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1. Introduction

Microporous zeolites with high surface area and well-defined pore dimensions have been widely used in the field of shapeselective catalysis, adsorption, and sensor technologies.^{1,2} In particular, the unique pore structure and strong acidity of zeolites lead to a wide range of applications as heterogeneous catalysts in petrochemistry and renewable energy areas.^{3,4} Cations (H^+) acting as the Brønsted acid sites in aluminosilicate zeolites are located at the oxygen atoms between the bridge Si and Al atoms in the crystalline framework, forming catalytically active sites.^{5,6} The acid sites located within the confined channels of zeolites ensure their prefect shape-selectivity, while acid sites on the external surface of zeolites always lead to a reduction in the product selectivity and confinement effects.^{7,8} Therefore, the location

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Fabrication of a core-shell MFI@TON material and its enhanced catalytic performance for toluene alkylation[†]

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Core-shell MFI@TON composites were designed and synthesized as a highly shape-selective catalyst for toluene alkylation with methanol by passivating the nonselective acid sites and tuning the diffusion behavior. The synthesis parameters were comprehensively investigated, indicating the importance of the Si/Al ratio compatibility of the ZSM-5 and ZSM-22 components on the formation of a core-shell structure. The synthesis process was systemically traced, which allowed the formulation of a crystallization mechanism involving the oriented crystal growth and selective fusion steps during the secondary crystallization. As a result, the MFI zeolites as the core were fully covered by the TON zeolites as the shell, yielding spherical morphology. When applied to toluene alkylation with methanol, the core-shell MFI@TON composite exhibited significantly improved *para*-xylene selectivity in comparison with the original, unattached, and physically mixed catalysts. The enhanced catalytic behaviors of the core-shell MFI@TON composite could be ascribed to the effective suppression of *para*-xylene isomerization as a result of the passivated acid sites on the external surface and the improved diffusion time and distance for the intermediates inside the channels due to the unique structure. The synthesis method for the MFI@TON composite described herein may provide a generic platform for the design of core-shell zeolites with potentially broader applicability to other porous materials with advanced applications.

of the acid sites is considered to be a very important factor affecting the catalytic performance.⁹ A typical acid-catalyzed reaction is toluene alkylation with methanol to obtain *p*-xylene, which is an important intermediate to produce terephthalic acid and downstream polyesters.^{10,11}

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The selective production of *p*-xylene via the alkylation of toluene with methanol using various zeolite catalysts has been intensively investigated.^{12,13} Among them, TON-type ZSM-22 zeolites have been effectively recognized as a shape-selective catalyst for toluene alkylation to p-xylene.^{14,15} The high paraselectivity of ZSM-22 zeolites in this reaction mainly results from the one-dimensional 10-membered ring channels (0.45 \times 0.55 nm) that run along the longest dimension of the crystals crystallographic *c*-axis direction). However, the (the distributions of acid sites for ZSM-22 zeolites are nonuniform due to the fact that the crystals have aluminum concentrated on the external surfaces.¹⁶ Hence, many modification methods have been developed to eliminate the acid sites on the external surface.17-19 However, it is often difficult to control such technologies that require complicated operations and posttreatments, invariably leading to decreases in framework stability and shape-selectivity. Moreover, diffusion plays an important role in the transport of xylenes from the channels due to the fact that the diffusion coefficient of *p*-xylene is much

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higher than those of *o*-xylene and *m*-xylene.^{20,21} Therefore, if the diffusion resistance of the formed *p*-xylene inside the ZSM-22 zeolite improves, the isomerization of *p*-xylene into these two isomers can be inhibited, consequently leading to enhanced *para*-xylene selectivity.

At this point, if the one-dimensional straight channels of the ZSM-22 zeolite can be perpendicular to a certain material as the core leading to the formation of a spherical morphology with largely exposed pore mouths, increasing the diffusion resistance and passivating the acidity on the external surface of ZSM-22 zeolites can be simultaneously resolved. The hydrothermal synthesis of core-shell zeolites has been demonstrated for a wide range of inorganic materials.²² Many core-shell zeolite-zeolite composites possessing cores and shells of different structural types have already been reported, such as MOR@MFI,²³ BEA@MFI,²⁴ FAU/BEA,²⁵ MFI@BEA.26 The shell layer can always be formed by the secondary growth of the preliminarily adsorbed seeds on the core crystals. During the adsorption step, the organic molecules and surfactants, such as poly(diallyl dimethylammonium chloride), are used. However, the high cost of the polycation agent and rigorous procedures may limit the large-scale applications and commercial development of such zeolite composites. Moreover, the key factor in the fabrication of coreshell zeolite composites is that the zeolites are metastable materials that can be easily transformed into other porous or nonporous materials under hydrothermal conditions.²⁷ It is well known that both ZSM-22 and ZSM-5 zeolites have a 10membered ring, and ZSM-5 zeolites are the most commonly occurring impurities during the crystallization procedure of ZSM-22 zeolites.^{28,29} Combining ZSM-5 and ZSM-22 zeolites as a core-shell material not only meets the aforementioned requirements and circumvents the side-effects of zeolite surface modification, but it also provides a deeper understanding into the crystallization mechanism of ZSM-22 zeolites.

Herein, the present work focuses on the formation of ZSM-5@ZSM-22 core-shell composites comprising ZSM-5 zeolites as the core and surface-inert ZSM-22 zeolite as the shell. Several synthesis parameters were investigated to understand the key factors affecting the crystallization process of the composite. The formation mechanism of this material was also systemically investigated. The core-shell material shows significantly improved *para*-xylene selectivity in toluene alkylation with methanol by suppressing the acid sites on the external surface and improving the diffusion resistance of the product molecules. This investigation may not only provide a direct and efficient route for the crystallization of core-shell zeolite composites but also prove the importance of acid site distribution and diffusion behavior on improving the *para*-xylene selectivity for alkylation.

2. Experimental

2.1 Chemicals and reagents

The detailed descriptions of the chemicals and reagents are available in the ESI.†

2.2 Synthesis

2.2.1 Synthesis of core ZSM-5 zeolites. ZSM-5 zeolites (about 10 μ m) with different Si/Al ratios used as the core of the composites were synthesized *via* a laboratory recipe by adding a solution of Al₂(SO₄)₃, NaOH, and *n*-butylamine (BTA) accompanied with deionized water to the solution of sodium silicate under stirring. The resultant homogeneous gel with a molar composition of 12Na₂O:1Al₂O₃: (80/250)SiO₂:100BTA: 1400H₂O was transferred into a stainless steel autoclave and subjected to hydrothermal treatment at 180 °C for 48 h in an oven under static conditions and autogenous pressure. After this hydrothermal treatment, the solid product was recovered by filtration, washed, dried at 120 °C overnight, and calcined at 550 °C for 10 h to remove the organic template. The dried and calcined MFI zeolites were named SDA-MFI and Na-MFI, respectively.

2.2.2 Synthesis of ZSM-22 nanorods. In the present work, 1,6-diaminohexane (DAH) was used as the organic template for the synthesis of ZSM-22 zeolites. ZSM-22 zeolite nanorods were prepared *via* the hydrothermal treatment of aluminosilicate solution with the following chemical composition: SiO_2 : $0.12K_2O:0.0067Al_2O_3:0.3DAH:40H_2O$. The synthesis processes were performed at 160 °C for 48 h in autoclaves under stirring at autogenous pressures. The solid products were recovered by filtration, extensively washed with deionized water, and dried at 120 °C. Finally, the organic template in the zeolites was removed by high-temperature calcination in air at 550 °C for 10 h. The dried and calcined ZSM-22 zeolites were named as SDA-TON and K-TON, respectively.

These Na-MFI and K-TON zeolites were converted into their protonic forms by ion exchange with NH₄NO₃, drying, and calcination at 550 °C for 4 h. These post-treatment steps were repeated three times. The corresponding protonic zeolites were denoted as MFI and TON.

2.2.3 Synthesis of the core-shell materials. The schematic diagram for the preparation process of the seed is shown in Fig. 1. Firstly, the big MFI crystal was hydrothermally treated in an aqueous solution of DAH (0.2 mol L⁻¹) for 12 h at 50 °C. This treated MFI was filtered and redispersed in distilled water and then a precalculated amount of SDA-TON crystals was adsorbed. Then, the mixture was subjected to ultrasonic treatment for 1 h and the upper suspension was removed. Finally, the drying and calcination of the pretreated seed at 550 °C for 4 h yielded seeds with TON nanorods firmly fixed on the surface of the ZSM-5 zeolites. The secondary growth of the preadsorbed seed was performed at 160 °C with a solution having the molar composition SiO₂:0.12K₂O: $xAl_2O_3:0.2DAH:40H_2O$, where x = 0-0.014. The resulting gel



Fig. 1 Schematic diagram of the preparation steps of the seed.

was aged for 8 h at room temperature before performing the crystallization procedure in a PTFE-lined stainless steel autoclave. After hydrothermal synthesis, the solid was washed with distilled water to neutral and dried at 120 °C for 12 h. The products were calcined at 550 °C for 8 h in air to remove the organic template. With this method, several typical samples were obtained after different secondary crystallization times to elucidate the growth process of the core-shell structure. The final composite was finally converted to its protonic form through the NH₃-exchange step, and it was denoted as MFI@TON.

The reference sample, termed as TON/MFI, was prepared by using the same components as those used for preparing the MFI@TON composite. The secondary crystallization of the TON sample was the same as that used for composites without the addition of MFI zeolites. After the crystallization process, the post-treatment steps were the same as those for the protonic zeolites. The resulting TON crystal (denoted as TON-SG) was mechanically mixed with the MFI zeolites based on the phase compositions of MFI and TON zeolites as calculated from the XRD patterns of the composite.³⁰

2.3 Preparation of catalysts

To obtain the catalysts for use in the catalytic tests for toluene alkylation with methanol, the TON, MFI, TON/MFI, TON-SG, and MFI@TON zeolites were extruded, crushed, and sieved to a particle size of 10–20 mesh.

2.4 Characterizations

Detailed characterizations are available in the ESI.†

2.5 Catalytic test

The catalytic performance of toluene alkylation with methanol over various catalysts was carried out in a continuous-flow fixed-bed reactor under atmospheric pressure. The sieved catalyst (2.0 g) was packed in the isothermal zone of the reactor tube. Before the catalytic test, the catalyst was activated in situ under a N2 flow at 500 °C for 1 h. After decreasing the reaction temperature to 420 °C, a mixture of toluene and methanol at a molar ratio of 4:1 as the reactant was pumped into the reactor at a WHSV value of 2.0 h^{-1} via a double-plunger pump. All the products were separated and the gas products were analyzed online by means of a gas chromatograph (Agilent 6890 A) equipped with a flame ionization detector and a capillary column (Al_2O_3, 30 m \times 0.32 mm \times 0.25 μm). The liquid products were collected with a cold trap and then kept in sealed vials for posterior analysis via offline gas chromatography (Agilent 7890A equipped with a flame ionization detector and a capillary column, DB-PONA, 50 m × 0.20 mm × 0.55 µm). In all these experiments, the carbon balance was maintained above 95%. Herein, toluene conversion was determined based on the weight of the converted toluene. Selectivity toward xylene was defined as the percentage of xylene in all the products.

3. Results and discussion

3.1 Synthesis of core-shell materials

Attempts to synthesize core-shell composites without using TON seeds have been unsuccessful in cases where only discrete MFI particles have been present. Therefore, TON seeds are necessary in order to obtain the core-shell structure. Meanwhile, the adsorption step of the TON nanorods on MFI crystals is the key parameter for the growth of TON nanorods and the full coverage of the MFI material. Therefore, the present study focuses on the effect of chemical compatibility and matching the crystallization field for the core-shell MFI@TON composite.

3.1.1 Influence of Si/Al ratios of the crystallization gel. Suppressing the growth of the core material and fabricating the secondary crystallization of the shell zeolite were considered to be important factors to prepare a core-shell composite. After varying the different parameters of the crystallization system, it was found that the chemical compatibility and matching degree of the Si/Al ratios of the initial gel with the seed were significant. Therefore, the preadsorbed seeds containing TON and MFI zeolites with different Si/Al ratios were prepared. Then, the prepared seed was added into the gels at different initial Si/Al ratios for the secondary synthesis process.

The obvious differences in the size and morphology of the MFI crystals core and TON nanorods shell facilitate distinguishing between these materials. Firstly, the seed containing the TON zeolite (Si/Al ratio: 71.5) and MFI zeolite (Si/Al ratio: 34) was used to prepare the composite. When the Si/Al ratio of the initial gel composition ranged from 35 to 70, the composite material with the aggregated MFI zeolite was obtained, as shown in Fig. 2a. Meanwhile, the diffraction peaks assigned to the ZSM-22 zeolites were much weaker than that for ZSM-5 zeolites, as shown in Fig. S1,† suggesting that secondary crystallization in such synthesis conditions is preferable for fabricating the MFI zeolite core. Closeup views of the synthesized sample (Fig. 2b) provide solid evidence of the crystallization of the MFI core sample. However, when the Si/Al molar ratio of the initial gel is above 71.5, the growth of the core is distinctly suppressed, leading to the formation of spherical morphology with a large amount of needle-like ZSM-22 zeolites, as shown in Fig. 2c. Furthermore, a similar experiment was performed to investigate the nature of this result. In this experiment, a seed with TON zeolites (Si/Al = 71.5) and MFI zeolites (Si/Al = 121.5) was used. When the Si/Al ratio of the initial composition was below 70, an amorphous material was obtained. As the Si/Al ratio was improved to 70-120, aggregated morphology and prominent diffraction peaks in the ZSM-5 crystallites reappear, as shown in Fig. 2d and S1,† respectively. As the Si/Al ratio increased above 120, the desired composite with the secondary-crystallized TON shell was obtained. Therefore, the growth of the MFI zeolite core could be effectively inhibited when the initial Si/Al ratio of the synthesis gel was higher than that of both the



Fig. 2 Scanning electron microscopy (SEM) images of the composite samples prepared under different conditions. Synthesis conditions: (a) Si/Al ratios of TON and MFI zeolites in the preadsorbed seed are 71.5 and 34, respectively; Si/Al ratio of the initial gel is 70. (b) Closeup view of Fig. 2a. (c) Si/Al ratios of TON and MFI zeolites in the preadsorbed seed are 71.5 and 34, respectively; Si/Al ratio of the initial gel is 75. (d) Si/Al ratios of TON and MFI zeolites in the preadsorbed seed are 71.5 and 121.5, respectively; Si/Al ratio of the initial gel is 120.

components of the seed. Therefore, it can be concluded that the Si/Al ratios compatibility of the seed and initial gel are the key parameters for the formation of MFI@TON core-shell materials.

3.1.2 Influence of crystallization temperature. То investigate the effect of synthesis temperature on the crystallization of the core-shell materials, the synthesis was carried out at different temperatures. The seed containing the TON zeolite (Si/Al ratio: 71.5) and MFI zeolite (Si/Al ratio: 34) was used in this case. The secondary crystallization is performed without the addition of Al. The XRD patterns are shown in Fig. 3, and the crystallization curves at different conditions are shown in Fig. S2 in the ESI.† At the lowest crystallization temperature (140 °C), the mixture of MFI@TON material and amorphous silica was obtained after 36 h, according to the relatively low intensity of the XRD patterns shown in Fig. 3a. With a further increase in the crystallization time to 60 h, the MFI@TON composite with high crystallinity could be observed, as shown in Fig. S2.† When the synthesis temperature improved to 160 °C, the



Fig. 3 XRD patterns of core-shell MFI@TON composites prepared at 140 (a), 160 (b), and 180 (c) $^{\circ}\text{C}.$

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MFI@TON composite indicated no evidence of the formation of amorphous silica, and the crystallinity reached 92% after 32 h. As the synthesis temperature further increased to 180 °C, the MFI@TON composite with high crystallinity (95%) was obtained after 24 h. The formation of a zeolite with poor crystallinity (Fig. S2† and 3a) and the amorphous phase at lower temperatures indicate that the solution system is only slightly favorable for the interactions between the organic template and silica sol.³¹ Furthermore, the structuredirecting formation of the composite requires higher temperatures. Nevertheless, as shown in the magnified SEM images (Fig. S3†) of the composites with similar crystallinity, the crystal of the TON shell prepared at 180 °C is much thinner than the sample synthesized at 140 °C, suggesting that an increase in crystallization time yields larger crystals.³²

3.2 Crystallization procedure of core-shell materials

The seed comprising TON (Si/Al ratio: 71.5) and MFI (Si/Al ratio: 34) zeolites was used to investigate the crystallization procedure of core-shell MFI@TON materials. To obtain the MFI@TON composite with a passivated surface, the molar composition of the initial synthesis mixture was SiO_2 : $0.12K_2O:0.2DAH:40H_2O$.

3.2.1 XRD and SEM. Fig. 3b shows the XRD patterns of the MFI@TON composite after different crystallization times at 160 °C. During the first 18 h, broad peaks between 10° and 40° and weak diffraction peaks attributable to MFI and TON phases suggest that the product is still largely amorphous. XRD intensities increase over the next few hours (24 h). The clear signals at 8.10°, 20.28°, 24.14°, and 25.66° appear, which are characteristic of the TON-type framework.33,34 After crystallization for 32 h, the XRD patterns of the final products reveal the intense diffraction peaks of the TON phase together with the characteristic peaks of the MFI phase. Moreover, Fig. S2[†] shows the dependence of crystallinity on the crystallization time. This curve indicates that the crystallization of the TON nanorods shell mainly occurs within 18-32 h. The introduction period ends at 18 h and the TON zeolite gets fully crystallized after 32 h.

Fig. 4 and S4† show the SEM micrographs of the MFI@TON composites after different crystallization stages at various magnifications. As shown in Fig. 4a and b, a large number of amorphous materials appear on the surface of the seed. After crystallization for 24 h, the MFI crystals are fully covered with elongated TON crystals, as shown in Fig. 4d and S4a,† indicating that at this crystallization stage, the TON nanorods shell grow along the needle axis, namely, the *c*-axisoriented growth is dominant during this crystallization process.³⁵ After synthesis for 32 h, the amorphous material is totally consumed and all the MFI crystals are fully covered with TON crystallites (width: 400-600 nm; length: 5-6 µm) (Fig. 4e and f). These observations suggest that the TON crystals bunched together perpendicular to the needle axis at this stage. Combined with the closer inspection of the TEM image (Fig. S5[†]), it is evident that the thickened crystals of



Fig. 4 SEM images of the core-shell MFI@TON composites at different crystallization times of 12 (a), 18 (b), 21 (c), 24 (d), 32 (e), and 36 (f) h.

the TON shell comprised thinner nanorods along the *a*- and *b*-axes. In summary, a growth model of the TON crystal shell, where nanorods grow along the rod direction until the medium is almost depleted and nanorods latterly fuse in an aligned manner, can be speculated from the XRD and SEM results supported by the TEM data.

3.2.2 UV Raman and magic-angle spinning nuclear magnetic resonance (MAS NMR). During the crystallization process, the liquid and solid phases coexist.³⁶ These phases are separated by centrifugation and independently analyzed. The Raman spectra of the solution throughout the synthesis process are shown in Fig. 5a. The bands at 460, 620, 780, 846, and 855 cm⁻¹ are observed in the Raman spectrum of the initial liquid phase, in which the bands at 846 and 855 cm⁻¹ can be ascribed to the DAH cation. The pH value of the



Fig. 5 UV resonance Raman spectra of the liquid solution (a) and solid phase (b) of MFI@TON composites after different crystallization times.

crystallization mixture is above 11, and the solubility of amorphous silica is high. Moreover, the high Si content in gel further increases the solubility. Therefore, it is not surprising to observe the bands at 460 and 780 cm⁻¹ in the liquid phase, which can be assigned to the presence of silicate species.^{37,38} The band at 620 cm⁻¹ can be attributed to the Al-O symmetric stretching mode of the Al(OH)₄ species in the solution,³⁸ which may originate from the partial dissolution of the seed zeolites. The spectrum of the liquid phase undergoes significant changes after crystallization for 24 h. The band at 620 cm^{-1} decreases, suggesting that a part of the Al(OH)₄ species in the solution is incorporated into the solid phase and then polymerized with the silicate species. However, the band of silicate species remains unchanged throughout the crystallization process, indicating that these dissolved Si species are not incorporated into the solid phase. No Raman bands assigned to the aluminosilicate species are detected in the liquid phase.

Fig. 5b shows the Raman spectra of the solid phase of the MFI@TON composite at various crystallization times. The Raman spectrum of the initial precursor is characterized by a broad band at 460 cm⁻¹, while the bands assigned to the seeds are not observed in the spectra due to low content. The band at 460 cm⁻¹ comes from amorphous or vitreous silica and has been assigned to the symmetric vibration of the Si-O-Si bond (v_s (Si-O-Si)) of the five-membered silicate rings.³⁹ The band at 847 cm⁻¹ observed in the Raman spectrum after heating for 18 h can be attributed to DAH cations. These cations cannot be extensively washed even after several centrifugation treatments, indicating the presence of strong interactions between the DAH cations with the framework. With an increase in the crystallization time, the enhanced intensity of the band at 460 cm⁻¹ corresponds to an increased amount of five-membered silicate rings in the amorphous gel. Meanwhile, this broad band (at 460 cm^{-1}) gradually becomes sharper and shifts to 446 cm⁻¹ after heating for 20 h. This result suggests that the siliceous species in the gel mixture connect with each other and further form a TON-like structure. The appearance of the band at 800 cm⁻¹, which is assigned to the symmetric stretching mode of T-O,40 indicates that the intermediate species containing fivemembered rings are obtained during the synthesis procedure. By increasing the crystallization time from 20 to 24 h, the band at 446 cm⁻¹ becomes much sharper, while the band of the amorphous gel at 460 cm⁻¹ rapidly decreases, indicating the formation of a large amount of TON crystals, which is in agreement with the XRD and SEM results. The Raman band at 407 cm⁻¹ associated with five-membered rings⁴¹ appears after heating for 20 h, which becomes narrower and stronger with an increase in the crystallization time, suggesting the growth of crystals along the *c*-axis as well as the formation of elongated crystals. The Raman band at 460 cm⁻¹ becomes undetectable for crystallization beyond 24 h, suggesting that all the five-membered rings get almost depleted and converted to form the TON-type structure. Notably, the band at 366 cm⁻¹, which can be attributed to the

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six-membered rings,⁴² becomes intense after the crystallization time exceeds 28 h, reflecting the growth and fusion of TON-type crystals in an aligned manner. This band becomes particularly prominent in the samples after the crystallization time over 28 h, indicating the alignment and fusion of the nanorods, which is in accordance with the SEM and TEM results.

 27 Al and 29 Si MAS NMR measurements were performed to determine the chemical states of silicon and aluminum species during the crystallization process. As shown in Fig. 6a, only one peak at around 54.6 ppm, which can be assigned to the four-coordinated aluminum species, could be detected throughout the synthesis procedure. Apparently, when the solid was still largely amorphous (from 12 to 22 h), the 27 Al NMR signal was substantially broadened, suggesting that the Al species from the MFI and TON of the seed were partially dissolved. Furthermore, it is notable that the full width at half maximum (FWHM) of the four-coordinated aluminum species gradually decreased during the crystal growth period (24–32 h) owing to the formation of a tetrahedrally coordinated aluminosilicates structure.⁴³

The ²⁹Si MAS NMR spectra of the samples obtained after various crystallization times are shown in Fig. 6b. Obviously, in the initial stage of the crystallization process, the resonance in the range from -107 to -100 ppm assigned to silanol groups distinctly appears.44 As the crystallization proceeds, the resonance of silanol groups gradually becomes weaker and completely disappears at 24 h, suggesting the transformation of the silica species into a highly ordered framework.45 Then, with a further increase in the crystallization time (28-36 h), the NMR signal sharpens and the intensity gradually increases. Combined with the above characterizations and the data from earlier reports,^{46,47} it can be concluded that the growth of ZSM-22 zeolites involves two steps. First, nanorods with the TON-type framework are formed from the initial gel with the assistance of ZSM-22 seeds. In the second stage, the nanorods fuse together perpendicular to the *c*-axis in an aligned manner, leading to the formation of thick and long nanorods.

3.2.3 Proposed mechanism. Herein, based on the XRD, SEM, TEM, UV Raman, and MAS NMR data, a growth mechanism for the MFI@TON composite was proposed (Fig. 7). During the initial stage, the precursor solution



Fig. 6 $\,\,^{27}\!\text{Al}$ (a) and $\,^{29}\!\text{Si}$ (b) MAS NMR spectra of MFI@TON composites at different crystallization stages.



Fig. 7 Schematic representation of the hydrothermal crystallization procedure of the core-shell MFI@TON composites.

mainly comprised amorphous silicate species with fivemembered silicate rings, DAH, and partially dissolved Al in the solution phase. The amount of five-membered silicate rings increased with the crystallization time (\sim 0–12 h). Then, the five-membered rings in the amorphous phase (some of which may be incorporated by the Al species and interacted with the structure-directing agent) link together to form the nuclei of the TON-type structure with the assistance of TON seeds. Simultaneously, TON-type nanorods grow along the c-axis direction, leading to the generation of a Raman band at 407 cm⁻¹. When the crystallization time exceeds 24 h, all the five-membered silicate and aluminosilicate rings in the amorphous gel are transformed into the TON-type structure. Then, these nanorods bunch together in an aligned manner to form larger crystals accompanied by the appearance of a Raman band at 336 cm⁻¹ along with the enhanced intensity of the XRD diffraction peaks as well as the sharp resonance in the ²⁹Si MAS NMR. Finally, the framework structures and coordination environment of the TON shell become more uniform after 32 h.

3.3 Characterization of core-shell materials

The XRD patterns of different samples are shown in Fig. 8. The sharper, better-defined Brägg diffraction peaks of MFI, TON, and TON-SG zeolites reveal higher crystallinities.48 No additional peaks can be observed in all the patterns, suggesting that these materials are free of any impurities. With regard to the core-shell MFI@TON composite, the most intense peaks of the TON-type material, in the ranges of 2θ = 7.0-10.0° and 20-22°, can be observed together with the characteristic peaks of the MFI-type structure framework. The signal-to-noise ratio of the diffraction lines in the patterns is similar to that of the MFI and TON zeolites and is indicative of a highly crystalline composite. In view of the diffraction peaks belonging to the MFI and TON phases as well as the physical mixtures using the pure TON and MFI phases as references (as shown in Fig. S6[†]), the TON contents in the MFI@TON composite can be estimated to be in the range of \sim 75-85%. Therefore, the reference sample (TON/MFI) exhibits similar XRD patterns as those of the MFI@TON composite. The similar Si/Al ratios of the TON/MFI and MFI@TON samples can also be observed, as listed in Table 1. The surface Si/Al ratios of the different samples determined by XPS are listed in Table 1, which confirm the uneven Al distributions in the TON zeolites due to the fact that the Al



Fig. 8 XRD patterns of TON, MFI, TON/MFI, TON-SG, and core-shell MFI@TON materials.

	Si/Al ratio	Surface areas ^d $(m^2 g^{-1})$			
Samples	Initial ^a	Bulk ^b	Surface ^c	$S_{\rm Micro}$	$S_{\rm Ex}$
TON	75	71.5	63.6	165.2	61.7
MFI	35	34.0	30.6	229.3	109.5
TON/MFI	_	179.6	_	210.6	54.0
TON-SG	_	572.2	_	169.5	42.8
MFI@TON	00	192.6	852.1	198.8	44.1

 a Initial composition during hydrothermal synthesis. b Resulting Si/Al ratio of the different samples determined by XRF. c Surface Si/Al ratio of the different samples determined by XPS. d Obtained by N₂ adsorption at –196 °C using a Micromeritics ASAP 2020 instrument.

species prefer to be located on the external surface.⁴⁹ Because of the extra-Al-free synthesis condition, the surface Si/Al ratio of the composite is really high.

Fig. 9 shows the typical SEM images of MFI, TON, adsorbed seed, TON-SG, and core-shell MFI@TON composite. The TON and MFI zeolites exhibit needle- and coffin-shaped crystals, as shown in Fig. 9a and b, which are the typical morphologies for ZSM-22 and ZSM-5 zeolites,^{50,51} respectively. Evidently, as shown in Fig. 9e, the MFI@TON composite displays chrysanthemum-like morphology with dimensions of 20–30 μ m, which is different from those of the TON- or MFI-type zeolites used in our experiment. Almost no unattached crystals with needle-shaped morphology could be found, indicating that all the TON nanorods were perpendicular to the core crystals. The bigger crystals of the core-shell composite compared to the original zeolites could be attributed to the growth of TON nanorods on the MFI crystals. The isolated needles of the TON-SG sample are shown in Fig. 9d, demonstrating the key role of the core ZSM-5 crystal in maintaining the spherical morphology of the MFI@TON composite.

Fig. 10 shows the representative high-resolution transmission electron microscopy (HRTEM) images of the core-shell materials before and after post-treatments. The uniform growth of the TON nanorod shells on the external surface of the MFI-type zeolites can be seen in Fig. 10a and b. The corresponding HRTEM image (Fig. 10c) for the TON shell reveals that the elongated crystals are made





Fig. 9 SEM images of TON (a), MFI (b), seeds (c), TON-SG (d), and core-shell MFI@TON (e) materials.

up of nanorods. However, the completely covered structure limits the observation for the combination of core and shell zeolites. Fig. 10d and e show the composite crystals after intensive post-treatment in order to destroy the core-shell structure. Apparently, the nanorod crystals of ZSM-22 zeolites as the shell are inserted in the ZSM-5 zeolite, forming bloomlike morphology, as shown in Fig. 10e. The EDX analysis of the Si and Al contents of different positions, as shown in Fig. 10d, suggests that the Si/Al ratio of the nanorods is 874.2, which is close to the value of the TON shell as



Fig. 10 HRTEM and HAADF-STEM images of the core-shell composite under different magnifications (a-c) and post-treated composites (d and e).

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determined by the XPS analysis. Meanwhile, the Si/Al ratio of MFI zeolites core is slightly higher than that of the parent sample, indicating that the formation of MFI layers might occur during the hydrothermal synthesis process. These results reveal that the secondary growth of the TON materials shell is dominant and the growth of the MFI material core is suppressed.

The N₂ adsorption-desorption isotherms of the protonic TON, MFI, TON/MFI, TON-SG, and the MFI@TON composites are shown in Fig. 11. All these isotherms are typical of microporous materials due to the steep rise at low relative pressures. The subsequent upswing can be attributed to the multilayer adsorption on the surface of the crystals.⁵² With regard to the isotherm of TON zeolites, the hysteresis loop mainly results from polycrystalline accumulation.⁵³ However, the composite exhibits a smaller hysteresis loop at higher relative pressures as compared to that observed in the TON/MFI sample, which is probably due to the densely stacked TON nanorods. A similar conclusion can be drawn by comparing the isotherms of the TON and TON-SG samples.

Nevertheless, in order to further verify the core-shell structure, the composites with a calcined core and uncalcined shell obtained after different crystallization times are investigated by N2 adsorption measurements. The isotherms for the calcined and un-calcined composites (36 h) are shown in Fig. S7.† Obviously, the un-calcined composite shows a much smaller hysteresis loop at higher relative pressure, and no steep uptake is observed. As listed in Table S2,† with an increase in the crystallization time, the microporous areas and volumes of the different samples gradually decrease due to which the organic template in the channels of the shell ZSM-22 zeolite inhibits N₂ adsorption. Therefore, the coverage of the shell correspondingly improves with an increase in the crystallization time. These results demonstrate that the MFI zeolite core with open channels is completely covered by the un-calcined TON shell. This result also further provides solid evidence of the formation of a core-shell structure with higher coverage.²⁶

The micropore diameters (as shown in Fig. S8a†) of all the samples are narrowly centered at about 0.5 nm, indicating the formation of a 10-membered ring. Furthermore, Fig. S8b† shows that the mesopore distributions are not observed in the TON, TON-SG, and MFI zeolites, as well as the TON/MFI sample. However, the mesopore distribution curve of the



Fig. 11 N₂ adsorption-desorption isotherms of different materials.

core-shell material with a maximum at about 4.0 nm does not suggest the "real" pores, which mainly results from the tensile strength effect of the adsorbed phase,⁵⁴ suggesting a strong interaction between the TON shell and MFI zeolite core.

The textural properties derived from the N_2 adsorptiondesorption isotherms are listed in Table 1. Expectedly, the external surface area of the core-shell material is much lower than that of the reference sample (TON/MFI) due to the totally covered MFI zeolites. To further confirm this, several samples after different crystallization times were obtained, as shown in Fig. S9,† and the textural properties are listed in Table S1.† When the crystallization time exceeds 24 h, fusion and aggregation led to a gradual decrease in the interspace between the individual TON nanorods. Therefore, the hysteresis loop and corresponding external surface area of the core-shell materials gradually decreased with an increase in the synthesis time. This result revealed that the growth of the TON shell could be performed through the aggregation of the formed nanorods.

Fig. S10 and S11[†] show the temperature-programmed desorption of ammonia (NH₃-TPD) and pyridine-adsorbed infrared (Py-IR) data for the different samples, and the acidity results are listed in Table 2. Among all the samples, the highest Al concentration in the MFI sample results in the largest amount of acid sites. TON zeolites exhibit a slightly higher amount of acid sites than that in the TON/MFI sample due to the comprehensive effect of the addition of MFI zeolites and high Si/Al ratio of the latter. Meanwhile, the MFI@TON composite exhibits a lesser amount of acid sites as compared to the physically mixed TON/MFI sample. This result suggests that the acid sites of the MFI zeolite core may not be detected by NH3 molecules due to the complete coverage by TON zeolites. As compared to the original TON zeolite, the TON-SG sample with a higher Si/Al ratio exhibits a lower amount of acid sites.

Py-IR results provide more information about the acidity of the various samples. The concentrations of Brønsted (B) and Lewis (L) acid sites for different samples increase with the Al contents, which is similar to the NH₃-TPD results. Apparently, the coverage of the TON shell with a high Si/Al ratio on the MFI zeolite results in a decreased amount of B acid sites over the MFI@TON composite as compared to that in the TON/MFI sample with exposed MFI zeolites. However,

Table 2 Acidity properties of the different samples determined by $\mathsf{NH}_{3}\text{-}\mathsf{TPD}$ and $\mathsf{Py}\text{-}\mathsf{IR}$

	Acid amount $(\mu mol g^{-1})$		Acid types (μ mol g ⁻¹)				
			B acid sites		L acid sites		
Samples	Weak	Strong	200 °C	350 °C	200 °C	350 °C	
TON	182	153	75	62	69	59	
MFI	385	327	187	159	115	96	
TON/MFI	136	128	62	69	58	48	
TON-SG	73	42	39	33	59	51	
MFI@TON	78	45	42	35	78	69	

the core-shell composite exhibits a higher amount of L acid sites as compared to the TON/MFI sample because of which the interaction between the MFI core and TON zeolite shell generates crystal lattice defects in the form of L acid sites.⁵⁵ Notably, the similar densities of B acid sites in the TON-SG and MFI@TON samples further indicate that the pyridine molecules do not reach the MFI zeolites core.

3.4 Catalytic performance

The catalytic performance of the composite catalyst is investigated in the alkylation of toluene with methanol. Since the alkylation reaction is typically an acid-catalyzed process, the activity and product selectivity are influenced by multiple factors, such as acidity, porosity, crystal size, and reaction conditions. Therefore, the MFI, TON, TON/MFI, and TON-SG catalysts are also evaluated under the same conditions.

The catalytic performance and detailed product selectivity are shown in Fig. 12 and listed in Table 3. All the catalysts exhibit high methanol conversion (above 99%) under these reaction conditions. The toluene conversion decreases in the order of MFI (26.67%) > TON (24.25%) > TON/MFI (21.15%) > TON-SG (18.02%) \approx TON/MFI (17.69%), directly validating the important role of the amounts of acid sites determined by NH₃-TPD and Py-IR techniques. When compared with the core-shell MFI@TON catalyst, the mechanically mixed TON/ MFI catalyst exhibits higher toluene conversion because of which the isolated MFI crystals can act as the active sites for the alkylation reaction, while in the core-shell structure, the MFI zeolites are completely covered by the TON shell. The similar toluene conversions of MFI@TON and TON-SG catalyst further indicate that the MFI zeolites core are inert in this reaction.

Significant differences in product selectivity and distribution are observed between these catalysts. With regard to the distribution of the aromatic products (Table 3), a certain amount of benzene is generated over the MFI and TON/MFI catalysts from toluene disproportionation. It is widely accepted that toluene disproportionation needs a stronger acid strength than toluene alkylation.⁵⁶ Therefore, no benzene is observed in the products over the TON, TON-SG, and MFI@TON catalysts, not only suggesting the much weaker acidity of the TON zeolites but also showing the



Fig. 12 Toluene conversion and aromatics selectivity over MFI, TON, TON/MFI, TON-SG, and MFI@TON catalysts (reaction conditions: 420 °C; $n_{\text{Toluene}}/n_{\text{Methanol}} = 4/1$; WHSV = 2.0 h⁻¹; atmosphere).

Table 3Catalytic performances of toluene alkylation with methanol overdifferent catalysts (reaction conditions: 420 °C; $n_{Toluene}/n_{Methanol} = 4/1$;WHSV = 2.0 h⁻¹; atmosphere)

Catalysts	MFI	TON	TON/MFI	TON-SG	MFI@TON
Methanol	99.96	99.85	99.68	99.84	99.92
conversion (%)					
Toluene	26.67	24.25	21.15	18.02	17.69
conversion (%)					
Selectivity	83.52	87.80	85.62	88.86	90.69
to xylene (%)					
para-Selectivity (%)	22.13	42.43	31.95	52.24	75.85
<i>p</i> -Xylene yield (%)	5.90	10.29	6.76	9.41	13.42
Aromatics					
Benzene (%)	4.89	0.10	3.56	0.10	0.10
<i>p</i> -Xylene (%)	22.13	42.43	31.95	52.24	75.85
<i>m</i> -Xylene (%)	32.53	25.28	28.87	19.62	8.02
o-Xylene (%)	18.71	16.31	16.82	13.45	4.14
C_9^+ hydrocarbons (%)	5.25	3.68	4.42	3.45	2.58

improved effect of TON shell on suppressing the strong acid sites of the MFI zeolites. This result also indicates that the MFI zeolites core does not directly participate in toluene alkylation. Apparently, the selectivity toward xylene, namely, *o-*, *m-*, and *p-*xylene, over the different catalysts under consideration follows the order of MFI@TON (90.69%) > TON-SG (88.86%) > TON (87.80%) > TON/MFI (85.62%) > MFI (83.52%), indicating the essential effect of the TON zeolite shell on the increase in xylene selectivity. Since the large crystals with enhanced diffusion resistance can suppress the further transformation of the as-generated xylenes to highly methylated aromatics, the MFI@TON and TON-SG catalysts exhibit lower C₉⁺ aromatics selectivity as compared to that by the original TON catalyst.

Within the distribution of xylene isomers, the para-xylene selectivity over different catalysts decrease in the order of MFI@TON (75.85%) > TON-SG (52.24%) > TON (42.43%) > TON/MFI (31.95%) > MFI (22.13%). In general, the increase for zeolite crystals is correlated with the increased diffusion length and resistance of the products, and the transport of *m*-xylene and *o*-xylene in the micropores is considerably inhibited, thereby resulting in the further isomerization of these isomers into *p*-xylene with a higher diffusion rate.⁵⁷ Therefore, the TON-SG catalyst with big crystals exhibits higher *para*-selectivity than the parent TON catalyst. Meanwhile, the acid sites also have an important role in affecting the product distribution. As determined by the XPS and TEM-EDX data, the composition of the preparation process results in almost no Al sites and correspondingly marginal amount of acid sites on the external surface of the shell component. Therefore, as compared to the parent TON catalyst, the enhanced selectivity toward p-xylene over TON-SG and core-shell MFI@TON catalysts can also be attributed to the almost inert external surface, which cannot isomerize the *p*-xylene diffused from the micropores into its isomers, consequently guaranteeing the high para-selectivity. Moreover, much higher para-selectivity can be achieved by the MFI@TON catalyst than that by the TON-SG catalyst,

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further suggesting the improved effects of spherical morphology and core-shell structure.

Furthermore, a significant difference between the TON/ MFI and MFI@TON catalysts can also be observed. Since these samples contain similar Si/Al ratios and pore channels, the key difference in these catalysts is the combination of the two zeolites components. The components of the TON/MFI catalyst prepared by mechanical mixing are randomly distributed, while the zeolite components of the MFI@TON catalyst yield spherical morphology with a core-shell structure. The uncovered MFI zeolite in the TON/MFI catalyst causes further conversion of the desired products and lower selectivity toward para-xylene in comparison to the MFI@TON catalyst. When combined with the catalytic performance of the TON-SG catalyst, it can be inferred that the reactant molecules have double diffusion resistance and longer diffusion times in the shell of the ZSM-22 crystals (of the MFI@TON catalyst) when they penetrate into the ZSM-22 channels and get converted at the interior acid sites. It should be noted that the spherical morphology of the coreshell MFI@TON composite also limits the further isomerization of the para-xylene products by exposing more pore mouths and lesser portion of the external surface. Therefore, the considerably enhanced para-xylene selectivity of the MFI@TON catalyst can not only be attributed to the passivation of the acid sites on the external surface of the TON shell by forming spherical morphology and inert surface but also resulting from the special structure with extended diffusion pathways of the TON crystals shell.

Fig. S11 and Table S3[†] list the catalytic performances of the MFI@TON composite and various zeolite catalysts found in the literature. The ZSM-5 zeolite catalyst in the present work exhibits a close performance value with the reported values, indicating the reliability of these experimental data. As compared to the 10- (MFI, SAPO-11) and 12-membered ring (SAPO-31, SAPO-5) zeolites, the considerably enhanced *para*-selectivity can be mainly attributed to the structural characteristics of the MFI@TON composite.

Based on the above discussions, the reaction pathway of the toluene alkylation with methanol over the core-shell MFI@TON composite is proposed, as shown in Fig. 13. Firstly, both toluene and methanol penetrate into the



Fig. 13 Simplified scheme of the diffusion pathways for the reactant (toluene and methanol) and products (*p*-xylene) over the core-shell MFI@TON composites.

microporous channels of the TON zeolites shell without reaching the MFI zeolite core. Then, the methanol molecules are converted into methoxonium ions on the interior acid sites. Subsequently, the formed methoxonium ions attack the aromatic ring of the toluene molecules with the assistance of acid sites, mainly forming *para*-xylene due to the steric hindrance of the channels and certain amounts of *m*-xylene and *o*-xylene. The much-improved diffusion time and distance lead to the further transformation of side products (*o*- and *m*-xylene) into *p*-xylene and a significantly increased *para*-selectivity. In addition, the *p*-xylene products diffusing from the microporous channels can hardly isomerize on the almost inert surface, and the high *para*-xylene selectivity can be largely maintained.

4. Conclusion

Core-shell MFI@TON composites with uniform morphology and well-ordered pore channel were successfully synthesized from precisely designed seeds using a hydrothermal crystallization method. Investigations about the synthesis conditions revealed the significance of the Si/Al ratios on determining the formation of a core-shell structure by suppressing the growth of the MFI zeolite core and ensuring the crystallization of the TON nanorods shell. A broad combination of characterizations assisted in formulating the crystallization mechanism of the MFI@TON composite, including the oriented crystal growth and selective fusion. TEM and N2-adsorption measurements provided solid evidence for the total coverage of the uniform TON shell on the MFI crystal. Both the pure silica composition and spherical morphology ensured the passivation of the surface acid sites as determined by the acidity measurements and XPS. As a result, the core-shell composite exhibited much higher para-xylene selectivity in the alkylation of toluene with methanol as compared to the original, unattached, and mechanically mixed catalysts. The enhanced catalytic performance can be attributed to the optimized acidity of the TON zeolites shell and the spherical morphology by suppressing the further isomerization of para-xylene as well as the considerably prolonged diffusion for the intermediates inside the channels due to the spherical structure with largely exposed pore mouths. The synthesis of core-shell MFI@TON composites offers a pathway to optimize the diffusion properties of a zeolite material, providing further insights into the growth of ZSM-22 zeolites.

Conflicts of interest

There are no conflicts to declare.

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