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Single-crystalline MFI Zeolite with Sheet-like Mesopores Layered along the *a* Axis

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Abstract: Designing a templating strategy for directing mesopore growth along different crystallographic directions is essential for fabricating two- or three-dimensional single-crystalline mesoporous zeolites. However, so far, the mesopores formed in MFI zeolites by soft templates have mostly been generated by disrupting growth along the *b* axis; generating mesopores by disrupting growth along the a axis is rare. Here, a single-crystalline mesoporous MFI zeolite (SCMMZ) with sheet-like mesopores layered along the a and b axes was synthesized using a triply branched surfactant with diquaternary ammonium groups connected to 1,3,5-triphenylbenzene by a sixand eight-carbon alkyl chain (TPB-6 and 8). The sheet-like mesopores were embedded in the MFI framework and were retained even after calcination. Molecular mechanics calculations provided evidence of low binding energy configurations of the surfactant that directed the growth of straight and zigzag channels along the b and a axes, respectively. The formation of nanosheets was attributed to the geometric matching of the arrangement of the aromatic groups to the zeolite framework.

Zeolites are widely employed in catalysis, separations and adsorption because of their open crystal structure, strong acidity and ion-exchange capacity.^[1] However, the small size of their pores (less than ~0.8 nm) and cavities $(typically < 1.5 \text{ nm})^{[2]}$ limit the diffusion of guest molecules through the pore channels in the catalytic inorganic framework.^[3] This disadvantage can be overcome by introducing mesopores into zeolites using post-synthesis treatments,^[4] soft templates (e.g., small molecules,^[5] surfactants,^[6] mesoscale polymers^[7]) and hard templates (e.g., carbon replicas,^[8] polystyrene spheres^[9]). The soft-template method, which involves self-assembling amphiphilic molecules and an inorganic source, is known to be the most promising method. Particularly, quaternary ammonium salts have been extensively used to generate numerous zeolite structures due to their strong interactions with the inorganic framework.^[10]

In the soft-template method, the templates not only direct the synthesis of the zeolite but also disrupt its growth through their hydrophobic parts, resulting in the generation of mesopores. Ryoo *et al.* successfully synthesized MFI zeolite nanosheets by disrupting the crystal growth along the *b* axis using a diquaternary ammonium-type surfactant.^[6, 11] We previously introduced aromatic groups into the hydrophobic tail of amphiphilic molecules to synthesize a single-crystalline architecture with mesostructured zeolite nanosheets layered

along the *b* axis, and we used a cylindrical azobenzene assembly in the hydrophobic part to generate quaternary, ordered, straight, square channels framed by MFI thin sheets in the *a*-*c* planes and joined by 90° rotations.^[12] We also found that an amphiphilic surfactant with three diquaternary ammonium-terminated alkyl chains connected uniformly to a benzene ring^[13] can direct the formation of single-crystalline mesoporous ZSM-5 with a sheet-like three-dimensional porous structure. The mesopores of all of these mesostructured MFI zeolites only opened at the (010) facets because the growth was disrupted along the *b* axis, which would limit the adsorption properties and shape selectivity.

It should be noted that tuning the hydrophobic part of the surfactant is the key factor for mesostructure formation and the structural matching between the mesopores and zeolite framework. The aromatic groups introduced into the hydrophobic tail of the surfactants not only provide π - π interactions that can stabilize the mesostructures but can also adjust their configuration to geometrically match the MFI zeolite framework, forming a single-crystalline lamellar MFI mesostructure. Until now, only one or two benzene groups have been introduced. Stronger π - π interactions and a more stable micellar structure can be formed by introducing larger aromatic groups, which would lead to the formation of mesoporous MFI zeolites with disrupted growth along other axes.

triply branched surfactants in which diquaternary Herein, ammoniums are connected to 1,3,5-triphenylbenzene by different carbon chain lengths to form C₆H₃{[C₆H₄-O-C_nH_{2n}-N⁺(CH₃)₂-C₆H₁₂- $N^{+}(CH_{3})_{2}-C_{6}H_{13}[Br^{-}]_{2}_{3}$ (denoted TPB-n, n = 4, 6, 8, 10) (Supporting Information, Figure S1) were designed. The three branches are preferentially stretched along three directions, in contrast to the bilayer configuration that extends in one or two opposite directions. Strong π - π interactions and a low stabilizing energy are achieved by introducing the larger aromatic "core". The different lengths of the alkyl chains of TPB-n ensure that the surfactants match mesoporous MFI zeolites (MMZs) with different structures. The MMZs templated by TPB-4, -6, -8 and -10 were denoted MMZ-4, -6, -8 and -10, respectively. Singlecrystalline mesoporous MFI zeolite (SCMMZs) with sheet-like mesopores layered along the a and b axes were fabricated with TPB-6 and -8.

The low-angle X-ray diffraction (XRD) pattern (Figure 1a) of calcined MMZ-6 exhibits a broad peak at approximately 1.44°, indicating the existence of less-ordered mesopores. Indexing this peak to the first-order reflection of layered MFI nanosheets gives a repeating unit of 6.1 nm. The mesostructure is retained even after the removal of the templates, in contrast to lamellar mesostructure zeolites that collapse to form polycrystals or single crystals.^[6a, 12a] The high-angle XRD pattern of MMZ-6 (Figure 1b) exhibits the same reflections as that of conventional MFI, indicating that a high-quality MFI zeolite structure is produced. SEM images (Figures 1c and 1d) show that the sample consists of interconnected primary particles with an irregular morphology and average size of a few microns (see also the low-magnification SEM images in Figure S2). These particles are composed of secondary particles that are compacted with thin sheet-like particles with a thickness of ~5 nm.

The N₂ adsorption-desorption isotherm of calcined MMZ-6 (Figure

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1e) is type IV(a) and exhibits an H4-type hysteresis loop.^[14] The uptake step below $P/P_0 = 0.02$ reveals the presence of a microporous structure.^[15] The H4-type hysteresis loop at relative pressures $P/P_0 = 0.4-0.9$ indicates the presence of slit-like mesopores. The pore size distribution of MMZ-6 (Figure 1f) indicates an average pore size of ~2.2 nm (obtained from adsorption branch), which is approximately equal to the diameter of the slit-like mesopores observed in the TEM images. The Brunauer–Emmett–Teller (BET) surface area, micropore volume and mesopore volume of MMZ-6 are measured to be 621 m²/g, 0.09 cm³/g and 0.45 cm³/g, respectively (Supporting Information, Table S1). The BET surface area and mesopore volumes of MMZ-6 are much higher than those of conventional ZSM-5, indicating a large number of mesopores in this material, whereas the micropore volumes of these two zeolites are comparable.



Figure 1. a) Low-angle and b) high-angle XRD patterns, c) low-magnification and d) high-magnification SEM images, e) N_2 adsorption-desorption isotherm and f) pore size distribution of calcined MMZ-6.

Meso- and microstructural information about MMZ-6 was obtained by transmission electron microscopy (TEM) observations of a slice of calcined MMZ-6 embedded in epoxy resin. The low-magnification TEM image (Figures 2a) shows the presence of sheet-like mesopores with a thickness of ~2 nm and length of 5-50 nm. The corresponding selected-area electron diffraction (SAED) pattern (Figure 2b) reveals a single-crystalline nature. Based on the indexing of the SAED pattern, the mesopores are layered along the [100] direction of the MFI framework, which disrupts the crystal growth along the *a* axis. The high-resolution TEM (HRTEM) image (Figure 2c) shows that many of the mesoporous structures are associated with the MFI lattice fringes; however, the pores do not have a well-defined shape. The mesopores in the MFI framework observed along the *a* and *b* directions are short (< 50 nm) and embedded in the MFI framework, and they are retained after calcination. Figure 2d shows a possible structural model of calcined MMZ-6, in which mesopores with a diameter of ~2 nm are formed by breaking the Si-O bond that located at the middle of the 10membered ring along both the *a* and *b* axes. The TEM image obtained along the *a* axis (Supporting Information, Figure S3) shows that mesopores are also formed by disrupting the growth of the MFI crystal along the *b* axis. Therefore, MMZ-6 is a mixture of MMZ with layered pores along both the *a* and *b* axes. As observed in several lowmagnification TEM images, the average thickness of the repeating unit is estimated to be 5.6 nm, which is similar to the result obtained from the XRD patterns (Supporting Information, Figure S4 and S5).



Figure 2. a) Low-magnification TEM image and b) corresponding SAED pattern obtained along the *b* axis of MMZ-6. c) Enlarged image of the area marked by the white box in (a). d) Proposed structural model of the pores layered along the *a* axis.

When the alkyl chain length C4 is used, a lamellar MMZ is synthesized (Supporting Information, Figure S6 and Table S1). Two well-resolved peaks at $2\theta = 1.88^{\circ}$ and 3.86° are indexed to the firstand second-order reflections of lamellar MFI nanosheets with a *d*-spacing of 4.7 nm, indicating a periodic interlamellar structural order. The high-angle XRD pattern of MMZ-4 confirms that the sample has a pure MFI zeolite structure. The N₂ adsorption-desorption isotherm of calcined MMZ-4 is type-IV(a) and exhibits an H4-type hysteresis loop. The BET surface area, micropore volume and mesopore volume of MMZ-4 are measured to be 409 m²/g, 0.10 cm³/g and 0.21 cm³/g, respectively. The SEM images of calcined MMZ-4 show a house-of-cards-like morphology, and the TEM images indicate that the lamellar structure collapses after calcination.

When the length of the alkyl chains is increased to C8, SCMMZ is also produced (Supporting Information, Figure S7). The XRD patterns show the formation of a mesostructured MFI zeolite, and the SEM images reveal that MMZ-8 has a spherical morphology. MMZ-8 has an N₂ adsorption-desorption isotherm (type IV(a)), hysteresis loop (H4-type), surface area (590 m²/g), mesopore volume (0.44 cm³/g), micropore volume (0.10 cm³/g) and pore diameter (~2.3 nm, obtained

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from adsorption branch) similar to those of MMZ-6 (Supporting Information, Figure S7 and Table S1). The SAED patterns of thin slices of calcined MMZ-8 indicate a single-crystalline nature (Supporting Information, Figure S8). Mesopores stacked along the [100] and [010] directions of the MFI framework are clearly observed, demonstrating that the growth of the MFI crystal along the *a* and *b* axes is disrupted, which is similar to the results for MMZ-6.

Increasing the length of the alkyl chains to C10 results in MFI nanosheets with a rotationally and sequentially intergrown structure (Supporting Information, Figure S9 and Table S1). A broad paeks centered at 1.5°□ is observed in the low-angle XRD pattern indicating the existence of less-ordered mesopores, whereas the high-angle XRD patterns indicate that high-quality ZSM-5 is obtained. The N2 adsorption-desorption isotherm of calcined MMZ-10 is type IV(a) with an H4-type hysteresis loop. The pore size distribution reveals a uniform mesopore size of approximately 2.6 nm (obtained from adsorption branch). The BET surface area, micropore volume and mesopore volume of MMZ-10 are 642 m^2/g , 0.11 cm³/g and 0.37 cm³/g, respectively. The SEM images show that MMZ-10 has an oval morphology with a size of ~300 nm. Both the atomic-scale crystalline structure of MFI and the mesostructure of MMZ-10 can be observed in the TEM image. The four diffraction spots (indicated by white triangles) correspond to the similar periodicity of sheet-like mesopores along two perpendicular axes. The possible formation mechanism of MMZ-10 might be the overgrowth of the (100) faces on the (010) faces via the c axis, with the zigzag channels of one nanosheet being interconnected with the straight channels of the other nanosheets. The connectivity at the intersections could be due to the formation of new Si-O-Si bonds.



Figure 3. Stabilizing energy calculations of four simulation models of the TPB-6-directed MMZ-6 system. a) The three branches are loaded in the zigzag channels (3*zigzag), disrupting the *a* axis. b) The three branches of TPB-6 are loaded in the straight channels (3*straight), disrupting the *b* axis. c) One branch of TPB-6 is loaded in a straight channel, while the other two branches are loaded in zigzag channels (1*straight+2*zigzag), disrupting both the *a* and *b* axes. d) Two branches of TPB-6 are loaded in the straight channels, while one branch is loaded in a zigzag channel (2*straight+1*zigzag), disrupting both the *a* and *b* axes.

To understand the formation mechanism and the relation between the mesostructure formation and the alkyl chain length of the surfactants, the relative stabilizing energies of the mesoporous MFI zeolite with different configurations of TPB-6 (Figure 3) were calculated using molecular dynamics (MD) simulations. The simulation model of MFI was constructed based on the pore size distribution of MMZ-6, which exhibits a broad peak centred at ~2.2 nm. For the single-crystalline MFI structure, the size of the mesopores must be an integral multiple of the length of half the unit cell along the *a* or b axis. Three structural models for SCMMZ were proposed (Supporting Information, Figure S10), and model ii, which has a wellmatched pore size, is the most appropriate structure. The results of the MD simulations are summarized in Table S2. The stabilizing energies of 3*straight and 3*zigzag are higher than those of the other two models (Figure 3). It can be concluded that the preferred arrangements for a single surfactant molecule in the synthesis of MMZ-6 are 1*straight+2*zigzag and 2*straight+1*zigzag, because it is then oriented to direct the formation of SCMMZ by disrupting the growth of the zeolite along both the *a* and *b* axes. Considering the aggregation behaviour of the surfactants, the 3*straight and 3*zigzag configurations facilitate the self-assembly of the templates in a more relaxed and symmetrical way and exhibit a suitable structural fit with the arrangement of the mesopores and zeolite framework, directing the growth of SCMMZ with sheet-like mesopores.



Figure 4. a) UV-vis spectra of the dilute aqueous solution of the assynthesized template (black line) and the as-prepared MMZ-6 (red line). b-d) Packing configurations of the surfactants in the as-prepared zeolite viewed along the *a*, *b* and *c* axes. d₁, d₂) Configurations of two adjacent templates viewed along the *c* axis.

UV-vis spectroscopy was used to investigate the stereoregularity of the TPB-6 molecules (Figure 4a). The UV-vis absorption spectrum of the template molecules (TPB-6) in dilute water clearly exhibits two absorption bands (198 nm and 274 nm), which are ascribed to the π - π * transitions of the aromatic moieties.^[16] In the solid crystalline state in MMZ-6, the template molecules are more densely packed, leading to obvious π - π stacking due to the overlap of the π molecular orbitals of the aromatic groups. The energy of the electron transition from the π highest occupied molecular orbital to the π * lowest unoccupied molecular orbital decreases, which leads to a red shift (213 nm and 291 COMMUNICATION

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nm) relative to the bands of TPB-6 in a dilute aqueous solution. These results provide evidence for the π - π interactions and stacking of TPB-6 in MMZ-6.^[17]

The intact configuration of TPB-6 template without decomposition in MMZ-6 was confirmed by ¹³C nuclear magnetic resonance (NMR) spectra (see Figure S12). The thermogravimetric analysis (see Figure S13) combined with elemental analysis data (ratio of N/Si = 0.043) indicate that not only that all micropores were directed by the quaternary ammonium groups, but also that one template corresponds to three micropores. The dual stabilization effects of the diquaternary ammonium head groups and the strong π - π interactions in the hydrophobic core may energetically favour the formation of micellarstructured zeolites, which can further facilitate the self-assembly of templates with aromatic moieties to geometrically match the zeolitic frameworks. Thus, a geometric matching model of the zeolite structure and the cooperative packing of the TPB-6 molecules was proposed based on the corresponding arrangements of the triply branched templates in the MFI framework along the a and b axes. As mentioned previously, model ii is the most suitable structural model of MMZ-6 (Figures 4b-4d). The TPB-6 molecules stack in the *b*-*c* plane of the MFI framework, and the angle between the aromatic group and b-c plane is ~23° or 157° (Figure 4b). The horizontal distance between two adjacent surfactants is ~10 Å, and the perpendicular distance is 3.8 Å.^[18] The aromatic groups of the TPB-6 molecules stack in the b-cplane of the MFI framework, forming a stable network through π - π stacking with an slipped configuration, which results in sheet-like micelles (Figure 4d). The diquaternary ammonium head groups tethered on triply branches of the template broke the extension of the nanosheets assembly along the a and b axes, which led to the formation of SCMMZ with sheet-like mesopores layered along the *a* and *b* axes.

It is demonstrated that the length of the alkyl chain between the diquaternary ammoniums and aromatic group plays an important role in the construction of the crystallographically correlated mesostructure. The relative stabilizing energies of the mesoporous MFI zeolite with different configurations of TPB-4 and TPB-10 were also calculated using MD simulations (Supporting Information, Table S2). The diameter of model ii (Supporting Information, Figure S10) is also suitable for the size of TPB-4; however, it is too small for TPB-10. Because the most common pore size of MMZ-10 is 2.6 nm, a new structural model in which the diameter of the mesopore is ~3 nm was built for TPB-10 (model iii, Supporting Information, Figure S10).

For TPB-4, the stabilizing energy of 1*straight+2*zigzag is the lowest, followed by that of 2*straight+1*zigzag and 3*zigzag. It can be concluded that when TPB-4 is loaded in the mesostructured MFI, a single TPB-4 molecule tends to stretch along the a-c or b-c plane of the MFI structure. However, C4 (Supporting Information, Figure S11) is just long enough to reach from the aromatic segment to the zeolite framework (~2 nm), which is too stretched and energetically unfavourable for the aggregation of the surfactants that direct the formation of SCMMZ. Therefore, TPB-4 only directs the synthesis of lamellar mesostructured MFI zeolites, because no substantial stretching is required in this system. When loading TPB-10 in the SCMMZ, the 3*straight, most stable configuration is followed bv 2*straight+1*zigzag, which indicates that mesostructured MFI is preferentially synthesized by disrupting crystalline growth along the baxis. Thus, it is concluded that the TPB-10 molecules stack in the a-cplane of the MFI framework, disrupting the growth of the MFI crystal along the *b* axis and directing the synthesis of an intergrown structure.

In summary, four different triply branched quaternary ammonium surfactants that can readily self-assemble and whose aromatic groups have a highly ordered orientation due to π - π stacking were designed. Lamellar mesoporous MFI, SCMMZ and MFI nanosheets with a rotationally and sequentially intergrown structure are obtained when

triply branched quaternary ammonium surfactants with different alkyl chain lengths are used as templates. For the synthesis of SCMMZ, one branch of TPB-6 or TPB-8 is loaded in the straight channel, whereas the other two branches are loaded in the zigzag channels of MFI. The key elements enabling the synthesis of SCMMZ, in which mesopores are formed by disrupting crystalline growth along the *a* axis, are the special configuration of TPB-6 and TPB-8 with the quaternary ammoniums located in the zigzag channels to direct the synthesis of the zeolite and the geometric matching between the assembled surfactants and the zeolite framework. After removing the surfactants, the mesostructures of MMZ-6, MMZ-8 and MMZ-10 are retained, whereas the lamellar mesostructure of MMZ-4 collapses. The proposed mechanism provides a new route for the generation of hierarchical zeolites with different mesostructures.

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Conflict of interest

The authors declare no conflict of interest.

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A single-crystalline mesoporous MFI zeolite with sheet-like mesopores layered along the *a* and *b* axes was templated by a triply branched surfactant with diquaternary ammonium groups connected to 1,3,5-triphenylbenzene by a six-carbon alkyl chain. The sheet-like mesopores were embedded in the MFI framework and were retained even after calcination.



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