

Preparation of MFI Nanosheets with Distinctive Microstructures via **Facile Alkaline Etching**

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ABSTRACT: Although zeolite nanosheets (NSs) exhibit great prospects for a wide range of applications due to microstructural superiority, their facile preparation and microstructural tailoring remain a great challenge. In this study, uniform coffin-shaped MFI microcrystals were subjected to hydrothermal treatment in the presence of different types of alkaline etching agents, i.e., TMAOH, TEAOH, and TPAOH, for preparing MFI NSs with distinctive microstructures. It was found that the morphological and textural properties of MFI NSs could be readily tuned by varying etching agent types, etching agent contents, and hydrothermal treatment parameters, thereby leading to the formation of 10 nm thick leaf-shaped MFI NSs, ellipse-shaped MFI NSs, and single-crystal-like MFI NS aggregates through an in-plane oriented attachment. Simultaneously, the possible mechanisms involved in the formation of MFI NSs with distinctive microstructures were proposed. Among the prepared MFI NSs, 10 nm thick (ca. 5 unit cell) leaf-shaped MFI NSs represented one of the thinnest MFI NSs ever reported by the top-down method, while single-crystal-like MFI NS aggregates were prepared for the first time, which may endow them with superior performances in relevant application areas.

INTRODUCTION

Zeolites possessing uniform pore size, high surface areas, robust rigid structure, and tailorable surface functionality are widely used as adsorbents, detergents, catalysts, ion exchangers, and separation membranes.^{1–8} However, zeolites in the form of bulk powders may exhibit a high diffusion barrier for guest molecules, thereby severely hindering their widespread application in the chemical and petrochemical industry.^{9–14} Compared with their bulk counterparts, zeolite nanosheets (NSs) have shown superior performances in various fields due to significantly reduced diffusion path length and, therefore, a much lower diffusion barrier.^{15–19}

Recent decades witnessed significant progress in zeolite NSs, whose synthetic protocols could be further classified into bottom-up and top-down methods. The bottom-up method involves the direct synthesis of zeolite NSs by accurate engineering of the crystallization process.^{5,20-23} For example, Tsapatsis et al. reported the direct synthesis of high-aspect-ratio MFI NSs of 5 nm thickness with improved yields via nanocrystal-seeded growth method triggered by a single rotational intergrowth.²⁰ Hedlund et al. achieved the one-pot

synthesis of defect-free monodispersed 10 nm thick MFI crystals through long-term aging in a fluoride-containing medium.²¹ Very recently, Valtchev et al. further produced plate-like MFI crystals with the thickness of several tens of nanometers by combining preliminary aging with fluoride-aided low-temperature crystallization.²² In contrast, the top-down method involves a multistep approach based on exfoliating the layered zeolite precursors. Ryoo et al. first exfoliated multilamellar MFI zeolites into 2 nm thick MFI NSs using deliberately designed $[(CH_3O)_3SiC_3H_6-N^+(CH_3)_2C_{16}H_{33}]Cl$ (TPHAC) surfactants as structure-directing agents (SDAs).¹⁸ Tsapatsis et al. further developed a polymer-melt-compounding technique integrated with a density gradient centrifugation to exfoliate multilamellar

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Figure 1. (a) SEM image, (b) TEM image, (c) XRD pattern, and (d) N₂ adsorption/desorption isotherm of B-MFI.

MFI zeolites into monodispersed 3 nm thick MFI NSs.^{24,25} However, most of these synthetic strategies either rely on the use of expensive organic templates/environmentally hazardous additives or involve complicated exfoliation and purification procedures, which negatively affects their practical applications.

Different from the above protocols, alkaline etching has been widely recognized as a convenient and efficient approach for preparing hierarchical zeolites.^{26–28} Very recently, we successfully prepared uniform 25 nm thick hierarchical MFI NSs maintaining high mechanical stability and structural integrity via simple anisotropic etching of coffin-shaped bulk MFI crystals in an aqueous TPAOH solution under hydrothermal conditions.²⁹ Nevertheless, it was envisaged that MFI NSs with distinctive microstructures could be facilely tuned by simply varying the etching agent types as well as the etching conditions.

In this study, coffin-shaped bulk MFI crystals were hydrothermally treated with varying etching agents (i.e., TMAOH, TEAOH, and TPAOH). The influence of etching agent types, etching agent contents, and hydrothermal treatment parameters on the microstructure of MFI NSs was studied in detail. Simultaneously, plausible mechanisms for the formation of MFI NSs with versatile microstructures were proposed.

EXPERIMENTAL SECTION

Materials. TEOS (Macklin, 98 wt %), TMAOH (Macklin, 25 wt % aqueous solution), TEAOH (Macklin, 25 wt % aqueous solution), and TPAOH (Macklin, 25 wt % aqueous solution) were used without further purification.

Preparation of Coffin-Shaped Bulk MFI Crystals. Coffin-shaped bulk MFI crystals (B-MFI) were synthesized following the procedures reported previously.³⁰ Briefly, a precursor solution with the molar composition of 1TEOS:0.32TPAOH:165H₂O was prepared by adding 4.0 g of TEOS to an aqueous solution of 5.0 g of TPAOH and 53.3 g of deionized (DI) water. After being aged under vigorous stirring at room temperature for 4 h, the mixture was directly loaded into a Teflon-lined stainless steel autoclave and crystallized in a rotational convection oven (60 rpm) at 165 °C for 3 h. Afterward, the obtained sample was recovered, thoroughly washed with DI water, air-dried overnight at 60 °C, and finally calcined at 550 °C for 6 h with a ramping rate of 1 °C/min.

Preparation of MFI NSs with Different Etching Agents. TMAOH, TEAOH, and TPAOH were used as the etching agents in this study. After mixing the given amount of etching agents in DI water (gross mass of 16.5 g), 0.2 g of calcined B-MFI was added in the above aqueous solution. After sonication for 20 min, the solution was loaded into a Teflon-lined stainless steel autoclave. Alkaline etching was conducted in a rotational convection oven under 60 rpm at 170 °C. Afterward, the obtained sample was recovered, thoroughly washed with DI water, and finally air-dried overnight at 60 °C. The obtained samples were named as MFI-x(y, z), with x, y, and z denoting the type of etching agent (TMA, TEA, or TPA, respectively), the concentration of the etching agent, and the reaction time, respectively. For example, B-MFI hydrothermally treated with 0.18 M TEAOH solution at 170 °C for 18 h were denoted as MFI-TEA (0.18 M, 18 h).

Characterization. Powder X-ray diffraction (XRD) patterns were obtained on a Rigaku SmartLab diffractometer using Cu K α radiation ($\lambda = 0.15418$ nm) at 45 kV and 200 mA. Scanning electron microscopy (SEM) images were recorded on a FlexSEM 1000 instrument (Hitachi Co.) with an acceleration voltage of 15 kV. Before SEM characterization, the obtained samples were subjected to gold-sputtering treatment for better electrical conductivity. Transmission electron microscopy (TEM) images were collected on a JEM-2000EX instrument

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Figure 2. (a) SEM image, (b) AFM image with a height profile extracted along the white dashed line, and (c) TEM image of MFI-TMA (0.18 M, 18 h). (d, e) SEM image and (f) TEM image of MFI-TEA (0.18 M, 18 h). (g, h) SEM image and (i) TEM image of MFI-TPA (0.217 M, 18 h). (j) XRD patterns, (k) N_2 adsorption/desorption isotherms at 77 K, and (l) TGA curves of MFI-TMA (0.18 M, 18 h) (black line), MFI-TEA (0.18 M, 18 h) (blue line), and MFI-TPA (0.217 M, 18 h) (red line). The inset in part (c) shows the SAED pattern of the corresponding rectangular area.

(JEOL Company) operated at 120 kV. AFM measurements were performed on a PicoScan 2500 instrument (MI Company) under ambient conditions. The N₂ adsorption–desorption isotherms were recorded on a Micromeritics ASAP 2020 Plus analyzer at 77 K. Prior to the measurement, the samples were degassed at 300 °C under vacuum for 12 h. The total surface area was derived using the BET model, micropore volume and external surface area were determined from the *t*-plot method, and the total pore volume was determined from a single point measured at $P/P_0 = 0.994$. The Saito–Foley (SF) method was applied to analyze the micropore distributions and the mesopore distributions were determined by the adsorption branch of the N₂ isotherm based on the Barrett–Joyner–Halenda (BJH) model. Thermogravimetric analysis (TGA) was obtained on a NETZSCH (TG 209) thermal analyzer by heating the samples in an airflow (100 mL/min) from 40 to 800 $^\circ C$ with a ramping rate of 10 $^\circ C/min.$

RESULTS AND DISCUSSION

Characterization of Bulk MFI Crystals. The B-MFI were synthesized following a procedure described in the literature.³⁰ As shown in Figure 1a,b, the obtained products exhibited a coffin-shaped morphology with an average size of $0.9 \times 0.45 \times 1.2 \,\mu$ m. XRD results confirmed that the above products indeed belonged to the pure MFI phase (Figure 1c).³¹ Furthermore, the prepared B-MFI presented a typical type I isotherm (Figure 1d), thereby confirming a well-defined microporous structure. The BET surface area and the micropore volume calculated by the *t*-plot method reached 444.7 m²·g⁻¹ and 0.2 cm³·g⁻¹, respectively (shown in Table S1).



Figure 3. SEM images of MFI-TMA (0.18 M, z) samples synthesized at etching times of (a) 0.75 h, (b) 6 h, (c) 12 h, and (d) 72 h. The inset shows the corresponding TEM image.

Impact of Etching Agent Type on the Microstructure of MFI NSs. Initially, the influence of etching agent type on the microstructures of MFI NSs was investigated. SEM results indicated that after being subjected to hydrothermal treatment with different etching agents, MFI NSs with different morphologies could be obtained. With TMAOH as an etching agent, under optimized etching conditions (Figure S1), uniform leaf-shaped 10 nm thick (ca. 5 unit cell thick) MFI NSs with an average grain size of 0.7 μ m along the *c*-axis (Figure 2a–c) were formed. Relevant selected-area electron diffraction (SAED) patterns demonstrated that the prepared MFI NSs maintained a single-crystal structure (inset of Figure 2c).³² As far as we know, this represented one of the thinnest MFI NSs ever prepared by the top-down method. In the case that TEAOH was employed as an etching agent, we found that maintaining an appropriate TEAOH concentration (denoted as [TEAOH]) was indispensable for preparing MFI NSs with the desired microstructure (Figure 2d,e); or else, incomplete etching of a/c facets of B-MFI or excessive etching of the prepared MFI NSs would occur (Figure S2). TEM results (shown in Figure 2f) further indicated that substantial large mesopores were generated spontaneously inside MFI NSs in the process of TEAOH etching. As shown in Figure 2g,h, upon using TPAOH as the etching agent, after hydrothermal treatment under optimized TPAOH concentration (denoted as [TPAOH]), uniform ellipse-shaped 25 nm thick MFI NSs with high uniformity could be obtained. The presence of abundant mesopores inside the NSs could be supported by the TEM image (Figure 2i).

The above products obtained by the hydrothermal treatment of B-MFI in the presence of different alkaline etching agents were also characterized by XRD. As presented in Figure 2j, no clear differences could be observed between MFI crystals before and after the hydrothermal treatment, implying that the crystallinity of MFI NSs after being subjected to hydrothermal treatment with the etching agents could be well-preserved.³³ Subsequently, the textural properties of the above MFI NSs were studied by conducting the N2 physisorption measurements. As shown in Figure 2k, after being subjected to TMAOH, TEAOH, or TPAOH etching, the obtained MFI NSs presented typical IV isotherms with significantly increased N₂ uptake at $P/P_0 < 0.1$, thereby indicating the presence of hierarchical micro-mesoporous structures. Simultaneously, the BJH pore size distribution curves depicted in Figure S3 suggested the presence of additional mesopores aside from intrinsic micropores (0.55 nm) in the etched samples, which unambiguously confirmed that substantial mesopores were generated in the etching process. Moreover, specific surface areas and pore volumes of the above MFI NSs were calculated, and the relevant results were listed in Table S1. We noted that both BET surface areas (441.5, 424, and 439.7 $m^2 g^{-1}$ for MFI-TMA, MFI-TEA, and MFI-TPA, respectively) and micropore volumes (0.17, 0.19, and 0.17 cm^3 · g⁻¹ for MFI-TMA, MFI-TEA, and MFI-TPA, respectively) of the above MFI NSs remained well-preserved, thereby confirming well maintenance of the microscopic structural integrity even under harsh etching conditions. In comparison with B-MFI, the experimental data also indicated that both mesoporous volumes and external surface areas were significantly increased due to the introduction of mesopores during the hydrothermal alkaline treatment process. To gain more insights into the structural properties of synthesized MFI NSs, all etched samples were further characterized by TGA. As shown in Figure 2l, the TG curves of all uncalcined samples exhibited significant weight loss peaks in the temperature range of 250-500 °C, indicating that the corresponding tetraalkylammonium

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Figure 4. SEM and TEM images of MFI-TEA (0.18 M, z) samples synthesized at etching times of (a, b) 0.5 h, (c) 1 h, (d) 6 h, and (e, f) 72 h.



Figure 5. SEM and TEM images of MFI-TPA (0.217 M, z) samples synthesized at etching times of (a, b) 0.5 h, (c) 1 h, (d) 6 h, (e) 72 h, and (f-h) 144 h. (i) SAED patterns derived from the rectangle frame in (h).

(TAA) species,^{34,35} which served as templates, were incorporated in MFI channels during the NS formation process.

Investigation of MFI NS Evolution Process. We observed that hollow-structured MFI crystals with smaller grain sizes (1

 μ m along the *c*-axis) would form at the early stage in case TMAOH was used as the etching agent (Figure 3a). Further prolonging the hydrothermal treatment duration resulted in excessive thinning of zeolite walls in all crystallographic

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directions and, subsequently, the formation of ring-shaped MFI NSs comprising pillared leaf-shaped MFI NSs with an intersheet distance of 170 nm (Figure 3b,c). It was worth mentioning that the preparation of the pillared leaf-shaped MFI NSs has never been reported before. Upon extending the etching time to 18 h, only the largest facet, which was vertical to the *b*-axis of B-MFI, survived, thereby resulting in the formation of uniform leaf-like MFI NSs. It should be noted that the surface morphology of the prepared MFI NSs remained unchanged even when the etching time was further extended to 72 h (Figure 3d), implying that a solubility equilibrium had been established in the etching solution.

Upon hydrothermal treatment in an aqueous TEAOH solution, the formation of hollow MFI crystals could be observed at the early stage (Figure 4a,b). As has been previously reported in the literature, a dissolution-recrystallization mechanism played a dominant role in the formation of hollow MFI crystals.^{26,27,36} Initially, the zeolite cores were preferentially dissolved because of the lower crystallinity of the core. Subsequently, leached silica species were recrystallized on the outer surface in the presence of TEA⁺ cations. Since TEA⁺ cations were too large to enter MFI pores, recrystallization occurred only on the outer surface, thereby leading to the formation of hollow-structured MFI crystals. Further extension of the etching time led to the progressive thinning of zeolite walls in all directions (Figure 4c,d). Finally, only the largest faces arranged vertically to the b-axis of B-MFI were preserved, leading to the formation of uniform ellipse-shaped MFI NSs with an average thickness of ca. 60 nm and a yield of 17.5%. Simultaneously, a few fragments, which were detached from the hollow-structured MFI crystals, were also generated. Further prolonging the reaction time to 72 h led to the formation of MFI NSs with a well-developed morphology and an increased thickness of 155 nm along the *b*-axis (Figure 4e,f). In addition, the yield of MFI NSs was increased to 37%.

Upon hydrothermal treatment in an aqueous TPAOH solution, the formation of hollow MFI crystals, which were formed following the dissolution—recrystallization mechanism, was observed at the early stage (Figure 5a,b). Progressive thinning of zeolite walls in all directions also occurred upon extending the etching time (Figure 5c,d). As the reaction time was extended to 18 h, uniform ellipse-shaped MFI NSs with an average thickness of 25 nm and a yield of 16% were obtained. However, further extending the etching time to 72 h led to a considerable increase in thickness along the *b*-axis (65 nm; Figure 5e) as well as yield (24%), thereby confirming the dominance of recrystallization rate over dissolution rate during this time interval.

It is of interest to note that when the treatment time was prolonged to 144 h, several monodispersed NSs would attach together along their a/c-facets, resulting in the formation of MFI NS aggregates of 130 nm thickness with larger *b*-axis crystal planes (Figure 5f,g). The TEM image indicated that some mesopores still existed inside the MFI NSs (Figure 5h) and the corresponding SAED pattern confirmed that the prepared twinned MFI NSs maintained a single-crystal structure (Figure 5i). To the best of our knowledge, this represented the first report on the oriented attachment of MFI crystals along the a/c-facets. The subsequent mechanical stability test indicated that the prepared MFI NS aggregates were mechanically robust since their morphology remained unchanged even after being subjected to strong sonication for 1 h (Figure S4a) or vigorous stirring (400 rpm) for 1 week (Figure S4b), which was quite

beneficial for their applications under harsh operating conditions.

Plausible Mechanism Associated with Different Etching Agents. To elucidate the roles played by different etching agents during the hydrothermal treatment of B-MFI, first the pH value of the corresponding aqueous solution was measured to verify whether it dominated the final microstructures of the etched samples. The experimental data summarized in Table S2 indicated that there was little difference among the above precursor solutions. Therefore, the influence of the pH value of the precursor solution was negligible.

It is well recognized that the hydrothermal treatment of zeolite crystals with alkaline templates may cause partial dissolution of silica species from bulk zeolites and, simultaneously, their recrystallization on the outer surface of bulk zeolites.²⁶ Therefore, the final microstructure is determined by their dissolution rate relative to the recrystallization rate during the etching process. Considering the similarity of the pH values among different precursor solutions, their dissolution rates during the etching process should be comparable to each other. Therefore, the recrystallization rate of dissolved silica species would be of vital importance to the final microstructure of the etched MFI crystals.

It has been reported that the TAA template with a more advantageous spatial configuration for MFI topology was preferred for the recrystallization of leached silica species into the MFI framework.³⁷ Since TPAOH has proven to be the most appropriate SDA to MFI zeolite synthesis,³⁸ the recrystallization rate during the etching process could be accelerated to a large extent so that the highest structural integrity could be guaranteed. Song et al. investigated the influence of organic template types (e.g., TMAOH, TEAOH, and TPAOH) on the final morphology of TS-1/SiO₂ extrudates. Experimental results indicated that the ability for the above templates to direct the Pentasil SBU followed the sequence TPAOH > TEAOH > TMAOH.³⁹ By analogy, herein we speculated that the ability of the above etching agents to direct the recrystallization of the etched MFI crystals reduced in the order $TPA^+ > TEA^+ >$ TMA⁺. In contrast to TPAOH, TEAOH showed a decent ability to tune the recrystallization process so that the prepared MFI NSs exhibited relatively intact surface morphology but inferior grain size uniformity. In comparison with TPA⁺ and TEA⁺, TMA⁺ has the lowest structure-directing ability so that the recrystallization of the dissolved silica species was inconspicuous. As a result, the dissolution rate was much higher than the recrystallization rate, leading to the formation of leaf-shaped ultrathin MFI NSs with low yields.

CONCLUSIONS

In this study, we demonstrated the preparation of MFI NSs with distinctive microstructures (including surface morphology, NS thickness, structural integrity, and mutual intergrowth) via etching coffin-shaped bulk MFI crystals in an aqueous solution containing TMAOH, TEAOH, or TPAOH. The etching agent type, etching agent content, and parameters relevant to hydrothermal treatment were found to exert great influence on the final microstructure of MFI NSs, resulting in the formation of 10 nm thick leaf-shaped MFI NSs (ca. S unit cell thick), ellipse-shaped MFI NSs, and single-crystal-like MFI NS aggregates formed through oriented attachment along the a/c-facets. Owing to the different structure-directing ability of the TAA⁺ for the MFI topology structure (TPA⁺ > TEA⁺ > TMA⁺), the etching agent types significantly affected the dissolution rate

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relative to the recrystallization rate during the etching process; as a result, the NS integrity increased with the enhanced structuredirecting ability of TAA⁺. It is anticipated that the obtained MFI NSs with unique microstructures could exhibit superior performances in relevant application areas.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.1c03634.

Characterization data, SEM images, pore size distribution curves, textural properties, and pH test (PDF)

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Author Contributions

Y.L.* and Y.L. formulated the project. Y.L. performed major experiments and analyzed the experimental data with assistance from T.J., T.Z., and J.L.H.L. helped with the AFM characterization. Y.L.* and Y.L. co-wrote the manuscript with contributions from all authors.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Roth, W. J.; Nachtigall, P.; Morris, R. E.; Čejka, J. í. Twodimensional zeolites: current status and perspectives. *Chem. Rev.* 2014, 114, 4807–4837.

(2) Li, S. Y.; Li, J. F.; Dong, M.; Fan, S. B.; Zhao, T. S.; Wang, J. G.; Fan, W. B. Strategies to control zeolite particle morphology. *Chem. Soc. Rev.* **2019**, *48*, 885–907.

(3) Přech, J.; Pizarro, P.; Serrano, D. P.; Cejka, J. From 3D to 2D zeolite catalytic materials. *Chem. Soc. Rev.* **2018**, *47*, 8263–8306.

(4) Liu, Y.; Li, Y. S.; Yang, W. S. Fabrication of highly *b*-oriented MFI film with molecular sieving properties by controlled in-plane secondary growth. *J. Am. Chem. Soc.* **2010**, *132*, 1768–1769.

(5) Shan, Z. C.; Wang, H.; Meng, X. J.; Liu, S. Y.; Wang, L.; Wang, C. Y.; Li, F.; Lewis, J. P.; Xiao, F. S. Designed synthesis of TS-1 crystals with controllable *b*-oriented length. *Chem. Commun.* **2011**, 47, 1048–1050.

(6) Wu, Q. M.; Ma, Y.; Wang, S.; Meng, X. J.; Xiao, F. S. 110th Anniversary: Sustainable Synthesis of Zeolites: From Fundamental Research to Industrial Production. *Ind. Eng. Chem. Res.* **2019**, *58*, 11653–11658.

(7) Wu, Q. M.; Liu, X. L.; Zhu, L. F.; Ding, L. H.; Gao, P.; Wang, X.; Pan, S. X.; Bian, C. Q.; Meng, X. J.; Xu, J.; Deng, F.; Maurer, S.; Müller, U.; Xiao, F. S. Solvent-Free Synthesis of Zeolites from Anhydrous Starting Raw Solids. *J. Am. Chem. Soc.* **2015**, *137*, 1052–1055.

(8) Corma, A. State of the art and future challenges of zeolites as catalysts. *J. Catal.* **2003**, *216*, 298–312.

(9) Yang, X. Y.; Chen, L. H.; Li, Y.; Rooke, J. C.; Sanchez, Cm.; Su, B. L. Hierarchically porous materials: synthesis strategies and structure design. *Chem. Soc. Rev.* **2017**, *46*, 481–558.

(10) Bai, R. S.; Song, Y.; Li, Y.; Yu, J. H. Creating Hierarchical Pores in Zeolite Catalysts. *Trends Chem.* **2019**, *1*, 601–611.

(11) Zhang, T. J.; Chen, X. X.; Chen, G. R.; Chen, M. Y.; Bai, R. S.; Jia, M. J.; Yu, J. H. Synthesis of anatase-free nano-sized hierarchical TS-1 zeolites and their excellent catalytic performance in alkene epoxidation. *J. Mater. Chem. A* **2018**, *6*, 9473–9479.

(12) Zhang, Q.; Mayoral, A.; Terasaki, O.; Zhang, Q.; Ma, B.; Zhao, C.; Yang, G. J.; Yu, J. H. Amino Acid-Assisted Construction of Single-Crystalline Hierarchical Nanozeolites via Oriented-Aggregation and Intraparticle Ripening. *J. Am. Chem. Soc.* **2019**, *141*, 3772–3776.

(13) Jiao, Y. L.; Forster, L.; Xu, S. J.; Chen, H. H.; Han, J. F.; Liu, X. Q.; Zhou, Y. T.; Liu, J. M.; Zhang, J. S.; Yu, J. H.; D'Agostino, C.; Fan, X. L. Creation of Al-Enriched Mesoporous ZSM-5 Nanoboxes with High Catalytic Activity: Converting Tetrahedral Extra-Framework Al into Framework Sites by Post Treatment. *Angew. Chem., Int. Ed.* **2020**, *59*, 19478–19486.

(14) Na, K.; Jo, C.; Kim, J.; Cho, K.; Jung, J.; Seo, Y.; Messinger, R. J.; Chmelka, B. F.; Ryoo, R. Directing Zeolite Structures into Hierarchically Nanoporous Architectures. *Science* **2011**, *333*, 328–332.

(15) Wang, N.; Sun, Q. M.; Zhang, T. J.; Mayoral, A.; Li, L.; Zhou, X.; Xu, J.; Zhang, P.; Yu, J. H. Impregnating Subnanometer Metallic Nanocatalysts into Self-Pillared Zeolite Nanosheets. *J. Am. Chem. Soc.* **2021**, 143, 6905–6914.

(16) Na, K.; Choi, M.; Park, W.; Sakamoto, Y.; Terasaki, O.; Ryoo, R. Pillared MFI Zeolite Nanosheets of a Single-Unit-Cell Thickness. *J. Am. Chem. Soc.* **2010**, *132*, 4169–4177.

(17) Na, K.; Jo, C.; Kim, J.; Ahn, W.-S.; Ryoo, R. MFI Titanosilicate Nanosheets with Single-Unit-Cell Thickness as an Oxidation Catalyst Using Peroxides. *ACS Catal.* **2011**, *1*, 901–907.

(18) Choi, M.; Na, K.; Kim, J.; Sakamoto, Y.; Terasaki, O.; Ryoo, R. Stable single-unit-cell nanosheets of zeolite MFI as active and long-lived catalysts. *Nature* **2009**, *461*, 246–249.

(19) Zhang, X. Y.; Liu, D. X.; Xu, D. D.; Asahina, S.; Cychosz, K. A.; Agrawal, K. V.; Al Wahedi, Y.; Bhan, A.; Al Hashimi, S.; Terasaki, O.; Thommes, M.; Tsapatsis, M. Synthesis of self-pillared zeolite nanosheets by repetitive branching. *Science* **2012**, *336*, 1684–1687.

(20) Jeon, M. Y.; Kim, D.; Kumar, P.; Lee, P. S.; Rangnekar, N.; Bai, P.; Shete, M.; Elyassi, B.; Lee, H. S.; Narasimharao, K.; Basahel, S. N.; Al-Thabaiti, S.; Xu, W. Q.; Cho, H. J.; Fetisov, E. O.; Thyagarajan, R.; DeJaco, R. F.; Fan, W.; Mkhoyan, K. A.; Siepmann, J. I.; Tsapatsis, M.

Industrial & Engineering Chemistry Research

Ultra-selective high-flux membranes from directly synthesized zeolite nanosheets. *Nature* **2017**, *543*, 690–694.

(21) Zhou, M.; Hedlund, J. Facile Preparation of Hydrophobic Colloidal MFI and CHA Crystals and Oriented Ultrathin Films. *Angew. Chem., Int. Ed.* **2018**, *57*, 10966–10970.

(22) Dai, W. J.; Kouvatas, C.; Tai, W. S.; Wu, G. J.; Guan, N. J.; Li, L. D.; Valtchev, V. Platelike MFI Crystals with Controlled Crystal Faces Aspect Ratio. *J. Am. Chem. Soc.* **2021**, *143*, 1993–2004.

(23) Zhou, Y. W.; Mu, Y. Y.; Hsieh, M.-F.; Kabius, B.; Pacheco, C.; Bator, C.; Rioux, R. M.; Rimer, J. D. Enhanced Surface Activity of MWW Zeolite Nanosheets Prepared via a One-Step Synthesis. J. Am. Chem. Soc. 2020, 142, 8211–8222.

(24) Varoon, K.; Zhang, X. Y.; Elyassi, B.; Brewer, D. D.; Gettel, M.; Kumar, S.; Lee, J. A.; Maheshwari, S.; Mittal, A.; Sung, C. Y.; Cococcioni, M.; Francis, L. F.; McCormick, A. V.; Mkhoyan, K. A.; Tsapatsis, M. Dispersible exfoliated zeolite nanosheets and their application as a selective membrane. *Science* **2011**, *334*, 72–75.

(25) Agrawal, K. V.; Topuz, B.; Jiang, Z. Y.; Nguenkam, K.; Elyassi, B.; Francis, L. F.; Tsapatsis, M.; Navarro, M. Solution-Processable Exfoliated Zeolite Nanosheets Purified by Density Gradient Centrifugation. *AlChE J.* **2013**, *59*, 3458–3467.

(26) Dai, C. Y.; Zhang, A. F.; Li, L. L.; Hou, K. K.; Ding, F. S.; Li, J.; Mu, D. Y.; Song, C. S.; Liu, M.; Guo, X. W. Synthesis of Hollow Nanocubes and Macroporous Monoliths of Silicalite-1 by Alkaline Treatment. *Chem. Mater.* **2013**, *25*, 4197–4205.

(27) Pagis, C.; Morgado Prates, A. R.; Farrusseng, D.; Bats, N.; Tuel, A. Hollow Zeolite Structures: An Overview of Synthesis Methods. *Chem. Mater.* **2016**, *28*, 5205–5223.

(28) Chen, L. H.; Li, X. Y.; Rooke, J. C.; Zhang, Y. H.; Yang, X. Y.; Tang, Y.; Xiao, F. S.; Su, B. L. Hierarchically structured zeolites: synthesis, mass transport properties and applications. *J. Mater. Chem.* **2012**, 22, 17381–17403.

(29) Liu, Y.; Qiang, W. L.; Ji, T. T.; Zhang, M.; Li, M. R.; Lu, J. M.; Liu, Y. Uniform hierarchical MFI nanosheets prepared via anisotropic etching for solution-based sub–100-nm-thick oriented MFI layer fabrication. *Sci. Adv.* **2020**, *6*, No. eaay5993.

(30) Dong, Y. J.; Peng, Y.; Wang, G. L.; Wang, Z. B.; Yan, Y. S. Corrosion-Resistant Zeolite Silicalite-1 Coatings Synthesized by Seeded Growth. *Ind. Eng. Chem. Res.* **2012**, *51*, 3646–3652.

(31) Feng, R.; Yan, X. L.; Hu, X. Y.; Zhang, Y. X.; Wu, J. J.; Yan, Z. F. Phosphorus-modified b-axis oriented hierarchical ZSM-5 zeolites for enhancing catalytic performance in a methanol to propylene reaction. *Appl. Catal., A* **2020**, *594*, No. 117464.

(32) Cao, Z.; Zeng, S. X.; Xu, Z.; Arvanitis, A.; Yang, S. W.; Gu, X. H.; Dong, J. H. Ultrathin ZSM-5 zeolite nanosheet laminated membrane for high-flux desalination of concentrated brines. *Sci. Adv.* **2018**, *4*, No. eaau8634.

(33) Li, T.; Ma, Z.; Krumeich, F.; Knorpp, A. J.; Pinar, A. B.; vanBokhoven, J. A. Properties Modification of Nanosized Hollow Zeolite Crystals by Desilication. *ChemNanoMat* **2018**, *4*, 992–999.

(34) Akouche, M.; Gilson, J.-P.; Nesterenko, N.; Moldovan, S.; Chateigner, D.; Siblani, H. E.; Minoux, D.; Dath, J.-P.; Valtchev, V. Synthesis of Embryonic Zeolites with Controlled Physicochemical Properties. *Chem. Mater.* **2020**, *32*, 2123–2132.

(35) Zhai, Y.; Zhang, X.; Wang, F.; Lv, G.; Jiang, T.; Wu, Y.; Li, M.; Li, M.; Zhang, Q.; Liu, Y. Racing Crystallization Mechanism for Economical Design of Single-Crystal Hollow ZSM-5 with the Broken Limit of Si/Al Ratio and Improved Mass Transfer. *ACS Appl. Mater. Interfaces* **2021**, *13*, 15246–15260.

(36) Liu, Y.; Li, M. R.; Chen, Z. G.; Cui, Y.; Lu, J. M.; Liu, Y. Hierarchy Control of MFI Zeolite Membrane towards Superior Butane Isomer Separation Performance. *Angew. Chem., Int. Ed.* **2021**, *60*, 7659–7663.

(37) Song, Y.; Bai, R. S.; Zou, Y. C.; Feng, Z. C.; Yu, J. H. Temperature-regulated construction of hierarchical titanosilicate zeolites. *Inorg. Chem. Front.* **2020**, *7*, 1872–1879.

(38) Tuel, A.; Ben Taarit, Y. Configuration of tertraalkyl ammonium and tetraalkyl phosphonium ions in the framework of silicalite-1 and -2. *Microporous Mater.* **1994**, *2*, 501–514.

(39) Song, W. C.; Xiong, G.; Long, H. Y.; Jin, F. Y.; Liu, L. P.; Wang, X. S. Effect of treatment with different bases on the catalytic properties of TS-1/SiO₂ extrudates in propylene epoxidation. *Microporous Mesoporous Mater.* **2015**, *212*, 48–55.