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Direct Synthesis of Nanosheets Stacked Hierarchical “Honey Stick-like” MFI Zeolite by Aromatic Heterocyclic Dual-functional Organic Structure-Directing Agent

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Abstract: Soft template designing is the most promised strategy for synthesis of zeolites nanosheets. So far, MFI nanosheets directed by soft templates (containing long chain alkyl groups or aromatic groups as hydrophobic component), can be found frequently. However, the MFI nanosheets synthesized by soft template with aromatic heterocycle groups (e.g. s-triazine groups) are rare. Herein, nanosheets stacked hierarchical MFI zeolite (NSHM) has been synthesized utilizing a triply branched s-triazine based surfactant as a bifunctional organic structure-directing agent. On the basis of geometrical match relationship, a formation model has been proposed. Synthesized NSHM was endowed with abundant mesopores stacked by nanosheets and exhibited a high surface area (430 $m^2 \cdot g^{-1}$). The 1 wt% Pd/NSHM attained a significant increase in cyclohexanol/cyclohexanone mixture yield (from 66% to 85%) in oxidation of cyclohexane compared with Silicalite-1 and SBA-15 as supports.

Zeolites, as a series of catalysts or catalytic supports, have extensive applications in catalysis, adsorption, and separation owning to their regular geometry structure, shape-selectivity, strong acidity and high hydrothermal stability .[1] However, microporous zeolites are difficult to adapt for heterogeneous catalysis involving diffusion of bulky molecules whose dynamic diameters are larger than 2 nm, since the sole narrow micropores (pore widths < 2 nm) and long transmission distance (Thiele module φ > 4 for conventional zeolites[2]) hinders the mass transfer during the limited diffusion processes.[1b, 3] The diffusion limitation of micropores could be effectively relieved by the introduction of mesopores into zeolites.[4] Several synthesis methods have been developed for producing hierarchical zeolites, such as post-synthesis treatments,[5] hard templating[6] and soft templating.[7]Among all of these routes, fabricating the hierarchical zeolites via soft templating based on mesoscale micellar structures self-assembled by amphiphilic molecules was expected as the most valuable route because of its tailorability.[4c]

In the soft templating method, hierarchical molecular sieves was firstly attempted to synthesize utilizing a combination of structure-directing agents (SDAs) and various amphiphilic molecules.[8] Unfortunately, during the synthesis process, two types of templates usually play competitive roles with each other, inevitably leading to phase separation. Recently, Ryoo et al. [9]made progress on fabricating multilamellar MFI nanosheets with unit-cell thickness stacking along b-axis through the rational design of Gemini-type surfactants with long hydrophobic alkyl chains. The introduction of second quaternary ammonium head groups play a significant role in stabilizing crystal lamellae during the formation period of MFI nanosheets. Compared to bulky MFI zeolite, ultrathin layered hierarchical MFI zeolite extremely reduced diffusion path lengths by single unit cell nanosheets, greatly improving mass transfer the efficiency of catalytic reactions.[9a] Moreover, Che et al. further found that aromatic groups which are grafted onto the hydrophobic alkyl chain tail can greatly improve the stability of micellar structure due to π–π stacking interaction between aromatic groups.[10] On the basis of this principle, they synthesized a variety of mesostructured zeolite nanosheets, such as SCZN-1[10a], SCZN-2[10a] and SSMZ[11]. Nevertheless, all of these zeolites generally have poor stability without pillared treatment, since the varying degrees of structural collapse of the parallel zeolite nanosheets after calcination, restricting their applications.[9c] Furthermore, Singh et al. designed a triple branched phenyl cationic surfactant. This method allowed the synthesis of single-crystalline cauliflower-like mesoporous ZSM-5 with three-dimensional pores.[12] They found that, due to the similar lattice parameters, (100) faces can facilely intergrow with (010) faces. This growth occurred via the common c-axis in the MFI framework. The introduction of crossed joints also improved the stability avoiding lamella collapse.[12] However, only phenyl and naphthyl groups have been introduced into the design of this series of amphiphilic surfactant until now. No successful examples exist demonstrating that hierarchical MFI nanosheets can be prepared by this type of amphiphilic surfactant with aromatic heterocyclic groups. Owing to the difference of electron clouds between aromatic and aromatic heterocyclic groups, micellar mesostructures morphology self-assembled via the π–π interactions are diverse. Furthermore, the geometrical matching relationship between the aromatic heterocyclic surfactant and zeolite framework remains unknown.

Herein, a triply branched s-triazine based surfactant template was designed to fabricate nanosheets stacked hierarchical MFI zeolite (NSHM). They exist 90° rotational intergrowth between the neighboring nanoflakes via conventional hydrothermal synthesis method. In this template, three diquaternary ammonium hydrophilic branches favoring to extend along three directions are connected to 1,3,5- triphenyl s-triazine to form the C_3N_3-{[*p*-C_6H_4-CH_2-$N^+(CH_3)_2$-C_6H_{12}-$N^+(CH_3)_2C_6H_{13}$][Br-]$_2$}$_3$ structure (Fig. S1~S2).

As shown in Fig. 1(a), wide-angle X-ray diffraction (XRD) patterns of the hierarchical MFI zeolite reveal that high-quality MFI structure has been fabricated with the OSDA involved. There are no observations of other zeolites or amorphous silica indicating the pure phase of NSHM. It is worth noting that most of representative diffraction peaks correspond to the *h0l* reflections of MFI structure. Such reflections demonstrate the formation of nanosheets on the *a-c* plane. No reflections were observedin the small-angle XRD patterns, which indicate that no ordered mesoporous structures formed in this sample.

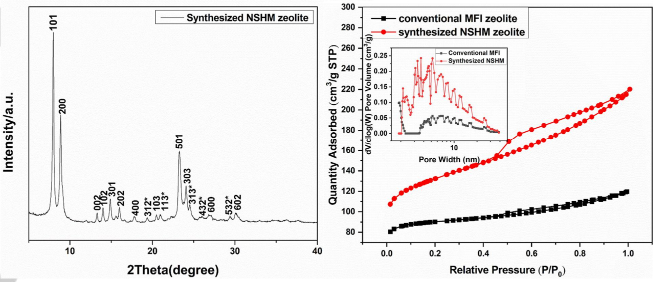


Fig. 1. (a) Wide-angle XRD pattern of the nanosheets stacked hierarchical MFI zeolite, (b) N_2 adsorption isotherms and DFT pore size distributions (inset) of the nanosheets stacked hierarchical MFI zeolite.

The N_2 adsorption–desorption isotherms and pore size distribution of the calcined sample are shown in Fig. 1(b). The isotherms exhibit type IV curve and H4-type hysteresis loop. The lifting parts below relative pressure (p/p_0) of 0.02 are attributed to the presence of abundant micropores,[13] which is similar to most of conventional MFI zeolites. The hysteresis loop at p/p_0=0.4-1.0 reveals the presence of sheet-like mesopores, which corresponds with the TEM figure. The mesopore size is mainly concentrated at 2.5 nm with a relatively broad peak, according to the calculation (on the basis of Barrett-Joyner-Halenda model) from adsorption branch. The Brunauer–Emmett–Teller (BET) surface area, micropore volume and mesopore volume of the sample are measured to be 430 m^2g^{-1}, 0.11 cm^3g^{-1} and 0.20 cm^3g^{-1} (Table S1), respectively, whose BET surface area and mesopore volumes are much higher than those of conventional MFI zeolite.

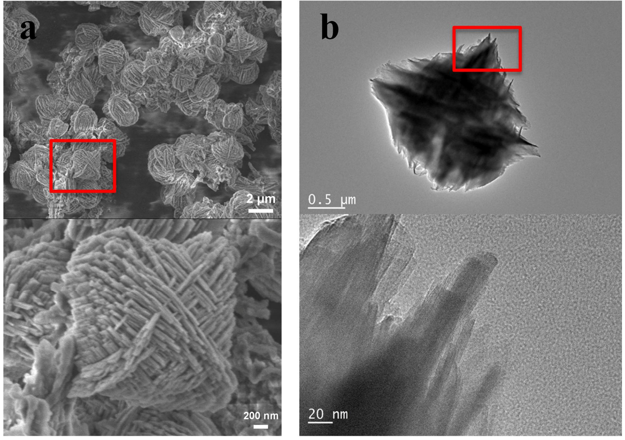


Fig. 2. (a) SEM and (b) TEM images of the nanosheets stacked hierarchical MFI zeolite.

Fig. 2(a) is a representative SEM picture of the synthesized hierarchical MFI zeolite. The sample particles exhibited a self-assembled “honey stick-like” morphology with a uniform diameter of 2 µm. Notably, the 90° rotational intergrowth can be observed distinctly in all the particles in the SEM image, the ellipsoidal structures are formed by MFI nanosheets piling up together vertically via intergrowth between them. The typical TEM image of the hierarchical MFI zeolite is provided in Fig. 2(b), the thickness of the primary MFI nanosheets are estimated to be 20 nm, presenting different stacking directions, which is consistent with the SEM picture. Between the layers, a mass of sheet-like mesopores are visually observed, which is attributed to the intergrowth of nanosheets along different directions 90° rotational stacking efficiently preventing the structure from collapsing by the removal of template during calcination.[10a] Considering the matching between surfactant geometry and zeolite framework, it could be speculated that the hydrophobic cores of OSDA prefer to arrange the micelle via partial face-to-face π–π interactions between adjacent aromatic groups in the MFI framework. Subsequently, the hydrophilic branches orient the nanosheets formation along the *a* and *c* axes in vertical direction, and form a brick masonry-like structure eventually (Fig. 3). On account of the stacking pattern inferred above, the nanosheet structure could take on extraordinary stability.

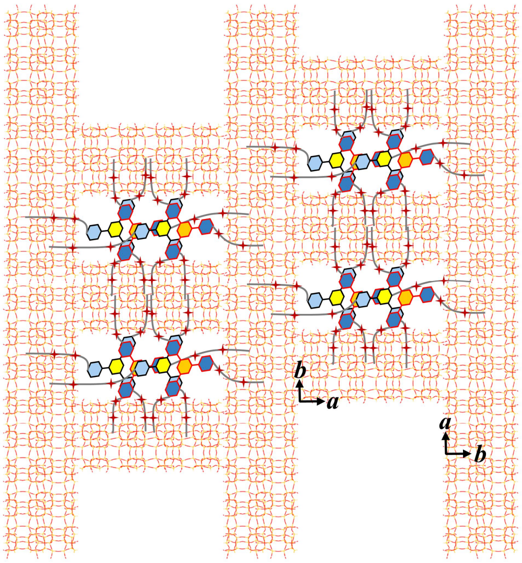
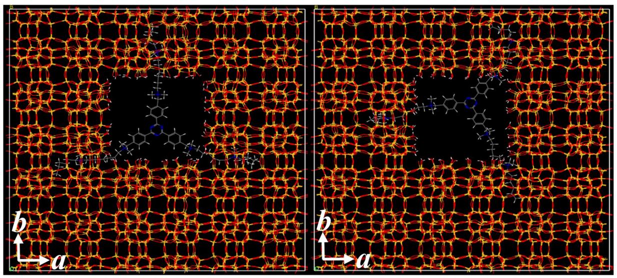
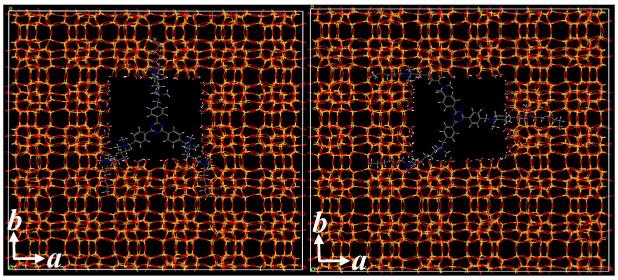


Fig. 3. Schematic representation of the packing configurations of the surfactants in the as-prepared NSHM zeolite and the possible formation model of the nanoflake intergrowth structure.

To confirm the speculation mentioned above, a series of binding energy calculations have been carried out (Fig. 4). Molecular dynamics (MD) simulations were applied to determine the optimized structure for OSDA with mesoporous MFI zeolite. MD simulations of the loading position model revealed that three straight occupied channels possess the lowest stabilizing energy. Thus, it could be concluded that extending along b axis is the preferred arrangement for OSDA in MFI zeolite. This conclusion is consistent with the XRD analysis (Fig. 1(a)) and the schematic diagram (Fig. 3). Because of ordered self-assemble of OSDA along *a-c* planes, the nanosheets configuration could be constructed facilely.



(a) One straight，two zig zag **(b) Two straight，one zig zag**



(c) Three straight **(d) Three zig zag**

Fig. 4. Diagram of results from binding energy calculations. According to the loading position of three hydrophilic chain of the OSDA in the MFI zeolite framework, four kinds of simulation models were constructed for binding energy calculation: one straight and two zig-zag channels occupied (a), two straight and one zig-zag channels occupied (b), three straight channels occupied (c), three straight channels occupied (d).

Table 1. Binding energies of four kinds of simulation models mentioned above.

Occupied Channels	One straight ， two zig zag	Two straight ， one zig zag	Three straight	Three zig zag
Binding energy △E^{a} (Kcal/mol)	360	-96	-384	-149

[a] △E = $E_{SDA+MFI}$ - E_{SDA} - E_{MFI}

To verify the internal surface accessibility, the as-made NSHM zeolite was loaded with 1 wt% Pd to obtain a supported palladium catalyst and evaluated in selective oxidation of cyclohexane (Fig. S3). By comparison, conventional Silicalite-1 and SBA-15 (textural parameters summarized in Table S1), which are well known as their monotonously micro- or meso-porous structure, are processed the same way. As shown in Fig. 5, a significant increase of the KA oil (Cyclohexanol/Cyclohexanone mixture) selectivity (from 66.1% for Silicalite-1/ 68.6% for SBA-15 to 85.4% for NSHM) was obtained for the NSHM zeolite. Such observation is probably attributed to the location of the Pd active sites in the shape-selectable micropore, instead of locating most likely on the external surface of bulk zeolite or non-selective mesopore of molecule sieve. Meanwhile, the considerable growth of cyclohexanone yield, implying the distinct improvement of oxidizing ability, is conjectured as the result of the higher dispersion of palladium clusters. To investigate the dispersion of Pd clusters, HR-TEM and STEM characterizations have been involved (Fig S4). Notably, Pd clusters were located more evenly inside NSHM particles and possessed a much smaller cluster diameter (1~5 nm) than that in Silicalite-1 (6~10 nm with uneven distribution), revealing that the better diffusion performance was obtained by NSHM.

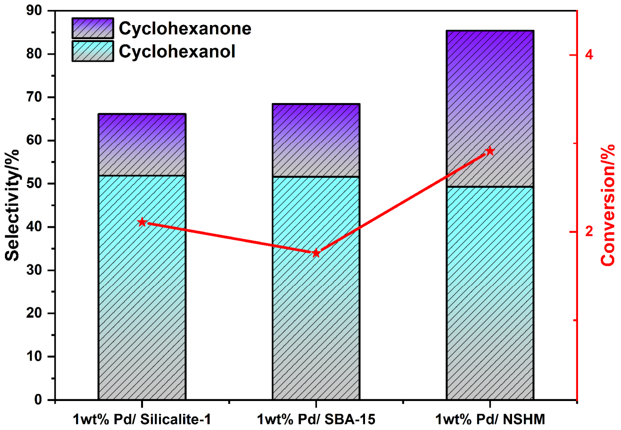


Fig. 5. Catalytic efficiency of conventional Pd/Silicalite-1, Pd/SBA-15 and Pd/NSHM in oxidation reaction of cyclohexane.

Therefore, on one hand, higher channel accessibility bring on the improved active site dispersion of Pd clusters. Thus the additional active sites could be obtained via the identical procedure. On the other hand, the existence of the abundant mesopores and larger specific surface area make the active sites located in the channels could be attached facilely by the reactants. Thus a superior performance in product selectivity could be acquired via the NSHM zeolite. To investigate the stability and recyclability of the Pd/NSHM, SEM characterization and repeat reaction have been performed by reused Pd/NSHM. Obviously, the nanosheets-stacked architecture of reused Pd/NSHM was maintained integrally (Fig. S5). It is worth noting that the reused Pd/NSHM remain superior catalytic performance (with total selectivity a bit raised) in the repeat reaction (Table S2), which has revealed that the NSHM possesses excellent stability.

In summary, by using a triply branched s-triazine based surfactant as a bifunctional structure directing agent with a conventional hydrothermal method, the hierarchical MFI zeolite was successfully fabricated through the 90° rotational intergrowth of nanosheets.The synthesized NSHM sample is made up of pure phase MFI nanosheet with high crystallity and exhibits a high surface area (430 m^2g^{-1}), a large mesopore volume (0.20 cm^3g^{-1}) and abundant mesopores around 2.5 nm stacked by nanosheets. Through the experiential evidence and Molecular dynamics (MD) simulations, the reasonable construction mechanism of NSHM has been proposed. Via a palladium loading process, the obtained Pd/NSHM possessed improved catalytic performance in cyclohexane oxidation reaction. The total selectivity to cyclohexanol and cyclohexanone increased to 85.4% while the conversion increased to 3%, which is superior over the conventional Silicate-1 and SBA-15 supported catalysts. All of these characteristics and evaluation results show promise for this hierarchical MFI zeolite to be used in the areas such as catalysis, catalyst supports or adsorbents.

Acknowledgements

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Conflicts of interest

The authors declare no competing financial interest.

Keywords: Heterocycles • MFI zeolite • Nanosheets • Self-assembly • Stacking interactions

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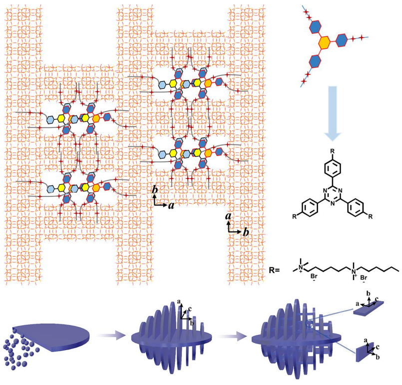

Nanosheets stacked hierarchical MFI zeolite (NSHM) has been synthesized utilizing a triply branched s-triazine based surfactant as bifunctional soft template, and the formation mechanism has been proposed. The obtained NSHM was endowed with abundant mesopores stacked by nanosheets and exhibited a high surface area (430 $m^2 \cdot g^{-1}$). Moreover, superior catalytic performance has been possessed by NSHM with palladium loading in oxidation reaction of cyclohexane.