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High ethylene selectivity in methanol-to-olefin (MTO) reaction over MOR nanosheets

Kun Lu^{†,+}, Ju Huang^{§,+}, Li Ren[†], Chao Li[‡], Yejun Guan[†], Bingwen Hu[‡], Hao Xu^{†,+}, Jingang Jiang[†], Yanhang Ma^{§,+}, Peng Wu^{†,+}

Abstract: Precisely controlled crystal growth endows zeolites with special textural and catalytic properties. A nanosheet mordenite zeolite with a thickness of ~11 nm, named as MOR-NS, has been prepared using a well-designed gemini-type amphiphilic surfactant as bifunctional structure-directing agent (SDA). Its benzyl diquarternary ammonium cations structurally directed the formation of MOR topology, whereas the long and hydrophobic hexadecyl tailing group prevented the extensive crystal growth along b axis. This kind of orientated crystallization took place through the inorganic-organic interaction between silica species and SDA molecules existing in the whole process. The thin MOR nanosheets, with highly exposed (010) planes and 8-membered ring (MR) windows therein, exhibited an extremely higher ethylene selectivity (42.1%) for methanol-to-olefin reactions when compared with conventional bulk MOR crystals (3.3%). Moreover, MOR-NS also possessed hierarchical structure and larger external surface area, making it a promising catalyst for processing bulky reactions like the alkylation of anisole with benzyl alcohol.

Zeolites are typical microporous crystalline materials that are widely used as catalysts in industrial processes, providing strong solid acidity and prominent shape-selective catalysis behaviors.^[1] The 3-dimensional (3D) micropore structures usually impose strong diffusion constrain in particular for bulky molecules, limiting the applications of conventional zeolite catalysts.^[2] To address this problem, hierarchical zeolites with secondary mesopore system or nanosized crystals have been synthesized, decreasing the diffusion length and enhancing the accessibility to the active sites.^[3] Nanosized zeolites, with significantly reduced crystal size along at least one dimension, always exhibit hierarchical porosity. The crystal size could be reduced through altering silica sources,^[4] gel compositions,^[5] or using hard templates,^[6] special organic templates^[7] to control initial nucleation and crystal growth thereafter. With strong structure-directing ability, organic quaternary ammonium cations are more possible to control the zeolite morphology or even to induce oriented crystallization and crystal growth under appropriate conditions. Taking the most studied MFI-type zeolite as an example, using different SDAs resulted in various morphologies, such as coffin crystals,^[8]

[†] Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, North Zhongshan Road 3663, Shanghai 200062, China E-mail address: hxu@chem.ecnu.edu.cn (H. Xu); pwu@chem.ecnu.edu.cn (P. Wu)

- [§] School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China
- E-mail address: mayh2@shanghaitech.edu.cn (Y. Ma) [[†]] Shanghai Key Laboratory of Magnetic Resonance, State Key
- [] Shanghai Key Laboratory of Magnetic Resonance, state Key Laboratory of Precision Spectroscopy, School of Physics and Materials Science, East China Normal University, Shanghai 200062, P. R. China
 [+] These authors contributed equally to this work.
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rectangular-shape crystals^[8] and nanocrystal aggregates.^[9] Reducing the particle size of MFI along desired axis could even achieved by adding modifiers of spermine, tributylphosphine oxide, etc.^[10] A major breakthrough was made by Ryoo et al. who succeeded in synthesizing unilamellar/multilamellar MFI nanosheets,^[11] using rationally designed Gemini-type amphiphilic surfactants with dual structure-directing functionalities. The MFI nanosheets exposed large amount of acid sites on the external surface, improving the catalytic conversion of large organic molecules. Using the similar strategy, the Beta,[12] MRE,[12] MTW, [11,12] MOR, [13] FAU[13], CHA[13] and MWW[14,15] zeolites with nanosheets, nanosponges, nanoparticles or nanorods morphologies were synthesized with two or more quaternary ammonium head group-containing amphiphilic surfactants.



Scheme 1. Graphic description for the formation of MOR nanosheet structure.

Mordenite (MOR), as a widely used solid acid catalyst, is characterized by a pore system composed of 12-MR main channel (0.65*0.7 nm) and elliptic 8-MR channel (0.26*0.57 nm) parallelly running along c axis, which are interconnected by 8-MR windows (0.34*0.48 nm) along b axis.^[16] Recently, it was reported that the 8-MR pores in MOR exhibited special shape-selective catalysis in the carbonylation of dimethyl ether to methyl $acetate^{\left[17,18\right]}$ and in the syngas conversion to ethylene $^{\left[19\right]}$ Thus, exposing more 8-MR windows by reducing the thickness along b axis of MOR topology would achieve specific catalytic selectivity. The MOR nanocrystals with 20 - 50 nm dimensions have been fabricated by using the amphiphilic templates with multiguaternary ammonium heads^[13] or the combination of tetraethyl ammonium hydroxide and commercial amphiphilic surfactants,^[20] but the crystal orientation and size were uncontrollable. Shen et al. synthesized the MOR nanosheets with of 20 - 40 nm thickness along c axis using a single quaternary ammonium surfactant.[18] Bearing these previous studies in mind, it is highly desirable to control the MOR crystals with further reduced size along b axis under rational expectation. We communicate here a high-silica aluminosilicate of MOR nanosheets, named as MOR-NS, using an amphiphilic bifunctional surfactant of C₁₆H₃₃-N⁺(CH₃)₂-C₄H₈-

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 $N^{+}(CH_3)_2$ -benzylamine (designated as Bza-4-16 hereafter) as SDA (Figure S1 and S2). Bza-4-16 with suitable spatial distance between two quaternary ammonium cations was designed to direct the formation of MOR structure while the hydrophobic tail of cetyl group to terminate the continuous crystal growth along *b* axis. This synthesis route gave rise to multilayer MOR nanosheeets with highly exposed (010) crystal planes (Scheme 1).

The PXRD pattern of MOR-NS was characteristic of the MOR topology, confirmed by Pawley refinement (Figure S3). However, the diffraction peaks especially those related to *b* axis were much broader for as-made MOR-NS-P in comparison to traditional MOR zeolite (Figure S4b and S4e), suggesting that MOR-NS probably possessed a *b*-axis orientated structure. The framework of MOR-NS was well-preserved after high-temperature calcination and hash acid treatment (Figure S4c and S4d), indicating it was thermally and hydrothermally stable.



Figure 1. SEM (a) and TEM images (b-d) of MOR-NS-P. The schematic diagram of MOR-NS-P structure viewed along c axis (e), in which the diquarternary ammonium cations are locked firmly by two 8-MR windows, with the benzyl headgroup pointing to 12-MR pore, whereas the long-chain cetyl tailing group to the opposite direction.

The SEM images revealed that MOR-NS exhibited a morphology significantly different from that of traditional MOR. The MOR-NS crystals were composed of flower-like thin nanosheets with a thickness around 10 nm (Figure 1a), whereas the traditional MOR zeolites showed nanoparticle or bulk morphologies, with the sizes ranging from 50 to several hundred nanometers depending on synthesis methods (Figure S5). The TEM images of MOR-NS were further collected to investigate its unique structure (Figure 1b and Figure S6), which were consistent with the SEM images indicative of highly ordered zeolite layers in MOR-NS. Under higher magnification along a axis, it was obvious that the as-synthesized MOR-NS-P composite was composed of alternating 2.0 nm-thick inorganic MOR layers and 1.1 nm-thick organic surfactant layers, possessing an overall thickness of ~ 11 nm (Figure 1c). Figure 1d further suggests that the MOR layers expanded within the (010) planes and stacked along b axis, in good agreement with the above mentioned PXRD patterns.

Considering the organic surfactant pillared the specific MOR layers as revealed by the TEM images, the organic-inorganic interaction was supposed to be crucial for the crystallization of multilamellar MOR zeolite. The elemental analysis and ¹³C NMR spectroscopy firstly proved that the chemical structure of SDA molecules was well-preserved in the crystallization process (Table S1 and Figure S7). The 2D ¹H-²⁹Si HETCOR NMR spectrum of MOR-NS-P revealed the essential role of the organic

surfactant molecules in supporting the inorganic MOR layers (Figure S8b). The ²⁹Si signals in the range of -118 to -105 ppm, assigned to the zeolite Q⁴ species,^[21] exhibited the strongest correlations with that of the $-N^+(CH_3)_3$ segment in Bza-4-16, implying the strong intermolecular interactions between the quaternary ammonium head groups and the zeolite frameworks. On the other hand, the ¹H NMR resonance at ca. 3.9 ppm, mainly due to the long chain of cetyl groups, had relatively weak correlation with either Q³ or Q⁴ inorganic framework silicon atoms. This indicated the tail groups of Bza-4-16 were spatially distant to the zeolite framework. This would further verify that the hydrophobic tails most possibly existed in the interlayer region but they were not embedded within zeolite pores. It should be noted that the benzyl head group of Bza-4-16 with a cross section of ~ 0.6 nm matches in size with the diameter (0.65 * 0.7 nm) of the MOR 12-MR pores. The most stable configuration of SDA in MOR structure was described using the molecular mechanics simulation (Figure S9). Considering the length of hydrophobic tail of SDA, the interlayer space would reach ~ 2 nm if the surfactant was packed in a vertical configuration. Hence, the alkyl chain groups were probably packed in an oblique or bended style in the interlayer space (Figure 1e). The two quaternary cations took the positions on the outsides of two 8-MR windows along b axis, with one in main 12-MR channel and the other one in broken 8-MR channel. This kind of configuration made the organic -(CH₂)₄butylene group between two quaternary ammonium cations firmly embedded within the inorganic framework. The location of Bza-4-16 was also confirmed by the TG-DTG analysis (Figure S10 and Table S2). The calculation based on the mass of organic SDA and inorganic zeolite indicated that MOR-NS-P contained about one SDA molecule per unit cell.

To investigate the structure evolution of MOR-NS, the solid products withdrawn from the synthetic mixture at different time were characterized by PXRD, SEM and TEM techniques. The PXRD pattern of initial synthetic gel of MOR-NS was corresponding to an amorphous phase (Figure S11a). After 24 hours, the diffraction characteristic of mesophase appeared in the low-angle region (Figure S11b), as a result of self-assembly between the micelle of amphiphilic SDA molecules and the silica/alumina sources. The mesophase disappeared after 96 hours (Figure S11d), while minor diffractions appeared in the high-angle region of $2\theta = 25 - 30^{\circ}$ after 192 hours (Figure S11e), implying that the meta-stable mesophase was dissolved or reorganized to provide the nutrition for the later zeolite crystallization. Highly crystalline MOR phase was obtained for MOR-NS after 504 hours (Figure S11i). The crystallization process was also traced by SEM and TEM images (Figure S12 and S13), revealing very similar results for the phase evolution. The crystallization process of MOR-NS was graphically described in Scheme 1.

A systematic study was conducted to determine the synthetic window for the phase-discrimination of MOR-NS (Table S3 and Figure S14). The crystalline phases of the products were largely affected by the Si/AI ratio in the initial gel, and MOR-NS with pure MOR phase was obtained in a relatively narrow Si/AI ratio range of 25 - 35 (Table S3, No. 3 - 5). At lower Si/AI ratios of 10 - 20, conventional MOR phase was obtained (Figure S15 and Figure S16. At higher Si/AI molar ratios of 45, layered silicate was formed as the major phase (Figure S15d and Figure S17). As reported in previous studies,^[22,23] traditional MOR zeolite was easily crystallized in the synthetic gel with lower Si/AI ratios, in good

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agreement with the phenomena observed in the present study. The effect of SDA, H_2O and Na^+ amount were also investigated in the supporting information.

The physicochemical properties of calcined MOR-NS nanosheets were compared with conventional MOR bulk crystals. The pristine conventional MOR was acid treated to achieve comparable Si/Al ratio as MOR-NS, and they exhibited wellpreserved crystallinity and morphology (Figure S5, e-g and Figure S18, e-g). The MOR-NS zeolite and its acid-treated derivative possessed both micropores and mesopores, while the traditional MOR zeolites exhibited only microporosity (Figure S19 and Table S4). The infrared spectra indicated that the dealumination procedure for MOR nanosheets was nonselective toward AI sites in 12-MR or 8-MR (Figure S20, a and b). With respect to the microporosity, MOR-NS and bulk MOR both showed the main peak around 6 Å in pore size distribution curves (Figure S21), due to the same main 12-MR channels of MOR topology. Meanwhile, the formation of mesopores in MOR-NS was highly related to the intergrown crystals, as the SDA species served as pillars to support each other and to prevent full condensation of the neighboring zeolite layers. On the other hand, the slight dislocation of the up-and-down layers would also cause the incomplete condensation.



Figure 2. (A) Conversion of methanol over the catalysts of MOR-C (a), MOR-NS-AT (b), MOR-D (c) and H-MOR-NS (d) in MTO reaction. (B) The comparison of low olefins ($C_{2.4}^{-1}$) selectivity between MOR-C and MOR-NS-AT. MTO reaction conditions: cat., 0.1 g; N₂ flow rate, 30 mL min⁻¹; temp., 673 K; WHSV, 1.0 h⁻¹.

The coordination environment of AI ions in MOR-NS and traditional MOR zeolites was revealed by ²⁷AI MAS NMR spectra

(Figure S22). A major resonance at 58 ppm, assigned to tetrahedrally coordinated AI species,^[24] was observed for the two kinds of MOR materials and their acid-treated derivatives, indicating almost all of the Al species were tetrahedrally coordinated in MOR framework. The IR spectra were further recorded in the hydroxyl stretching region to confirm the Al coordination (Figure S23). The IR band at 3610 cm⁻¹ was associated with the bridging hydroxyls of framework aluminum (Si-OH-AI), which proved that the AI species mainly existed in framework. H-MOR-NS showed a more intense 3740 cm⁻¹ band, attributing to isolated terminal silanol groups,^[25] which should be contributed by its highly exposed external surface on ac planes. The catalytic properties of aluminosilicates greatly depend on their Brønsted and Lewis acidity. Thus, pyridine adsorbed IR spectra were measured (Figure S24) and revealed that the amount and strength of Brønsted and Lewis acid sites were very similar for the two kinds of MOR materials with comparable Si/Al ratios of 31 and 28. The NH₃-TPD investigation also gave similar results (Figure S25).

The MOR-NS, with comparable acidity but greatly different crystal morphology and porosity in comparison to traditional MOR, is expected to exhibit distinct catalytic properties, which were probed in methanol-to-olefins (MTO) and Friedel-Crafts alkylation reactions. Figure 2 shows the time courses of methanol conversion and product selectivity of MTO over the MOR zeolites. The methanol conversions over MOR-NS-AT and MOR-C were kept over 97% for 360 min, indicating a slow deactivation rate. However, the corresponding samples with lower Si/Al ratios deactivated rapidly after 90 min (Figure 2A), due to the severe carbon deposition aroused by high acid density.^[26] The main products of MTO reaction were lower olefins ($C_2^{=} - C_4^{=}$), with MOR-NS-AT showing a higher total olefins selectivity close to ca. 80% (Figure 2B). More interestingly, the lower olefin distribution varied with the morphology of MOR zeolites. The MOR-NS-AT had unexpectedly high selectivity for ethylene (42.1%), while the main product of MOR-C was propylene (45.3%) and butene (24.3%) (Table S5). For the currently used zeolites (such as SAPO-34, MOR and MFI) as MTO catalysts, propylene was the primary product. These results demonstrated that the structural features of MOR-NS had obvious effects on the hydrocarbon product selectivity. The previous researches showed that the acid site distribution within MOR pores has a significant impact on ethylene production. Bao et al.^[19] provided experimental evidence that the high selectivity of ethylene in the syngas conversion was achieved more likely over the 8-MR sites in MOR framework. Similarly, the C-C coupling to produce light olefins in MTO reaction was controlled by the confined environment of zeolite pores and acid sites.^[27] The MOR-NS nanosheets, possessing highly exposed (010) planes as a result of crystal thinning along the *b*-axis, not only enhanced the accessibility of methanol to 8-MR windows, but also increased the diffusion rate of smaller olefin molecules along the *b*-axis, giving rise to a higher ethylene selectivity than conventional MOR zeolite at comparable Si/AI ratio. To confirm this, four MOR zeolites with different crystal morphologies were investigated in the MTO reaction at comparable Si/Al ratios of 85 - 91. As shown in Figure 3, all the MOR catalysts achieved 100% methanol conversion, and MOR-NS-AT showed higher light olefins selectivity than the other three conventional MOR zeolites. Especially, the ethylene selectivity in lower olefins decreased monotonically with increasing thickness

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Figure 3. The dependence of product distribution (Stacked-Column) and C₂= selectivity in low olefins (curve) on the crystal thickness along the b axis of MOR zeolites with different crystal morphologies. The comparison was made at comparable Si/Al ratios of around 90 and 100% MeOH conversion. MTO reaction conditions: cat., 0.1 g; N₂ flow rate, 30 mL min⁻¹; temp., 673 K; WHSV, 1.0 h⁻¹; time-on-stream, 60 min. The TEM images show the image of representative primary crystal of each MOR sample.

along the *b*-axis. By contrast, it had no relevance to the thickness along the c-axis (Figure S26). More detailed investigations were performed to disclose the relationship between the special acid site located in 8-MR pockets and high ethylene selectivity. When the H⁺ species in the 8-MR pockets of MOR-NS-AT were partially exchanged by Na⁺, the ethylene selectivity was declined from 42.1 % to 24.5 % (Figure S27, a and b). However, selectively shielding the acidic sites located within the 12-MR channel only slightly decreased the ethylene selectivity by introducing pyridine in the reaction feedstock (Figure S27, a and c). Figure S28 displays the GC-MS chromatograms of organic species retained in spent catalysts. More lower methylbenzenes retained in spent promoted MOR-NS-AT. which ethylene formation as intermediates. Besides, the ethylene in the reaction system could not be converted to propylene by methylation (Figure S29). The above results demonstrated that the formation of ethylene was mainly driven by aromatic-based pathway over the exposing specific 8-MR acid sites in MOR framework. The TG-DTG curves proved that the used MOR-NS-AT catalyst possessed smaller amount of carbon deposition (7.25 wt.%) than that of MOR-C (8.35 wt.%) (Figure S30), mostly because the former had a hierarchical porosity composed of micropores and mesopores that were useful for releasing diffusion constrains in MTO reaction.

The MOR-type catalysts were further evaluated in the alkylation of anisole with benzyl alcohol (Table S6). The reaction product of benzyl methoxybenzene with a diameter of ~0.8 nm was unable to fit inside the 8- or 12- ring pores, therefore the catalytic processes mainly occurred on the outer surface of MOR nanosheets. The catalytic activities of H-MOR-NS was much higher than that of MOR-C in terms of TON value (16 vs 3.5). H-MOR-NS and MOR-D had roughly the same acid amounts and acid strength. Hence, the higher activity of H-MOR-NS was attributed to its hierarchical pore system, offering a large number of acid sites on the external surface and favoring the diffusion of bulky molecules.

In conclusion, the bifunctional amphiphilic surfactant allowed us to synthesize multilamellar MOR-type zeolite. The Si/AI ratio was critical for the formation of monolayers stacking along *b* axis. The multilamellar structure was converted to 3D MOR nanosheets with highly exposed (010) crystal planes, which favored the ethylene production in the MTO reactions. Moreover, the hierarchical pore system of MOR-NS was beneficial to depress the coke formation in the MTO reaction and also to enhance the catalytic activity in the alkylation of anisole with benzyl alcohol.

Experimental Section

Experimental details are provided in the Supporting Information.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: MOR zeolite, nanosheet, orientated crystal growth, hierarchical structure, MTO reaction

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