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Hierarchical MFI Zeolites with A Single-Crystalline Sponge-like Mesostructure

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Abstract: Single-crystalline sponge-like MFI mesoporous zeolites (SSMZs) have been synthesized by using bolaform surfactants with axial chiral binaphthyl core in the hydrophobic tail and triguaternary ammonium head groups as bifunctional organic structure-directing agents (OSDAs). By changing the length of alkyl chain between triquaternary ammonium head group and binaphthyl group from 4 to 10 carbons, SSMZs with high specific surface area (382-434 m²/g), abundant micropore-mesopore connectivity and uniform mesopore diameter (4-10 nm) were obtained. While the OSDAs with an alkyl chain length of 11 and 12 carbons led to the formation of nanorodsconstructed mesoporous MFI zeolites. A geometrical matching between the cylindrical arrangement of binaphthyl groups and the zeolitic framework is speculated to be the key factor for the formation of mesoporous zeolites. The SSMZ zeolites, with abundant mesopores beneficial for the diffusion of reactants, exhibited significantly higher catalytic efficiencies than those of the conventional ZSM-5 with a microcrystal morphology (~1.5 µm).

Introduction

document.

Zeolites are inorganic crystals with regular microporous structures commonly used as commercial adsorbents and catalysts.^[1] However, the larger mass transfer resistance and long transmission path proposed by the small aperture of micropore (< 2 nm) severely hampered their applications.^[2] Recently, great efforts have been devoted to the synthesis of zeolites with mesopores, which greatly improved the mass transportation and enlarged the external surface area.^[3] So far, the assembly of zeolitic nanocrystals.^[4] demetallation,^[6] hard^[6] and soft^[7] templating methods have been studied extensively. Among those, the soft templating method shows great advantages as it can synthesize various mesoporous zeolites through the versatile molecular self-assembly.

Ryoo et al. have synthesized lamellar mesostructured zeolites,^[7b] polycrystalline zeolites nanosponges^[7]-I] and hexagonally ordered MFI zeolite-like mesoporous zeolites^[7c] by

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using designed soft templates, in which the connection of the multiple quaternary ammoniums head group to hydrophobic alkyl chains is the principal factor for the effective structuredirection of MFI zeolite and simultaneous formation of a mesoscale micellar structure. Xiao et al. synthesized singlecrystalline zeolites ZSM-5 with mesopores aligned along b-axis using a designed cationic amphiphilic copolymer as a mesoscale organic structure-directing agent (OSDA) and single-crystalline zeolites beta with disordered mesopores using polymers as a dual-functional SDA.^[7h, 8] An development of the soft templating methods has attempted by introducing benzene^[7e-g] and azobenzene^[7k] to the hydrophobic centre of bifunctional OSDAs in our previous works, which the single-crystalline mesoporous zeolite nanosheets^[7f, 7g] and single-crystalline mesoporous ZSM-5 with three-dimensional pores^[7e] have been synthesized by benzene rings centered molecules with quaternary ammonium head groups. The OSDAs used in those systems were composed of aromatic hydrophobic centre which can selfassemble through strong π - π interaction, while the quaternary ammonium head groups direct the growth of MFI zeolites. Recently, we successfully synthesized a hierarchical MFI zeolite with a two-dimensional (2D) square mesostructure by using rational designed templates with azobenzene segment in the hydrophobic tail.^[7m] It is worth noting that the surfactant-type OSDAs with a chiral hydrophobic center would self-assemble to form helical cylindrical assembly units and then lead to 2D or three dimensional (3D) interrupted zeolite growth.

Here we attempt to build helical cylindrical assembly by introducing axis chiral binaphthyl into the hydrophobic tail of the surfactant with quaternary ammonium head groups to form $[C_{10}H_6-O-C_nH_{2n}-[N^+(CH_3)_2-C_6H_{12}]_{m-1}-N^+(CH_3)_2-C_6H_{13}\cdot mBr^-]_2$ (denoted B_{n-mN} , see Table 1). It has been shown that the two naphthyl groups of the binaphthyl molecule can rotate along the C-C single bond and the dihedral angle between the naphthalene groups depends on the solution system and adjacent functional groups.^[9] The binaphthyl-containing surfactants can adjust their spatial conformations to form a helical cylindrical assembly.^[9b, 10] The quaternary ammonium groups pendant on binaphthol can interact with the inorganic source to form a zeolite framework. These assemblies would disrupt the zeolite growth into bulk crystals and also adjust the pitch length to geometrically match the MFI framework, leading to the formation of single-crystalline sponge-like mesostructure.

 $\label{eq:table_table_table} \begin{array}{l} \textbf{Table 1.} \\ \textbf{Multiquaternary ammonium surfactants containing binaphthyl tail groups.} \end{array}$

Surfactant structure	Notation
$R=C_{n}H_{2n}-[N^{+}(CH_{3})_{2}-C_{6}H_{12}]_{m-1}-N^{+}(CH_{3})_{2}-C_{6}H_{13}$ 3Br	B _{n-mN} n=4, 6, 8, 10, 11, 12. m=1,2,3

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Results and Discussion

The surfactants with different alkyl chain length and quaternary ammonium head groups were used to direct the mesoporous zeolite structures. Bulk ZSM-5 zeolite crystals were formed by the surfactants with one quaternary ammonium head group (B_{n-1N}) and two quaternary ammonium head groups ($B_{4.2N}$) as OSDAs (see Figure S1-S3), while hybrid hierarchical ZSM-5 zeolites with a crystalline core and nanosheet shell were obtained with $B_{6,8,10,11,12-2N}$ as OSDAs (see Figure S4-S7).By increasing the quaternary ammonium head groups of the surfactants to three (B_{n-3N}), SSMZ and nanorods constructed mesoporous MFI zeolites have been obtained. Figure 1 shows low- and high-angle X-ray diffraction (XRD) patterns of calcined



Figure 1. Low- (a) and high-angle (b) XRD patterns of calcined mesoporous MFI zeolites templated by B4-3N, B6-3N, B8-3N, B10-3N, B11-3N and B12-3N surfactants.



Figure 2. Low-magnification (a₁, b₁, c₁, d₁, e₁ and f₁) and corresponding high-magnification (a₂, b₂, c₂, d₂, e₂ and f₂) SEM images of calcined mesoporous MFI zeolites templated by B_{4-3N}, B_{6-3N}, B_{6-3N}, B_{1-3N}, B_{11-3N} and B_{12-3N} surfactants, respectively.

samples. Broad reflections were observed in the low-angle XRD profile of the zeolites templated by B_{4, 6, 8, 10-3N}, which indicate the presence of mesoporous structures in these samples. No reflection was observed in the low-angle XRD pattern of zeolites templated by B_{11, 12-3N} implying the absence of ordered mesoporous structures in these samples. High-angle XRD patterns show that the samples with ZSM-5 structure (MFI) were produced. The reflections in the high-angle region reflect the presence of reflections (*hkl*) with wide FWHM and low intensity, corresponding to the crystal structure with limited repeating unit (small size).^[7c, 7g]

The scanning electron microscopy (SEM) images show that all the samples templated by B_{n-3N} exhibit an octahedral-like morphology (Figure 2a₁, b₁, c₁, d₁, e₁, f₁). High resolution SEM image reveal that the samples templated by $B_{4, 6, 8, 10-3N}$ are composed of stacking of nonuniform nanoparticles with spongelike morphology. Abundant intraparticle mesopores with a diameter of 5-20 nm were observed and randomly distributed on the crystal surface (Figure 2a₂, b₂, c₂, d₂). After ultrasound treatment, the fracture of sample templated by B_{10-3N} also shows abundant mesopores randomly distributing inside the particles a sponge-like feature (see Figure S8). The crystal surface structure of the sample templated by B_{11-3N} were composed of crisscross-shaped nanorods with uniform diameter, while for that of B_{12-3N} , scattered nanorods with non-uniform diameters were observed(Figure 2e₂, f₂).

Figure 3 shows transmission electron microscopy (TEM) images of sliced thin sections of the calcined SSMZ sample templated by B_{10-3N}. As shown in the low-magnification TEM images (Figure 3a₁, 3b₁ and 3c₁), the presence of abundant randomly distributed mesopores can be confirmed, in agreement with the results obtained from XRD and SEM images. Figure 3a₄, 3b₄ and 3c₄ show the selected-area electron diffraction (SAED) patterns taken from the area of Figure 3a1, 3b1 and 3c1, respectively, which correspond to [100], [010] and [001] directions of MFI zeolite, revealing the single-crystalline nature of the particles. Figure 3a₂, 3b₂ and 3c₂ reveal the TEM images of the typical MFI lattice with single crystal nature, which the Fourier diffractograms (FDs) show sharp spots. As the white contrast in the images corresponds to areas of low electronscattering density, namely, the mesopores are randomly distributed in the whole particle. The high-resolution TEM (HRTEM) images are shown in Figure 3a₃, 3b₃ and 3c₃ respectively, the crystalline MFI lattice can be clearly observed along with abundant mesopores. The mesoporous structure is stable and does not collapse after calcination, which can be attributed to the 3D mesoporous structure with continuously grown zeolite framework. The samples templated by B_{4-3N}, B_{6-3N}



Figure 3. Low- and high-magnification TEM images (a_{1-3} , b_{1-3} and c_{1-3}), and SAED patterns (a_4 , b_4 and c_4 corresponding a_1 , b_1 and c_1) taken along the [100], [010] and [001] directions of sliced SSMZ templated by B_{10-3N} , respectively.

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and B_{B-3N} show similar structural feature as observed in that of B_{10-3N} (see Figure S9-S11). Furthermore, the TEM images of sliced thin sections of the calcined samples templated by B_{11-3N} and B_{12-3N} are shown in Figure S12, which contains the configurations of the nanorods stacking. Particles with a rectangular cross section that constructed by crossed nanorods are observed from the low-magnification TEM images. The voids between the nanorods show long slits morphology. Due to the dense arrangement of the nanorods and the overlap problem in the TEM images, it is difficult to observe the nanorod stacking in thick sections of the particles.

Figure 4a shows the N₂ adsorption/desorption isotherms of the calcined SSMZ and nanorods constructed mesoporous ZSM-5. Samples templated by B_{4-3N}, B_{6-3N}, B_{8-3N}, B_{10-3N} exhibit type IV isotherms and a type H2 hysteresis loops. The adsorption amount showed a steep increase in the region of $0 < P/P_0 < 0.01$, implicating the adsorption of the micropores,^[11] while hysteresis loops close to H2 type in the region of $0.4 < P/P_0 < 0.8$ indicate the

presence of ink-bottle type mesopores due to the stacking of nanoparticles.^[12] The pore size distributions (Figure 4b) calculated from desorption branches with BJH methods show relatively uniform pore size distribution. The BET specific surface area (Table 2) of these mesoporous ZSM-5 zeolites are higher than that of the conventional ZSM-5 zeolites. In particular, the mesopore volumes of these mesoporous ZSM-5 zeolites are much higher than that of conventional ZSM-5, while the micropore volume is comparable between these two kinds of MFI zeolites. For samples templated by B_{11-3N} and B_{12-3N}, similar microporous adsorption, type IV isotherms and type H3 hysteresis loops were observed. The type H3 hysteresis loop at relative pressure in the range of 0.4-0.9 indicates the presence of disordered lamellar or slit-type mesopores, which is consistent with the TEM observations. In addition, samples templated by B_{11-3N, 12-3N} possess much higher BET surface area and mesoporous pore volume than that of SSMZ samples (Table 2).



Figure 4. Nitrogen adsorption-desorption isotherms (a) and pore size distribution curves (b) of calcined mesoporous MFI zeolites templated by B_{4-3N}, B_{6-3N}, B_{3-3N}, B_{10-3N}, B_{11-3N} and B_{12-3N} surfactants.

Surfactants	Zeolites materials	$S_{BET}(m^2/g)^{[a]}$	Pore diameter ^{b]}	V _{micro} (cm ³ /g) ^[c]	V _{total} (cm ³ /g) ^{[c}
B4-3N	SSMZ	382	3.7	0.10	0.25
B6-3N		428	5.6	0.10	0.32
B _{8-3N}		434	5.9	0.10	0.35
В10-3N		427	6.6	0.11	0.34
B _{11-3N}	Nanorods constructed mesoporous zeolites	484	-	0.11	0.40
B _{12-3N}		530	-	0.10	0.49

[a] Given by BET method. [b] The pore size distributions were converted from the desorption (samples templated by B_{4-3N}, B_{6-3N}, B_{8-3N}, and B_{10-3N},) or adsorption (samples templated by B_{11-3N} and B_{12-3N}) branch according to the BJH algorithm. [c] Determined by *t*-plot method. [d] Obtained by the single-point method.

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To confirm the π - π stacking arrangement of the template molecules in the synthesis system, we measured UV-Vis and DRUV adsorption spectra of the B_{10-3N} template in aqueous form and in as-prepared SSMZ (Figure 5a). In a dilute water solution, B_{10-3N} molecules are isolated from each other, resulting in absorption bands from the molecule at 230, 287 and 337 nm. It was reported that the band at 230 nm corresponds to a long axis of a naphthyl group, while the band at 287 nm corresponds to its short axis^[9b] and the crucial electron transition feature of the band at 337 nm is due to the fact that the orbitals involved are mainly localized on two naphthalene moieties with π - π * character.^[13] Templates in SSMZ showed an obvious red shift, indicating the long-range ordered assembly of binaphthyl core through π - π interaction. The peaks at 230 and 287 nm shifted to 257 and 297 nm for SSMZ, respectively, indicating that the status of original conjugated templates have changed during the zeolites growing process. The peak at 337 nm shifted to 343 nm for SSMZ due to the π - π interaction of the assembled templates in the zeolites. The displacement of the absorption peak is due to the energy transition from the π -HOMO to the π^* -LUMO decreases as two π - π molecular orbitals from the aromatic groups overlap, which usually leads to a red shift of the absorption bands.^[13] The mirror imaged CD signals of asprepared samples templated by enantiomeric S-B_{10-3N} and R-B_{10-3N} were obtained in the corresponding UV/Vis absorption region (Figure S13), which indicates the helical assembly of surfactants.

The integrity of template molecule was confirmed by ¹³C NMR spectroscopy, while the content of template was obtained from thermogravimetric analysis (TGA) (see Figure S14, S15 and Table S1). The N/Si ratio of 0.051 obtained from TGA is relatively high compared to the reported value of the conventional MFI zeolites^[14], since partial ammonium groups in the mesoporous zeolites did not direct the formation of the zeolite framework and thus did not occupy the micropores of



Figure 5. Schematic representation of the formation of SSMZ. UV-DR spectra (a) of template molecules in a diluted water solution (black line, i), and in asprepared SSMZ solid (red line, ii). Schematic diagram of the formation of SSMZ (b, c), diquaternary ammonium groups of the template direct the formation of the MFI framework while one quaternary ammonium stabilises the negative charges of the zeolite framework viewed along the [001] and [010] directions, respectively. Structural model (d) of the arrangement of binaphthyl groups along a tilted (101) plane (The cylinder represents parts of the mesopores in the SSMZ).

zeolites. To investigate the formation mechanism and the relationship between the surfactants and the derived SSMZ, the relative binding energies between the templates with different configurations and the mesoporous MFI were calculated using. molecular dynamics (MD) simulations. The calculation indicates that the binding energies of 2*zig-zag-s (two branches of B_{10-3N} loading in zig-zag channels of MFI zeolite with same direction) and 2*zig-zag-o (two branches of B_{10-3N} loading in straight channels with opposite direction) are the lowest. The 2*straight-s (two branches of B_{10-3N} loading in straight channels with same direction) shows slightly increased binding energy, while the values of 2*straight-o (two branches of B_{10-3N} loading in zig-zag channels with opposite direction) and 1*straight+1*zig-zag (one branch of B_{10-3N} loading in zig-zag channels) are much higher (Table S2 and Figure S16). Considering the helical cylindrical assembly of surfactants, the conformation of 2*zig-zag-o will lead to the fact that one alkyl chain would be too stretched while the other chain is highly relaxed in the structure, which would be energetically unfavorable than that of 2*zig-zag-s and 2* straight-s. Therefore, it can be concluded that the arrangements of 2*zig-zag-s and 2* straight-s are preferential in the synthesis of SSMZ. These results are in accordance with the experimental results that the surfactants can disrupt the growth of zeolite MFI along a- and b-axis simultaneously, which provided the evidence for the geometric matching between the templates and the zeolites.

Based on the surfactant geometry and the zeolite structure, it can be speculated that the mesostructure is formed by cylindrically assembly units of the surfactant, and the structural matching between the mesostructure and zeolite framework is the key factor for the synthesis of SSMZ. The two naphthol groups of the axis chiral OSDAs are connected by one C-C single chain, which rotate easily and form a scissor-like spatial conformation.^[9b, 9c] The scissor-like binaphthyl unit with a noncoplanar molecular conformation can pack into helical cylindrical assembled micelles in a cooperative manner with the inorganic species.^[10, 15]. Therefore, we propose a geometrical matching model between the arrangement of the assembly units and the zeolite structure with the cooperative self-assembly process (Figure 5b-d). Presumably, each straight or sinusoidal channel of five pentasil layers contains four quaternary groups belonging two opposite stretching hydrophilic chains of one template molecule (Figure 5b, 5c). Four quaternary groups of the B_{10-3N} stay inside the channel of the framework directing the zeolite growth and the other two locate in the micelle stabilizing the (010) and (100) surface, which is in accordance with the N/Si ratio (0.051) obtained by TGA. To illustrate the assembly behavior of the templates, the structural model of the arrangement of the binaphthyl groups along a tilted (101) plane is presented in Figure 5d. Naphthol groups of the template molecules aligned parallel to [001] axis, while triquaternary groups stay in the corresponding channels. The distance between adjacent two naphthol groups is ~3.3 Å, which is within the range of the theoretical distance of π - π stacking.^[16] Therefore, the structural matching of the assembly unit and the sponge-like mesoporous structures in MFI can be established. It is speculated that π - π stacking exists between the adjacent

naphthol groups and those in neighboring pitch, which effectively stabilizes the helical structure. By increasing the length of alkyl chain between triguaternary ammonium head group and binaphthyl group to 11 and 12, mesoporous zeolites with nanorods stacking were formed, which may go through a surface-to-core growth process as reported in other nanorods zeolites formation.^[17] The template molecules with long chain may have difficulties in keeping its helical assembled micelle aggregation, which results in relatively loosely distribution on the surface of the primary zeolite crystal and direct the MFI zeolites growth from surface to core. The different assembly behaviors of binaphthyl centred surfactants may derive from the structural features of the axial chiral molecule. The helical assembly of the binaphthyl group can only be formed with certain attached groups, such as azobenzene $^{\scriptscriptstyle [9b]}$, poly(aryl carbonates) $^{\scriptscriptstyle [10a]}$ and stilbenes^[10b]. While other attached groups, such as anthracene^[15] and tetrathiafulvalene^[13] do not exhibit helically self-assembly properties. Taking the structural feature of the binaphthyl group into consideration, we speculate that the suitable length of alkyl chain is the key point to direct the SSMZ, which tend to form helically assembly units and geometrically match the MFI zeolite framework.

Catalytic properties of SSMZ zeolites. Firstly, to investigate the catalytic performance for the reactants with relatively small molecular sizes, the SSMZ zeolite was compared with conventional ZSM-5 in the methanol to propylene (MTP) reaction (Figure 6a). The Si/Al ratio of SSMZ zeolite was adjusted to 104, which is generally considered to be suitable for MTP. The MTP reaction includes an initial step from methanol dehydration to dimethyl ether (DME) and then the subsequent step of producing ethylene, propylene and other small hydrocarbons such as alkanes and aromatics.[18] The SSMZ zeolite showed a greatly prolonged lifetime than the ZSM-5 bulk crystals, which should be attributed to the mesoporosity in the former catalyst. The selectivity of these intermediate products is intensively related to the catalyst structure, the acidity and the operational conditions. SSMZ shows a high selectivity for propylene (44.6%) in comparison with that of the conventional ZSM-5 (see Figure S17 for textural properties) and a high propylene to ethylene (P/E) ratio (see Table S3 for the product distribution of methanol to propene reaction), which were predominately attributed to its optimal combination of acidity and mesopores.

Secondly, the catalytic activities of SSMZ and conventional bulk ZSM-5 were tested for the acetalization of benzaldehyde with pentaerythritol to compare their performance in converting bulky molecules (Figure 6b, and Figure S18 for textural properties). In this case, the diffusion of the large molecules, such as the diacetal product, determine the reaction rate. The SSMZ showed distinctly increased catalytic activities compared with those of the conventional ZSM-5 (Figure 6b, and Figure S18 and S19). This result is due to the existence of the abundant mesopores and larger specific surface area of the SSMZ.

Thirdly, the gas-phase cracking of 1,3,5-triisopropylbenzene (TIPB) was also carried out to investigate the possibility of mesoporous ZSM-5 zeolites for processing bulky molecules

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Figure 6. Catalytic efficiency of SSMZ and conventional ZSM-5. Conversion and selectivity for methanol to propene and the ratio of propylene to ethylene (P/E ratio) (a). Conversion of the acetalization of benzaldehyde with pentaerythritol (b). Conversion and selectivity of cracking of 1,3,5-triisopropylbenzene (c).

(Figure 6c, Figure S18 and S20), as this reaction occurs predominately on the external surface of ZSM-5 as TIPB is too large to enter its micropores. The main products were diisopropylbenzene (DIPB) isomers, isopropylbenzene (IPB) and benzene (BZ), formed by successive cracking. The catalytic activity for TIPB cracking reflects the Brønsted acidity solely presenting on the external surfaces of the ZSM-5. The SSMZ shows a high catalytic activity compared to the bulk conventional ZSM-5, which clearly demonstrates the catalytic advantage of SSMZ with hierarchically mesoporous structure to bulky molecules.^[19]

The SSMZ ZSM-5 with a larger surface area and similar micropore volume to conventional ZSM-5 exhibits excellent catalytic activity in both small and relatively large molecule reaction. The improved performance of SSMZ would be attributed to the facile diffusion through the mesopores in SSMZ, strong acidities of their crystalline zeolitic frameworks, and high concentrations of surface acid sites that are accessible to organic substrates particularly with bulky molecular dimensions.

Conclusions

We have synthesized a series of SSMZ and nanorods constructed mesoporous zeolites by the templates composed of an axis chirality hydrophobic centre and two hydrophilic alkyl chain. Various mesoporous zeolite with different structures can be tuned by different length of alkyl chain between triquaternary ammonium head groups. It has been demonstrated that different self-assembly behavior of the binaphthyl-type templates play an important role in the structural formation, which direct the nanosponge and nanorods constructed mesoporous zeolites, respectively. This finding would provide new strategies to synthesize highly ordered mesoporous zeolites by using delicately designed templates.

Experimental Section

Synthesis of binaphthyl core surfactants: The surfactants used in this work were synthesised according to the methods reported in previous report^[20], their structures are listed in Table 1. In a typical synthesis, (S)-(-)-1,1'-bi-2,2'-naphthol (1.43 g, 5 mmol) and 1,10-dibromodecane (30 g, 100 mmol) were mixed in 100 mL of acetone containing 12.42 g (90 mmol) of K₂CO₃ of and refluxed under N₂ atmosphere for 24 h. The product was filtered to remove K₂CO₃ and vapored to obtain a light yellow viscous crude product. The crude product was chromatographed on a silica gel column (petroleum ether/ethyl acetate, 100:1). The pure intermediate B₁₀ was obtained as colourless oil (68% yield). Then 2.6 g (3.6 mmol) of B₁₀ and 12.4 g (72 mmol) of N,N,N',N'-tetramethyl-1,6-hexanediamine were mixed in 150 mL of acetonitrile and refluxed at 83 °C for 24 h. After cooling to room temperature, the intermediate B₁₀₋₁ was filtered, washed with diethyl ether, and dried in a vacuum oven

overnight (3.4 g, 91%). Then 3.4 g (3.2 mmol) of B₁₀₋₁ and 16.6 g (68 mmol) of 1,6-dibromohexane were mixed in 150 mL of acetonitrile and refluxed at 83 °C for 24 h. After cooling to room temperature, the intermediate B₁₀₋₂ was filtered, washed with diethyl ether, and dried in a vacuum oven overnight (4.3 g, 98%). Then 4.3 g (3.1 mmol) of B₁₀₋₂ and 1.2 g (9.3 mmol) of N,N-dimethylhexylamine were mixed in 150 mL of acetonitrile and refluxed at 83 °C for 24 h. After cooling to room temperature, the product B_{10-3N} was filtered, washed with diethyl ether, and dried in a vacuum oven overnight (5.5 g, 98%). The expected structures of the final organic products were confirmed by ¹H NMR. The other surfactants were synthesised in similar process but with different raw materials.

Synthesis of mesoporous and conventional ZSM-5: The mesoporous zeolites were prepared by hydrothermal synthesis using different B_{n-mN} as templates or OSDAs. In a typical run, the mesoporous zeolites were synthesised at an original gel composition of 1 B_{10-3N}: 50 SiO₂: 12.4 Na₂O: 0.5 Al₂O₃: 200 EtOH: 4000 H₂O. Tetraethyl orthosilicate (TEOS) was used as a silica source, while ethanol (EtOH), with a stoichiometric amount of four times, came from TEOS hydrolysis. To be specific, 0.18 g surfactant, 0.0082 g sodium aluminate and 0.09 g sodium hydroxide were added to 7.2 g deionized water to form a homogeneous gel. When the gel was well mixed after stirring for 30 min, 1.04 g TEOS was quickly added to the gel. Then the gel was stirred for another 5 h in water bath pot at 60 °C. Next, the mixture was transferred to a Teflon-lined stainless steel. Then, the autoclave was tumbled at 413 K and 40 rpm to carry out the crystallization for 4 days. Finally, the zeolite products were filtered, washed with distilled water, and dried at 373 K overnight. Other samples were synthesised accordingly, with different surfactants and molar ratio. Before examing catalytic properties, the zeolites were ion-exchanged with 2M NH₄Cl for 2 h at 353 K and then converted into proton form by calcination in air at 823 K for 6 h. The whole ion-exchanged process repeated twice to obtain the final product for catalytic reaction.

Conventional ZSM-5 with bulk crystals was synthesised as control through colloidal seed assisting method using tetraethylammonium bromide as OSDA as in the previous reports.^[21]

Characterizations: The synthesised surfactants were analysed by ¹H nuclear magnetic resonance (NMR) and UV/visible (UV/vis) spectroscopies, whereas X-ray diffraction, scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and N2 adsorption/desorption analysis were applied to the characterization of synthesised zeolites. Powder XRD patterns were recorded on a Rigaku X-ray diffractometer (D/MAX-2200/PC) equipped with Cu Ka radiation (40 kV. 30 mA, λ = 1.5418 Å) at a rate 1°/min in a 2θ range of 0.8-5° and 5-40°. Observation via scanning electron microscopy (SEM) was performed with a JEOL JSM-7800 Prime microscope operating at 0.5 kV with a stage bias of -5 kV, using upper electron detector with 4 mm working distance. Observation via transmission electron microscopy (TEM) was performed with a JEOL JEM-2100 microscope operated at 200 kV (Cs 1.0 mm, point resolution of 2.3 Å). Images were recorded with a TENGRA CCD camera (2304 × 2304 pixels with a 2:1 fiber-optical taper and an effective pixel size of 18 $\mu m^2)$ at 30000-500000 magnification under low-dose conditions. The specific surface area, pore volume, and pore size distribution were analysed with N2 adsorption/desorption isotherms, which were measured at 77 K using an ASAP 2010 M+C analyser. Prior to the adsorption measurements, all the samples were degassed under a vacuum for 3 h at 423 K. The surface area was calculated from the desorption branch in the P/P0 range from 0.05 to 0.30 using the Brunauer-Emmett-Teller (BET) equation. The pore size distributions were calculated from the entire adsorption or desorption branch according to the Barrett-Joyner-Halenda (BJH) algorithm for approximation. The diffuse-reflectance UV/vis (DRUV) spectra were recorded on a PerkinElmer Lambda 20 UV/vis spectrometer, whereas the UV/vis absorption spectrum of the filter was measured with a Shimadzu UV-2450 spectrophotometer. The absorbance spectra were obtained from the reflectance spectra through Kubelka-Munk transformation. The ¹H NMR spectra were recorded on an AVANCE III 500 (500 MHz) spectrometer with chemical shifts reported in parts per million relative to the residual deuterated solvent and the internal standard tetramethylsilane (TMS)

Catalytic reactions

Methanol to propene (MTP) reaction: MTP reactions were performed in a fixed-bed quartz reactor over the catalyst at 450 $^{\circ}$ C, atmospheric pressure, and a WHSV of methanol of 8 h⁻¹. All samples were calcined under nitrogen flow at 550 $^{\circ}$ C for 1 h before commencing the MTP reaction. The reactor temperature was decreased to 450 $^{\circ}$ C, where methanol was fed to the reactor together with carrier gas. The effluent products from the reactor were maintained at 140 $^{\circ}$ C and analysed by an online gas chromatograph (GC) equipped with a Plot-Q capillary column and a FID detector. In the reaction, dimethyl ether (DME) was considered as reactant in the calculation.

Acetalization of benzaldehyde with pentaerythritol: Acetalization of benzaldehyde with pentaerythritol reactions were carried out under slurry phase reaction conditions using a conventional oil bath attached with condenser. A typical reaction mixture in a 25 mL round bottle flask contained benzaldehyde (20 mmol), pentaerythritol (10 mmol), toluene (8 mmol) and a freshly activated catalyst (50 mg). Activation of the catalyst was done by calcination at 550 ℃ for 5 h. The reaction was carried out at 120 ℃ for 5 h. After cooling to room temperature, the flask was washed several times by acetone. All the mixture was collected and separated by centrifugation. The liquid mixture was analysed on a Shimadzu GC-2014 gas chromatograph using an Rtx®-Wax capillary column with FID detector. The conversion was calculated based on benzaldehyde using the internal standard method, where toluene was applied as the internal standard. The formation of diacetals of pentaerythritol was confirmed by the GC-MS.

Cracking of 1,3,5-triisopropylbenzene: The cracking reaction of 1,3,5-triiaopropylbenzene (TIPB) was conducted using a continuous system in fixed-bed quartz reactor (i.d.8 mm) under atmospheric pressure with nitrogen as a carrier gas. The catalyst was first activated at 823 K in a N₂ flow rate of 30 mL min⁻¹ for 1 h, and then decreased to the reaction temperature (573 K), where the TIPB was fed into the reactor at a rate of 1.7 mL h⁻¹. The typical catalyst loading and carrier gas flow were 0.2 g and 30 mL min⁻¹, respectively, which corresponded to a weight hourly space velocity (WHSV) of 7.18 h⁻¹ for TIPB. The liquid product was collected with an ice-water trap and then analysed on A Shimadzu 14B gas chromatograph equipped with FFAP capillary column and FID detector.

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Keywords: MFI Zeolite, hierarchical structure, sponge-like structure, single-crystal.

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Single-crystalline sponge-like MFI mesoporous zeolites (SSMZs) have been synthesized by using bolaform surfactants with axial chiral binaphthyl core in the hydrophobic tail and triquaternary ammonium head groups as bifunctional organic structure-directing agents (OSDAs).



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