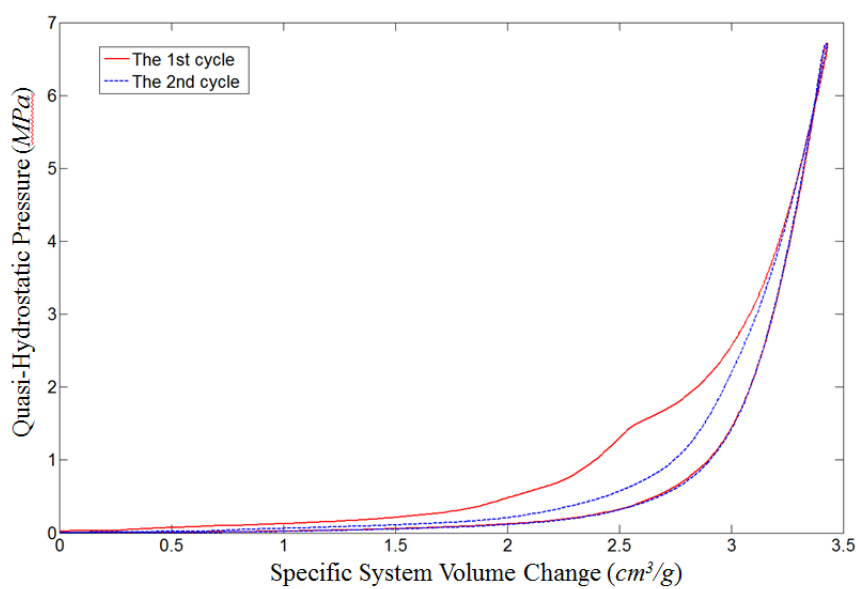


Figure 8-11 : Energy absorption behaviors of NMF liquid based on C₁-endcapped, C₈-surface treated synthetic nanoporous SiO₂

8.4 Concluding Remarks

A nanoporous silica was synthesized by phase separation method, which is cost-efficient and simple. The pore size and pore connectivity can be precisely controlled.

The NMF liquids based on the synthesized materials shows significant energy absorption characteristics. However, the motion of confined liquid is irreversible.

9 CONCLUSIONS

The energy absorption behavior of a NMF liquid is dependent on the pore structure (pore size, pore volume, pore connectivity, etc), the surface properties, the particle size, the liquid composition, and the loading mode (e.g. the loading rate).

In an investigation on a ZSM-5 zeolite, it is noticed that when the anion concentration is relatively low, its influence on the ion transport pressure is negligible; when the anion concentration is relatively high, its effect becomes significant. The ion size also has a pronounced influence on the system free energy. These phenomena can be attributed to the confined ion structures in nanopores.

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 related to the chainlike 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 indispensable factor that must be taken into account.

Repeated energy absorption is achieved by using either HMS or ZY. As the loading cycle continues, no system degradation can be observed for ZY, but the effective compressibility of HMS decreases as the number of loading cycles exceeds 10,000, probably due to leaching.

As the particle size of a silica gel is increased, with the pore size. And the pore volume remained the same, the infiltration pressure rises significantly, which is contradictory to the conventional theory. This should be associated with the column resistance between the nanopore wall and the confined liquid, suggesting that increasing particle size can be beneficial to the energy absorption efficiency.

The hydrophobicity of the surface of nanoporous carbon can be controlled electrically. The inner surface group was grafted by surface modification with trimethylsilyl group and MHA, so the inner surface groups are partly crooked at initial stage, and the nanopore walls are hydrophobic. Through an electric field, the surface properties can be controlled, as the negatively charged carboxylate groups are repelled or attracted by the surface charges. Thus, the surface wettability can be controlled electrically.

The infiltration pressure and the excess solid-liquid interfacial tension considerably increase with surface treatment time of silica gel, which indicate that the enhanced hydrophobicity in nanopore wall can dominate the infiltration pressure (P_{in}) and the excess solid-liquid interfacial tension ($\Delta\gamma$).

Nanoporous silica can be synthesized through phase-separation method, which is cost effective, simple and controllable compared with the templating technique. The so-prepared NMF liquids behave similarly at the first loading. However, in order to achieve reversible confined liquid motion, the interconnectivity among nanopores as well as the crystalline properties should be enhanced.

APPENDIX A. LOADING RATE EFFECTS

A.1 Introduction

Molecular dynamics simulations show that liquids in nanopore tends to have much smaller viscosity compared with their bulk counter parts [52, 93, 94].

For instance, Li[95] reported the damping properties of a hydrophilic nanoporous silica plate in water. When a pressure was applied on the plate, water transported from the compressive parts to the tensile parts. As a result, a certain amount of energy was dissipated. The energy absorption efficiency, which was measured by the amount of energy absorbed by a unit mass of material, however, was lower than the expected level, indicating that the effective liquid viscosity in nanopores was smaller than that of the bulk phase.

In our experiments discussed in previous chapters, we reported that the capillary effect of nanoporous materials is more pronounced and controllable[96]. When applying a quasi-static pressure on a system containing hydrophobic nanoporous silica particles, the liquid phase could be forced into the nanopores. In the dynamic experiment, the energy absorption efficiency was considerably increased, suggesting that viscosity effects might be significant as the loading rate is high.

We investigated the confined liquid motion in a Zeolite Y (ZY). ZY has a FAU (faujasite) structure and its 3-dimensional pores are perpendicular to each other. The pores consist of 12-membered oxygen rings (7.4 Å), 6-membered oxygen rings, and 4-membered oxygen rings. Each member represents a tetrahedral unit (the secondary building unit, TO_4 , where T is Si or Al as shown by Figure A-1, Figure A-2 and Figure A-3[97, 98]). A cavity in a ZY is surrounded by ten sodalite cages (truncated

octahedra) connected on their hexagonal faces. The unit cell is cubic ($a = 24.7\text{\AA}$), with a $Fd3m$ symmetry. ZY typically has an effective pore surface area of $710\text{ m}^2/\text{g}$, an effective pore volume of $0.22\text{ cm}^3/\text{g}$ [99] and a Si/Al ratio of 80[87]. It thermally decomposes at 793°C [98].

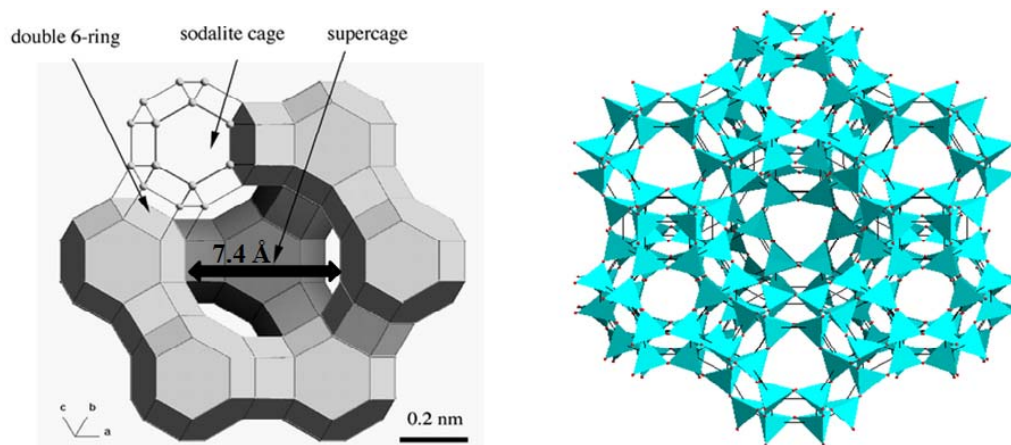


Figure A-1 : Illustration of Zeolite Y (FAU) structure [97]

ZY is mainly used as cracking catalyst, e.g. in the acidic form in the petroleum refinery catalytic cracking units. ZY is also used in hydrocracking units as a platinum/palladium support to increase the aromatic content [100].

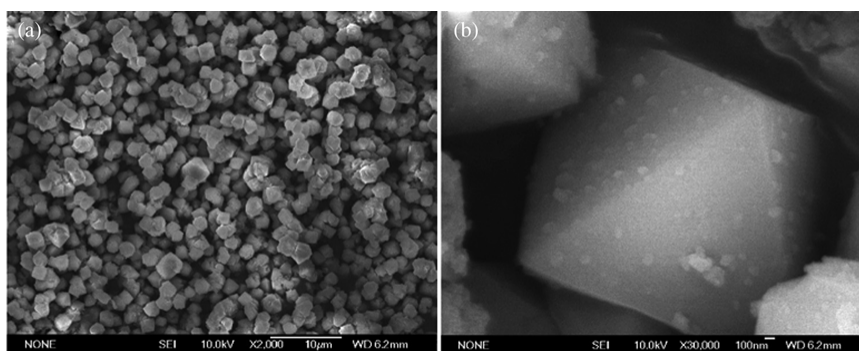


Figure A-2 : SEM images of Zeolite Y : (a) x2,000, (b) x3,000 [101]

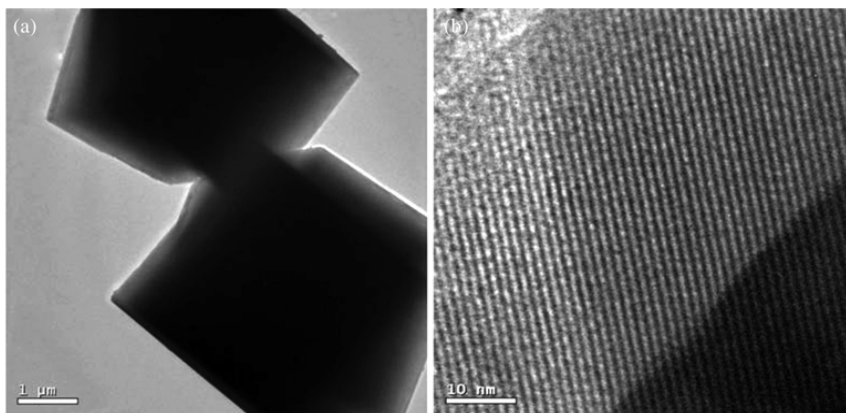


Figure A-3 : (a) TEM and (b) HR-TEM images of zeolite Y [101]

A.2 Experimental

Zeolite Y (CBV901) was obtained from Zeolyst International Co. (Chicago, IL). Ethylene diamine tetraacetic acid (EDTA, M.W. 292.24 g/mol), potassium chloride (KCl, M.W 74.55 g/mol), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 46.07 g/mol) were obtained from Sigma-Aldrich Chemical Co. (St. Louis, MO).

The Zeolite Y sample was treated as following:

- a. 5 g of zeolite Y (CBV901 from Zeolyst) was added to a 100 mL aluminum crucible and dried at 120 °C for 10 h.
- b. The aluminum crucible was placed in a tube furnace (Figure 7-4).
- c. At 400 °C, ZY was treated in a N_2 flow with saturated silicon tetrachloride vapor for 0.5 h and then cooled down to room temperature.
- d. The heat treated ZY was washed with distilled water and dried at 120 °C for 10 h.
- e. The dried ZY was added to an aluminum crucible and placed into a tube furnace.

- f. The temperature was kept at 500 °C for 1 h and then cooled down to room temperature.
- g. The heat treated ZY was added to a hydrothermal reactor at 650 °C for 48 h in a saturated steam flow.
- h. 100 mL of 7.5 wt % ethylenediaminetetraacetic acid (EDTA) aqueous solution and the treated ZY were added to a 250 mL 3-neck round-bottomed flask, and the mixture was refluxed at 120 °C for 12 h.
- i. The mixture was filtered by an aspirator and the pre-treat ZY was washed with water and ethanol repeatedly.
- j. The filtered ZY was dried in vacuum at 80 °C for 12 h.

The testing cell was prepared by sealing 0.7 g of the heat treated ZY and 7 g of 26 wt% aqueous potassium chloride (KCl) solution in a stainless steel cylinder (Figure 2-3). The cross-sectional area of the stainless steel cylinder was 286.52 mm². The testing cell was tested in a type 5580 inston machine at various loading rate.

A.3 Results and Discussion

Figure A-4 shows the gas sorption analysis result of ZY. The porous structure was characterized by a Trister 3000 analyzer (micromeritics). The average pore size is 0.74 nm, the specific pore volume is 0.22 cm³/g and the specific surface area is 700 m²/g.

Figure A-5 shows the sorption isotherm curves of ZY in 26 wt % potassium chloride solution at various loading rates.

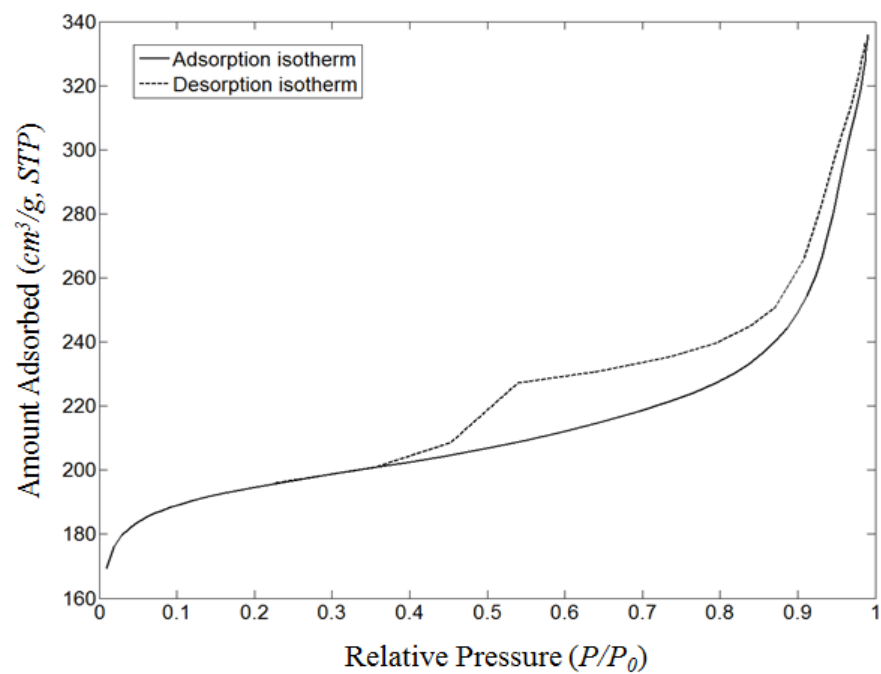


Figure A-4 : The N₂ sorption isotherm curve at 77 K

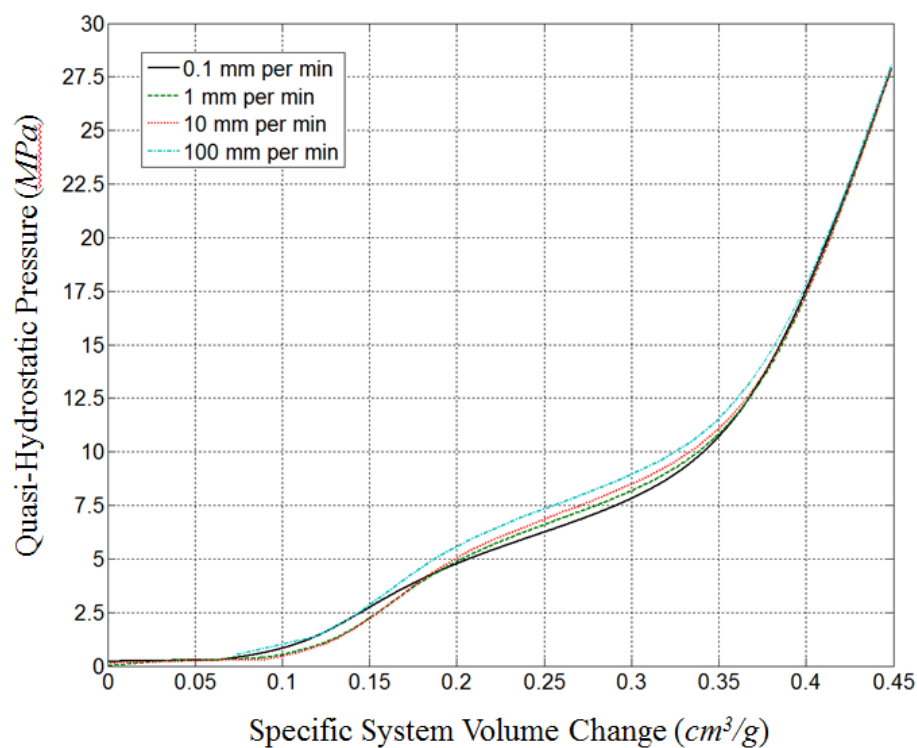


Figure A-5 : The loading rate effect

The pressure was calculated as $P=F/A_0$, with F being the force applied on the piston and A_0 the cross sectional area of the testing cell. The specific system volume change was defined as $\Delta V = A_0 d / m$, with d being the piston displacement and m being the mass of the ZY.

It can be seen clearly that the nanopores are hydrophobic. As the pressure is relatively low, the compression of the system is similar with that of pure liquid, indicating that the liquid phase cannot enter the nanopores. As the pressure is sufficiently increased, the pressure induced infiltration takes place.

According to Figure A-6, The relationship between the loading rate and P_{in} is quite linear, as the loading rate increases, the infiltration pressure (P_{in}), which is taken as the pressure at the middle of point of infiltration plateau becomes higher. That is, $P_{in} = P_{in0} + \delta p$, where P_{in0} is independent of the loading rate and δp is the additional infiltration pressure related to the loading rate effect. Based on the classic circular Poiseuille flow solution[102, 103], as the first-order approximation, we have $\delta p = 128\mu QL / \pi D^4$, where μ is the effective liquid viscosity in nanopores, Q is the flow rate, and L is the effective nanopore depth. During the infiltration experiment, since the effective flow velocity, v , is constant, the overall flow rate can be assessed as vA_0 , and the total infiltration time is $t_0 = V_p / vA_0$, with $V_p = 0.22 \text{ cm}^3/\text{g}$ being the specific nanopore volume.

Thus, the flow rate in a nanopore can be assessed as $Q(D) = (fV_p) / (t_D N) = \pi v A_0 D^2 L / 4 f V_p$, with $N = f V_p / (\pi D^2 L / 4)$ and f being the number and the volume fraction of the nanopores of size D , respectively.

Consequently, $\mu = \alpha(\delta p/v)D^2 f(D)$, where $\alpha = V_p / 32 A_0 L^2$. When L is taken as

one-half of the average ZY particle size, the effective viscosity of confined liquid can be calculated based on the measurement value of δp and v . The results are shown that μ is 0.3326 mPa·s as $\delta p = 0.5$ MPa and $v = 1$ mm/min; μ is 0.0056 mPa·s as $\delta p = 0.85$ MPa and $v = 10$ mm/min; μ is 0.0090 mPa·s as $\delta p = 1.35$ MPa and $v = 100$ mm/min.

The viscosity of 26 wt% (4.82 mol/Kg) potassium chloride solution is 0.9662 mPa·s [104]. The effective viscosity of the liquid in nanopores is much lower than this value. Depending on the pore size, the additional infiltration pressure, and the loading rate, μ varies in the range of $10^{-3} \sim 10^{-1}$ mPa·s.

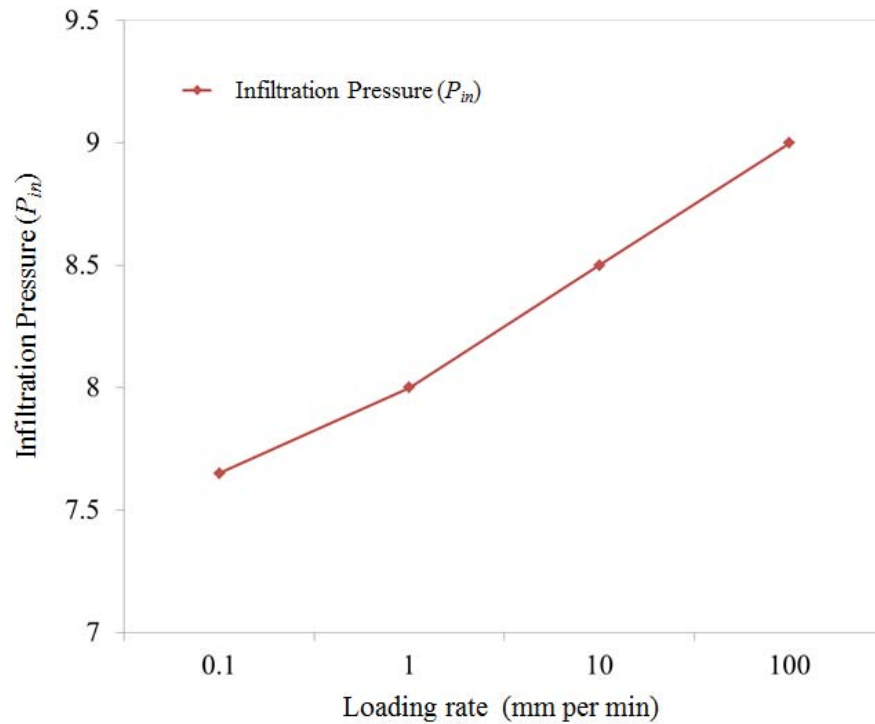


Figure A-6 : The infiltration pressure as functions of the loading rate.

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