Ordered Hierarchical Porous Materials: Towards Tunable Size- and Shape-Selective Microcavities in Nanoporous Channels**

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Size and shape selectivity plays a very important role in a wide range of industrial and biological processes involving molecular transport, adsorption, catalysis, and separation. In industrial processes, the most widely used approach towards selectivity is to take advantage of well-defined cage structures in microporous zeolites.[1] Zeolites are made of three-dimensional crystalline frameworks containing interpenetrating pore channels, usually less than 10 Å in size. The crystalline structure and the pore size depend on the chemical composition as well as the processing conditions. A wide range of cations and polycations is known to stabilize certain pore structures, but a one-to-one "templating" relationship between the cations and the pore size is normally not apparent.[1] Selective transport and separation in biological processes are usually performed by soft lipid membranes containing microporous channels and pores.[2] These membrane channels and pores are self-regulated through conformational changes of membrane proteins that precisely control the ion and molecular permeability across the membrane surfaces. The self-regulating (or responsive) properties of the membrane transport process are not commonly observed in zeolites or other synthetic microporous materials.

Since 1992, the synthesis of ordered mesoporous materials using surfactants as pore-directing agents has attracted wide attention.[3] Precise control of the pore size and the ability to vary the pore size and pore geometry are highly desirable for many applications. A wide range of mesoporous materials have been synthesized as demonstrated by the large number of papers published in this area.[4] However, few reports have been published concerning the size and shape selectivity of these mesoporous materials because of the large pore size and the amorphous nature of the materials. The efforts to synthesize bimodal mesoporous materials (mesoporous materials with microporous walls) have met with limited success.

Functional groups and molecules can be incorporated into mesoporous materials to modify the surface properties for a wide range of applications, as extensively review by Möller and Bein.[5] Several approaches have been reported, including direct silanation,[6, 7] surface rehydration and silanation,[8] co-condensation,[9] and molecular imprinting.[10] A mesoporous organosilicate with bridge-bonded ethene (and other) groups was also synthesized with the co-condensation method.[11]

Recently, Katz and Davis reported molecularly imprinted bulk microporous silica using a series of imprinting molecules (carbamate bound with one, two, or three aminopropyltriethoxysilane groups).[12] The imprinted microporous material showed novel selective catalytic properties as well as selective adsorption, compared to previous molecular imprinting studies on silica materials.[13, 14]

Herein, we report on a new approach to synthesize a hierarchical porous material containing a rigid mesoporous oxide frame coated by a soft, "microporous" molecular monolayer (Figure 1). Unlike in zeolite and microporous materials, the size and the shape of the cavities embedded in the long-chain molecular monolayers determine the size and shape selectivity of the new material. The size and shape of the cavities can be systematically varied by properly choosing the template molecules. Zeolite-like properties, such as size and shape selectivity have been demonstrated. Furthermore, we can take advantage of the conformational changes of the long-chain molecules in the monolayer coating to regulate the accessibility of the microporous cavities, a property usually observed in biomembranes, but not in inorganic microporous materials. The microcavities are accessible in the open position and partially accessible or inaccessible in the closed position.

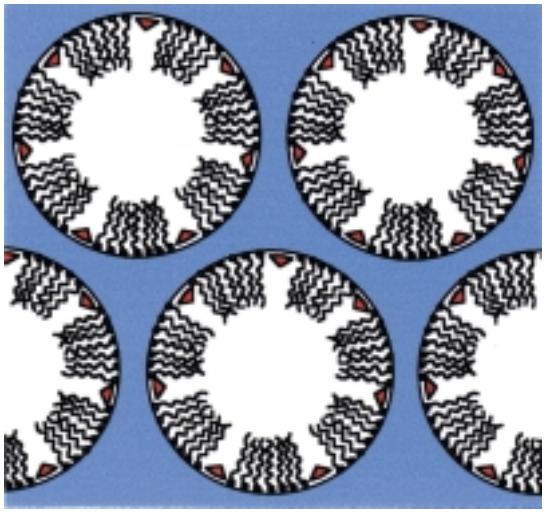

Figure 1. Schematic representation of the hierarchical porous materials with ordered nanoporosities and microcavities in the long-chain molecular monolayer coatings. The red triangular shape in the cavity represents the template molecules, or the idealized shape of the cavity.

The synthetic procedure is illustrated schematically in Scheme 1. This process was developed from widely investigated molecular imprinting techniques[15, 16] and involves the formation of heterogeneous molecular monolayers. Selectively removing the template molecules gives rise to cavitated patterns within the organic coating material. Nominally triangular, linear, and point cavities were created by first binding short aminopropyltrimethoxysilane (APS) chains to the template molecules, followed by the deposition of the template-bound silanes. Subsequently, long-chain molecules

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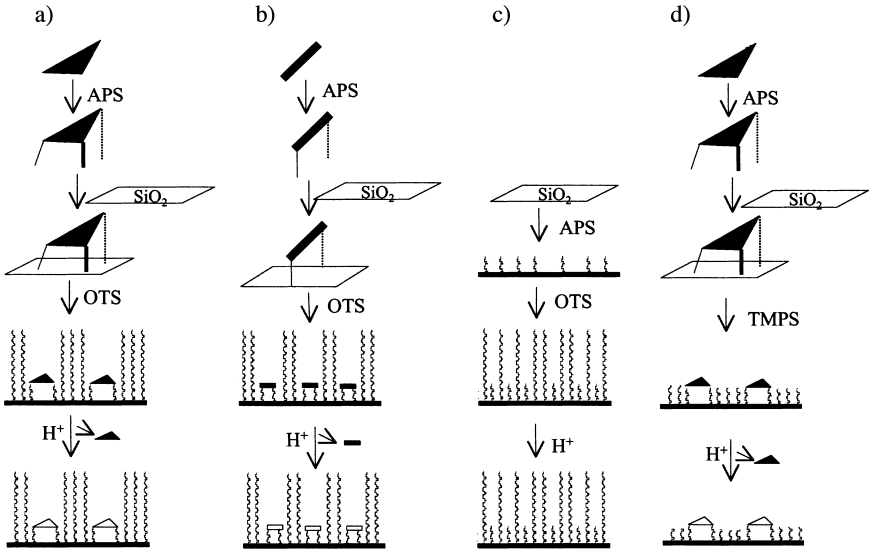

Scheme 1. Molecular imprinting approach for creating microcavities in the monolayer with controlled shape and size: a) triangular cavities, b) linear cavities, c) point cavities, d) triangular binding sites with short-chain capping layers. The solid triangular and rectangular shapes represent the template molecules, and the empty triangular and rectangular shapes represent the shape of the cavities after the template molecules are removed.

were deposited on the unoccupied surface of the silica substrates. The template molecules were later removed from the substrates with a mild acid wash to leave the desired cavities in the monolayer coating.

The mesoporous silica was prepared according to a method[17] using a triblock copolymer surfactant (Pluronic P123, $EO_{20}PO_{70}EO_{20}$, M.W. 5800), tetraethyl orthosilicate (TEOS). The block copolymers give more uniform pore channels for large pore sizes than the MCM-41-type mesoporous materials using a cationic surfactant. A mesoporous silica with a surface area of 517 $m^2 g^{-1}$ (corrected for microporosity) and an average radius of 48 Å was obtained. Triangular template molecules (tripod, 2,4,6-tris(*p*-formylphenoxy)-1,3,5-triazine) were synthesized by the reaction of cyanuric chloride with three equivalents of *p*-hydroxybenzaldehyde, a procedure first reported by Tahmassebi and Sasaki.[18] Linear template molecules (dipod, 2,4-bis(*p*-formylphenoxy)-6-methoxy-1,3,5-triazine) were synthesized by the same procedure using 2,4-dichloro-6-methoxy-1,3,5-triazine instead of cyanuric chloride as a starting material with two equivalents of *p*-hydroxybenzaldehyde (see the Experimental Section).

The tripod or dipod molecules were then treated with 3-aminopropyltrimethoxysilane (APS) to form tripod-APS or dipod-APS through the formation of Schiff bases.[18] The Schiff base was added to a suspension of mesoporous silica in toluene. The tripod templates should bind to the substrate with a face-on conformation through the amine groups on the three corners, and the dipod templates should bind to the substrate through the amine groups on the two ends. Long-chain organic silanes, such as octadecyltrimethoxysilane (OTS), were then added to the solution mixture to form the long-chain molecular monolayer coating.[8] The template molecules were subsequently removed by acid hydrolysis.

Ideally, these procedures should produce triangular cavities (10 Å wide, based on the dimension of the template[18]) and linear cavities (10 Å long). Gravimetric measurement suggested complete removal of the template molecules by the acid wash. For point cavities, APS molecules were first deposited on the porous substrate, followed by the deposition of OTS. The dimension of the point cavities was determined from the area an APS molecule would occupy on the surface (about 4.5 Å for one point cavity).[8] The concentrations of the template molecules (or the APS) were controlled during the sample preparations so that about 20% of the available surfaces was covered, which corresponds to 1.5 mmol APS per gram of silica. A full surface coverage would give a surface concentration of 7.5 mmol g^{-1} (SiO_2), based on the closest packing of the APS molecules.[8]

A Quantachrome instrument was used to measure the Brunauer-Emmett-Teller (BET) surface area and pore size. The pore-size distributions were obtained from the adsorption branches using the standard Barrett-Joyner-Halenda (BJH) method.[19] The adsorption branch is found to give representative results about the pore-size distribution of ordered mesoporous materials.[20] The N_2 adsorption isotherms, as well as the pore-size distributions of several samples, are plotted in Figure 2. The nitrogen adsorption usually shows a typical rectangular hysteresis loop, as previously reported.[17] This hysteresis shape represents a uniform tubular capillary pore geometry with wide and narrow regions in the pore channels.[19]

After the deposition of the templates, or the long-chain molecular coatings, the hysteresis loops were shifted to smaller pore sizes. The surface area A was also reduced, depending on the amount of silane molecules incorporated and the remaining pore diameter. Figure 2b also includes the idealized monolayer structure of the corresponding samples in a vacuum environment. The thickness of the monolayer can be estimated from the chain lengths. Here a collapsed conformation is assumed for the long-chain molecules with the triangular cavities and an extended conformation assumed for those over the point cavities on the basis of packing considerations and the space available in the nearest neighbor. The final pore radius R_e (estimated) is the difference between the initial pore radius (48 Å) and the monolayer thickness. The expected pore radii (R_e; Figure 2b) are very close to the pore radii derived from the adsorption branches. These results confirm that the suggested monolayer structures are reasonable. The desorption branches also provide useful information about the uniformity of the monolayer. The results will be published separately with more detailed analysis of the N_2 adsorption data.

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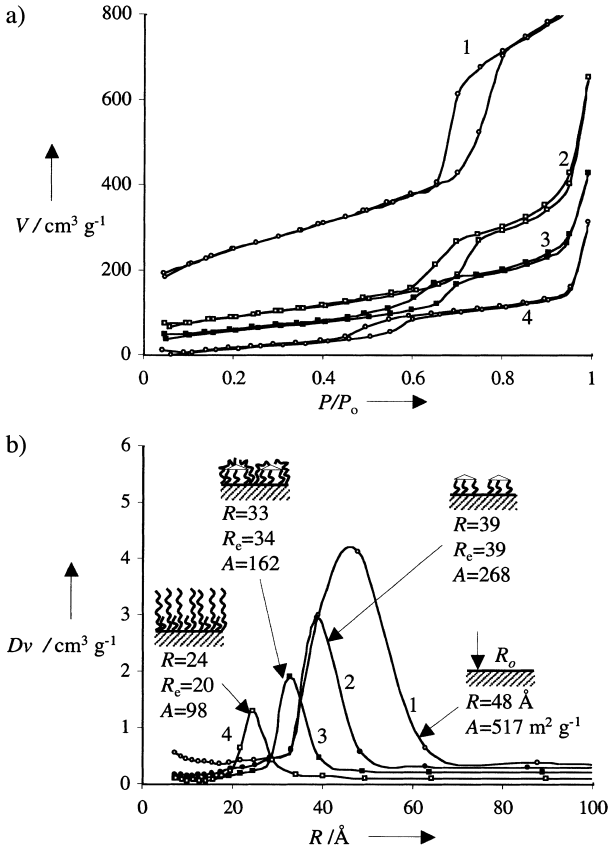

Figure 2. N_2 adsorption results: a) N_2 adsorption volume V as a function of the relative pressure P/P_o, b) pore-size distributions (incremental pore volume Dv as a function of the pore radius R): 1: native mesoporous silica, 2: mesoporous silica templated by the tripod, without OTS chains, 3: mesoporous silica with triangular cavities in OTS monolayer, and 4: mesoporous silica with APS and OTS (point cavities). The solid triangular shape represents the space initially occupied by the templates. The template molecules were removed in these samples. The expected monolayer conformations, the measured pore radii R, the expected pore radii R_e, and the measured surface area A are also included.

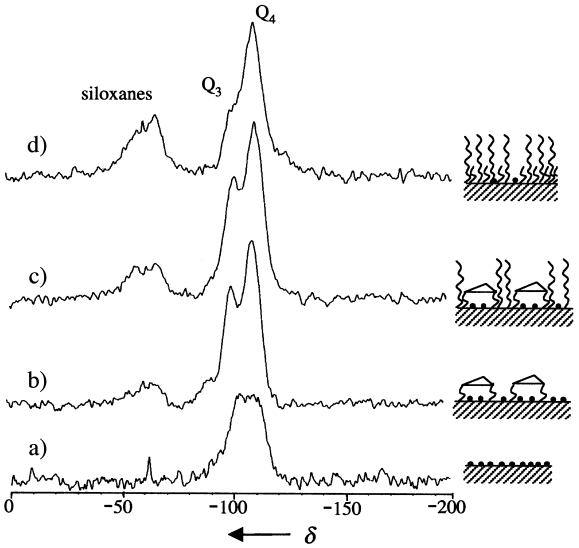

Figure 3. Single-pulse ^{29}Si spectra: a) native mesoporous silica; b) mesoporous silica templated by the tripod, without OTS chains; c) mesoporous silica with triangular cavities in the OTS monolayer; d) mesoporous silica with APS and OTS (point cavities). The triangular shape represents the space initially occupied by the templates. The template molecules were removed in these samples. The solid dots represent the surface hydroxy groups.

Single-pulse ^{29}Si NMR studies (Figure 3) provide further information about the resident chemical environments on the surfaces. A Bloch decay-pulse sequence (single-pulse excitation) with long recycle times (30 s) was used to obtain the spectra. The initial silica substrate contains significant contributions from both Si atoms with one free hydroxy group (Q_3) at -100 ppm and cross-linked silicon atoms (Q_4) at -110 ppm ($Q_3/Q_4 \approx 0.87$). The high Q_3 component is typical of the mesoporous materials prepared following ref. [17]. The deposition of silanes (APS or OTS) is accompanied by the appearance of additional siloxane peaks from -50 to -80 ppm, and reduction (for partial-surface coverage) (Figure 3b and c, $Q_3/Q_4 \approx 0.55$) or significant reduction (for high-surface coverage) of the peak for Q_3 (Figure 3d, $Q_3/Q_4 \approx 0.27$).

Part of the silica surface in both the dipod- and tripod-templated monolayers was covered with the template molecules, so that part of the surface was not available for surface silanation with OTS (Figure 3c). Therefore, Q_3 is still present in significant amounts. The shape of the siloxane peaks from $\delta = -50$ to -80 also suggests a mixture of terminal and cross-linked siloxane chains.[8] The APS molecules have less tendency to block silanation with OTS in the mixed monolayer with APS and OTS (point cavities). Q_3 is significantly reduced. The concentration of siloxane peaks from $\delta = -50$ to -80 was also found to be higher, with a more significant contribution from the cross-linked siloxane chains. These results suggest a higher packing density of OTS and a higher degree of cross-linking. In such closely packed monolayers, the molecular chains are more likely to be vertically oriented, giving a monolayer thickness roughly corresponding to the chain length. This result is consistent with the N_2 adsorption data. However, even in this case, a considerable number of free-silanol groups are still on the surface ($Q_3/Q_4 = 0.27$). The sites occupied by the template molecules in the tripod- and dipod-templated monolayers were not accessible to OTS. The OTS molecules are flexible and will give a monolayer thickness less than the full chain length unless the chains are supported and fully extended, such as in a good solvent.

The tripod and dipod molecules, which were used as the templates to create the microcavities in the monolayers, were used as probe molecules to test the size and shape selectivity of the material. Figure 4a shows the adsorption of tripod molecules onto the three cavitated substrates in toluene. The adsorption of tripod molecules on the triangular cavities (tripod templated) is two times higher than the adsorption of the same molecules on the linear cavities (tripod templated), or the substrate with point cavities (formed by APS). Similar results were also observed for the dipod adsorption studied (Figure 4b).

There are several noticeable features of these adsorption results. First is the precise nature of the selectivity. The difference between the tripod and dipod molecules is not great. The former has three benzaldehyde arms and the latter two. The rest of the molecular structures are similar. In

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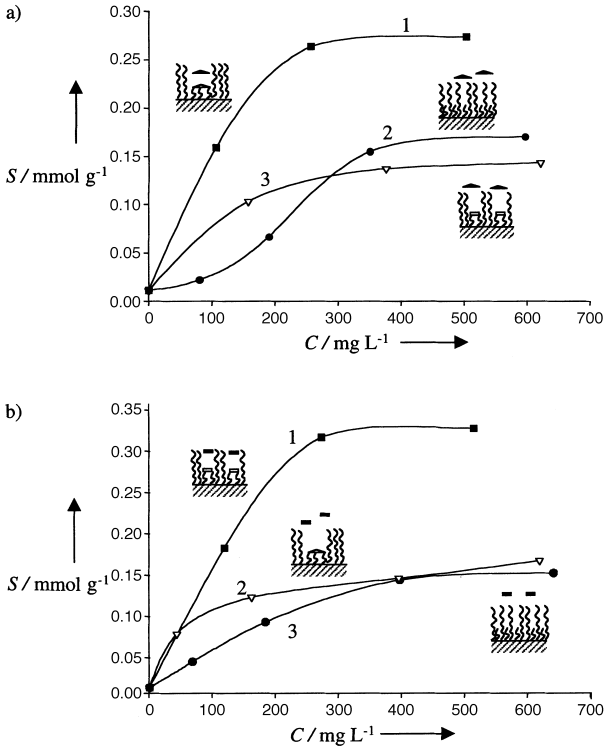

Figure 4. Specific adsorption S of dipod or tripod molecules as a function of equilibrium concentration C. a) Tripod molecules on triangular cavities (1), linear cavities (2), and point cavities (3). b) Dipod molecules on linear cavities (1), triangular cavities (2), and point cavities (3).

principle, the dipod molecules can easily fit into the triangular cavities and conform to the majority of the cavities nicely. The two aldehyde groups can also bind with the two amine groups at the corner of the cavity (through hydrogen bonding or formation of a Schiff base). We would expect the dipod molecules to adsorb on triangular cavities as well as on linear cavities. The large difference in the adsorption behavior of dipod molecules on triangular and linear cavities demonstrated that the shapes of the cavities are very important.

Second, the three-dimensional nature (arising from the long-chain molecule coating) of the cavities is critical. A one-to-one correspondence of the binding sites alone does not give any selectivity. Materials have been prepared using the same procedure without the long-chain molecule monolayer coating or with a coating layer made of small molecules (hexamethyldisilazane, or trimethoxypropylsilane (TMPS)) (Scheme 1 d). These materials contain exactly the same bindings sites (amine groups from the APS) arranged in the same way as in the long-chain monolayers. No selectivity was observed on any of these materials without the long-chain capping. If the selectivity were just attributed to the matching of the binding sites, the materials without capping or with the short-chain capping layer should have a similar selectivity as the long-chain materials. Therefore, we can conclude that the steric effect of the cavities in the long-chain monolayers largely contributed to the selectivity of such materials.

One unique feature of the new material is that the accessibility of the microcavities can be changed. This property is demonstrated with adsorption studies conducted in mixed solutions of toluene and ethanol. Pure ethanol was not used because most of the probe molecules studied were not soluble in ethanol. Generally, whether the long-chain molecules assume an extended or a collapsed conformation depends on the inter- and intramolecular forces. Toluene and long-chain hydrocarbons are hydrophobic molecules and have similar dielectric constant (ε) and refractive indices (n) ($\varepsilon_{toluene} \approx 2.37$, $\varepsilon_{C18} \approx 2.0$, $n_{toluene} \approx 1.49$, $n_{C18} \approx 1.44$). The interactions within and between the hydrocarbon chains in toluene are greatly reduced.[21] Therefore, the hydrocarbon chains will assume a more extended conformation, thus making the microcavities accessible. However, ethanol is a hydrophilic solvent and has a different dielectric constant and refractive index ($\varepsilon_{EtOH} \approx 26$, $n_{EtOH} \approx 1.36$).

The attractive forces within and between the hydrocarbon chains increases in a solvent containing ethanol.[21] This will cause the hydrocarbon chains to form a more-compact (collapsed) conformation, which blocks the microcavities from molecules in the solvent. This kind of change in molecular conformation when the solvency of the solution is changed is well documented in textbooks.[22] Figure 5 a compares the results of tripod adsorption on triangular cavities in toluene and in toluene/ethanol mixture. The adsorption in the mixture is greatly reduced. It is interesting to compare Figure 5 a with Figure 5 b (dipod adsorption on linear cavities): in the latter the adsorption in the mixture was nearly turned off. The linear cavities are much narrower than the triangular cavities and when the hydrocarbon chains curl over, the accessibility to the linear cavities can be completely shut off.

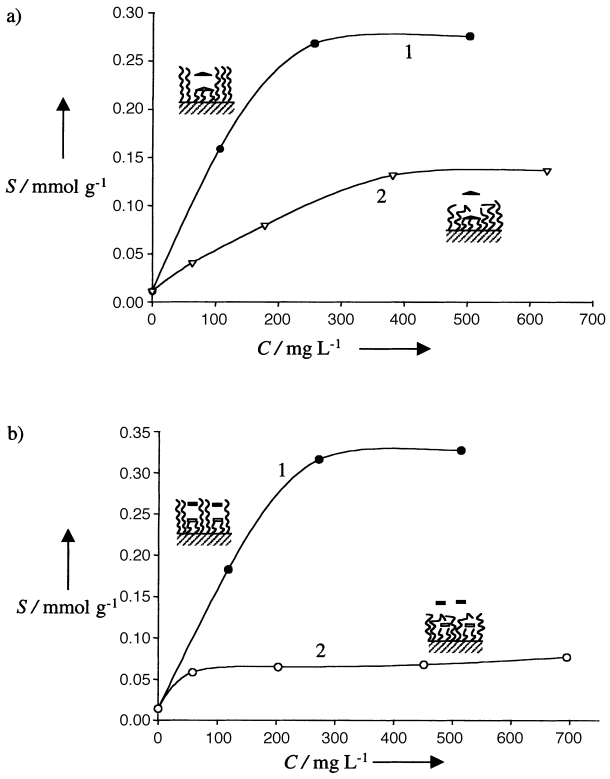

Figure 5. Solvent effects on adsorption behavior on adsorption isotherms. a) Tripod molecules on triangular cavities in toluene (1) and in toluene/ethanol (2). b) Dipod molecules on linear cavities in toluene (1) and in toluene/ethanol (2).

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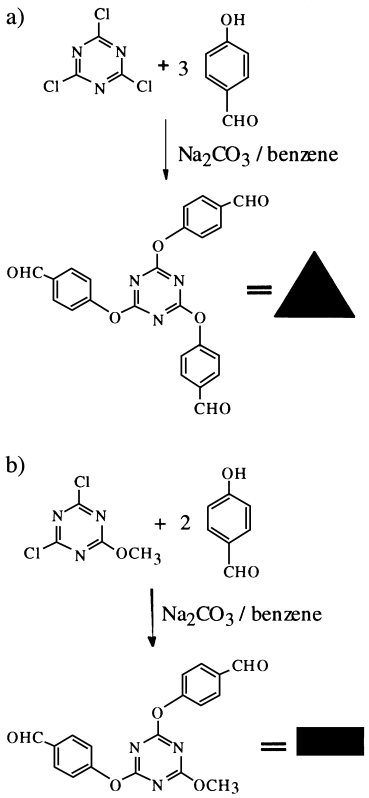
We should point out that the molecular conformation and the monolayer chemistry discussed herein are still under more detailed investigation. The drawings in the figures are meant to be schematic, not mechanistic or quantitative. For example, we can easily speculate that dimers, trimers, or even high-order clusters could form when APS or the template molecules were initially deposited, rather than being uniformly distributed on the surface. The aggregation of these molecules on the surface would have a negative effect on the selectivity, based on the size and shape of the cavities. The possibility also exists of forming more than one molecular layer, or aggregation of the monolayer molecules. There is also evidence that the deposition of OTS molecules can be affected by the predeposited template molecules, and therefore the long-chain monolayers may not be as well organized. Furthermore, the exact shape and size of the cavities should also be the subject of a future study, maybe using techniques such as atomic force microscopes (AFM) and flat substrates as model systems. The shape and the size of the cavities described here are based on the shape and size of the templates, and may not reflect the exact size and shape of the cavities.

The fact that we indeed observed significant selectivity and the consistency between the N_2 adsorption, NMR results, and many other properties of the materials suggests that the material does behave as we expected, and the rationale used is reasonable. This new class of hierarchical porous materials with tunable microporosities are attractive for many applications. The principles used in the synthesis should be applicable to the creation of a wide range of microcavities and patterns within a confined space. The combination of tailored nanoporosity and tunable micropatterns within the nanoporosity may lead to novel properties and applications that will even mimic the structures and functions of sophisticated biological materials.

Finally, we would like to discuss the possibility of selective catalysis based on the size of the micropores. Preliminary results on the Knoevenagel condensation[23–26] between malononitrile and benzaldehyde or 3-pentanone showed that a larger microcavity size (triangular cavities) favored the reaction of the large molecule (benzaldehyde). Although further research is needed to understand the reaction pathways and to optimize the materials properties, we believe that we can selectively enhance or reduce the reaction rate by manipulating the monolayer chemistry and the size and shape of the cavities.



Scheme 2. a) Synthesis of the triangular template (tripod). b) Synthesis of the rectangular template (dipod).

Experimental Section

Synthesis of the tripod and dipod:[18] The tripod and dipod were synthesized as illustrated in Scheme 2. The tripod: cyanuric chloride (1.20 g, 6.50 mmol) and *p*-hydroxybenzaldehyde (3.20 g, 26.2 mmol) were added to a suspension of Na_2CO_3 (20.0 g) in benzene (100 mL). After the reaction mixture had refluxed for 24 h at 100 °C, the white solid was removed by filtration and washed with ethyl acetate (EtOAc) three times. The filtrate was washed with 10 % Na_2CO_3 and H_2O three times. The organic layer was dried over $MgSO_4$ and then concentrated under reduced pressure. The crude white powder was recrystallized from EtOAc (30 mL). The dipod: the synthesis was identical to the tripod, but using 2,4-dichloro-6-methoxy-1,3,5-triazine (3.0 g, 16.7 mmol) and *p*-hydroxybenzaldehyde (4.50 g, 36.8 mmol) in a suspension of Na_2CO_3 (30.0 g) in benzene (200 mL) instead of cyanuric chloride.

Synthesis of mesoporous materials: The mesoporous silica was prepared according to a method[17] using a triblock copolymer surfactant (Pluronic P123, $EO_{20}PO_{70}EO_{20}$, M.W. 5800), tetraethyl orthosilicate (TEOS). The sample was treated at 40 °C and 100 °C and then calcined at 500 °C.

Imprinting approach for microporous monolayers in mesoporous silica: The tripod or dipod molecules were treated with 3-aminopropyltrimethoxysilane (APS) at room temperature to form tripod-APS or dipod-APS through formation of Schiff bases.[18] This Schiff base was added to a suspension of mesoporous silica in toluene and refluxed at 150 °C for 6 h. The long-chain organic silanes, such as octadecyltrimethoxysilane (OTS), were then added to the mixture to form the long-chain molecular monolayer coating.[8] The template molecules were subsequently removed by acid hydrolysis (HCl) of the Schiff bases with aqueous methanol (1/1 (v/v)) over a period of 4 h at room temperature.

Adsorption study of the tripod and dipod: The adsorption capacity toward the dipod or tripod was determined on a UV/Vis spectrophotometer. In all experiments, each sample (0.02 g) was equilibrated with different concentration solutions (10.0 mL) of dipod or tripod in toluene in stoppered glass vials, and these mixtures were stirred for 4 h on the Environ Shaker at room temperature. The difference in the template concentrations before and after equilibrium gave the adsorbed amount on the solid samples. The adsorption study of the tripod and dipod in mixed solvents was performed similarly to the above, except that a mixture of ethanol and toluene (50/50 (wt/wt)) was used as the solvent.

Knoevenagel condensation on tripod and dipod:[23] In a typical procedure, each catalyst (0.05 g) and benzaldehyde (0.212 g, 2.0 mmol) were stirred in dry toluene (10.0 mL). To this solution malononitrile (0.126 mL, 2.0 mmol) was added, and the mixture was stirred at room temperature. The reaction was monitored periodically on a UV/Vis spectrophotometer (285 nm for benzaldehyde and 314 nm for product). A similar procedure was used for 3-pentanone, except that the reaction was carried out at 110 °C.

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Hierarchical Pore Structures through Diatom Zeolitization**

Michael W. Anderson,* Stuart M. Holmes, Noreen Hanif, and Colin S. Cundy

There has been considerable effort recently to devise routes to hierarchical porous structures, which aid the diffusion of guest species through an inorganic network of pores and channels. In order to optimize the performance of a material for a specific application, it is desirable to combine different levels of porosity into one hierarchical porous material. In applications such as catalysis, where the diffusion of molecules through the pore structure, called "molecular traffic control",[1] is vital for optimum performance, a highly ramified network of macro- and micropores is desired. Further, for bulk processes, again such as catalysis or ion-exchange, then any hierarchical porous material must be both facile and cheap to construct. Herein, we report the use of diatomaceous earth for the controlled synthesis of ordered mesoporous/microporous composites which may have considerable utility for bulk industrial processes.

Diatoms are single-celled algae,[2] microscopic plants which secrete and are enclosed by an intricate silica shell. When these aquatic plants die, their shells collect on the ocean or lake floor, eventually forming the material called diatomaceous earth (kieselguhr) or the more light weight rock called diatomite. Diatomite is used in sound and heat insulation, as filters, abrasives, and in the manufacture of explosives. One unique feature of diatoms is their macroporous channel structure with pore sizes ranging from the submicron to tens of microns scale. As diatoms make up about a quarter of plant life by weight, they are an extremely abundant and cheap source of silica. The purpose of this work is to try to utilize the inherent macroporosity of diatoms in the construction of hierarchical composite materials by their "zeolitization".

Hierarchical pore networks have been predicted for some time to have enhanced diffusion properties, whether the networks are ordered or disordered.[3] Indeed, much of the preparation of working catalyst particles involves the treatment of the active component with a suitable binder (usually a form of clay) such that good diffusion is maintained. However, the control over the level and degree of porosity is somewhat arbitrary and depends upon processing conditions. Recently, elegant efforts to synthesize controlled hierarchical materials have resulted in composites with a pore size distribution spread over up to three orders of magnitude. However, the processing conditions are complicated and

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