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Synthesis and catalytic properties of multilayered MEL-type titanosilicate nanosheets

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Multilayered MEL-type titanosilicate nanosheets (MTS-2) were hydrothermally synthesized through a dualtemplate method, using cetyltrimethylammonium tosylate (CTATos) and tetrabutylammonium hydroxide (TBAOH) as templates for mesopores and micropores, respectively. The mismatch of nanocrystals and mesophase was minimized by decreasing the size of primary zeolite particles, taking advantage of MELtype zeolite that tends to form nano-sized crystallites. The titanosilicate nanosheets possess both MEL zeolitic structure and large volume of intersheet mesopores without the formation of a physical mixture of bulky zeolites and mesoporous materials. Moreover, it exhibited improved catalytic activities for bulky molecules compared to those of other ordered mesoporous materials and conventional MFI- and MELtype titanosilicates, where post-treatment of as-made MTS-2 samples using NH₄F could reduce the silanols, and thus enhance their hydrophobicity and epoxidation activity.

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1. Introduction

Zeolites with crystalline framework, high stability and specific active sites are widely used in petro-chemistry and fine-chemical synthesis and often show size- and shape-selectivity.1-3 However, the very presence of the micropores, with aperture diameters often below 1 nm, always goes hand-in-hand with diffusion limitations,^{2,4,5} which adversely affects their catalytic activity. The problem can be overcome by decreasing the size of zeolite crystals, synthesizing zeolites with larger pores and introducing mesopores/macropores into the zeolite particles.4,6 Within the past few decades, nanozeolites have been prepared by hydrothermal synthesis at relatively low temperatures with or without the addition of a growth inhibitor or nucleation promoter, confined-space synthesis and two-step seeded growth synthesis.7-11 However, zeolite crystals smaller than 100 nm might be thermodynamically unstable due to the high surface energy and vast amounts of surface defects. Meanwhile, highly dispersed nanocrystals are quite difficult to handle and generally have low yields during the synthesis, in which the majority of the building units are left unused in the mother liquid. The nano-sized zeolite crystallites could be assembled by adding mesoporogens, in which the mesopores are formed among the crystallites. An alternative method is to directly synthesize hierarchical zeolite with inter-crystalline and/or intra-crystalline mesoporosity, where mesoporogens and microporogens are used simultaneously in one system. A number of hard or soft templates have been used as mesoporogens. Most of the hard

templates, such as carbon particles,^{12,13} carbon aerogels,¹⁴ 3DOM carbon^{15,16} and monodisperse polystyrene (PS) spheres,¹⁷ serve as scaffolds, through either endo- or exo-templating.¹⁸ Nevertheless, some mesoporous zeolites with isolated and closed secondary porosity so far have been unsuitable for the diffusion of large molecules. Furthermore, high cost and the complexity in the fabrication of hard templates limit their industrial applications.

Compared with hard templates, soft templates may offer a more promising alternative approach for the preparation of hierarchical mesoporous zeolites through diverse interactions with zeolite precursors. However, two different templating systems of micropore and mesopore worked in a competitive manner rather than in a cooperative manner, which easily results in the formation of physical mixtures of amorphous mesoporous material and bulky zeolite.5,19-21 To prevent phase separation, Ryoo et al. directly synthesized mesoporous MFI and LTA zeolites with tunable mesostructure using specifically designed amphiphilic organosilanes.22 Later, stable single-unitcell nanosheets of zeolite MFI were successfully fabricated with the specially designed and synthesized bifunctionalized agent C₂₂-H₄₅-N(CH₃)₂-C₆H₁₂-N(CH₃)₂-C₆H₁₃(C₂₂₋₆₋₆), which possesses two quaternary ammonium groups spaced by a C₆ alkyl linkage and a long chain alkyl group (C_{22}) on the end.²³ Very recently, zeolite ZSM-5 nanosheets with the thickness of ~10 nm could be directly synthesized using multiquaternary ammonium surfactants, based on 1,4-diazabicyclo[2.2.2]octane, as structure-directing agents.²⁴ Alternatively, various polymers were used as mesoporogens to enhance their interaction with zeolitic precursors. For example, Park et al. used silylated polypropylene oxide diamine and polyethylenimine polymers as templates to synthesize MSU-MFI with intracrystalline

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mesopores of 2.2 and 5.2 nm.^{25,26} Xiao *et al.* synthesized hierarchical zeolites beta and ZSM-5 by using the cationic polymers polydiallyldimethylammonium chloride (PDADMAC) and dimethyl diallyl ammonium chloride acrylamide copolymer (PDDAM) as mesoporogens, respectively, and sometimes the mesopore size could be tuned by the amount of polymers used.²⁷ Based on the suitable interactions between the zeolite precursor and mesoporogen by either chemical bonding or enlargement of charge densities, the hierarchical structures could be created without phase separation between the mesophase and crystalline zeolite. Unfortunately, the synthesis of these unique templates is very complex, leading to a high cost for the synthesized mesoporous zeolite materials. To synthesize hierarchical zeolites using commercially-available templates is still highly anticipated.

Shi and coworkers reported that direct synthesis of mesoporous zeolite ZSM-5 with MFI structure, using commercially available TPAOH and cetyltrimethylammonium bromide (CTAB) as microporogen and mesoporogen, respectively, could be achieved by finely tuning the degree of polymerization and then the size of subnanocrystals, which could enhance the interaction between zeolitic precursors and CTAB and then prevent the phase separation of mesoporous material and bulk zeolite.²⁸

Both zeolites MEL and MFI belong to the pentasil family. It is well known that zeolites with MEL structure tends to form nanosized primary particles.²⁹ The small crystallite size of MEL-type zeolite could thus minimize the mismatch of zeolitic particles and mesophase, make the templates for zeolite and mesoporous materials work cooperatively so as to prevent the formation of physical mixtures.

Long and coworkers hydrothermally synthesized colloidal silicalite-2 particles with the size of ~ 100 nm in a very simple reactant system of TBAOH-TEOS-H2O.29 Under certain conditions, colloidal silicalite-2 particles were the agglomerates composed of nano-crystals with the size of ~20 nm. Very recently, Tsapatsis and coworkers reported that tetrabutylphosphonium (TBP) hydroxide or tetrabutylammonium (TBA) hydroxide could be used as a single template to synthesize a hierarchical zeolite MEL/MFI made of orthogonally connected microporous nanosheets during one-step hydrothermal crystal growth at 388 K.³⁰ The 'ultrathin' zeolites with thickness around 2 nm resulted in a large number of active sites on the external surface and then rendered them highly active for the catalytic conversion of large molecules. However, the size of zeolite aggregates obtained from both systems ranged from 60 nm to 400 nm, which still was very difficult for the separation and recovery.

The object of this study is to use normal TBAOH and CTATos as dual templates for micropores and mesopores, respectively, to synthesize mesoporous MEL-type zeolites with sizes of several microns with combined advantages of reduced diffusion limitation and easy recovery, where the enhanced interactions between small nanocrystals of MEL-type zeolite and CTATos effectively prevent the formation of a physical mixture of mesoporous materials and the bulk zeolite. In addition, the catalytic reactions involving relatively large molecules, including the hydroxylation of phenol and the epoxidation of cyclohexene, were tested. The effect of post fluoride treatment was also discussed.

2.1. Synthesis of MTS-2

In a typical synthesis, 9.11 g of cetyltrimethylammonium tosylate (CTATos, Merck, 99%) was dissolved in 108 mL of water to obtain a clear CTATos solution A. 45.41 g of tetramethylammonium hydroxide (TBAOH, 40 wt%, Alfa) aqueous solution was added to 41.67 g of tetraethyl orthosilicate (TEOS, SCRC, >97%). After complete hydrolysis under vigorous agitation, the silicate solution was further stirred at room temperature for 30 min and cooled to 0 °C, then tetrabutyl titanate (TBOT, SCRC, 98%) isopropanol solution containing 1.70 g of TBOT and 15 g of isopropanol was added slowly and continued to stir for 30 min at 0 °C. After the removal of alcohol at 80 °C for 2 h, the above obtained solution was dropwise added to CTATos solution A. The molar composition of the final synthetic mixture was $SiO_2 : 0.025TiO_2 : 0.1CTATos : 0.35TBAOH : 50H_2O$. The mixture was stirred continuously for 2 h at 60 °C and then divided into several aliquots and loaded into teflon-lined steel autoclaves. The final mixture was heated in the autoclave under static conditions at different temperatures for 12 days. The asmade solid was recovered by filtration, fully washed with water, and dried at 100 °C in the oven overnight.

The post fluoride treatment of the MTS-2 with NH₄F (SCRC, AR) was performed at 100 °C for 12 h using the as-made samples before the removal of organic templates, and the molar composition of the final mixture was $100SiO_2 : 25NH_4$ -F : $6000H_2O$. After the treatment, all the samples were filtered, washed thoroughly with distilled water, and dried at 100 °C for 12 h. Subsequently, the dried products were calcined at 550 °C for 5 h under air for the removal of organic templates before characterization and catalytic use.

2.2. Characterization

Powder X-ray diffraction patterns (XRD) were collected on a Bruker D8 Advance powder diffractometer using Cu Ka radiation ($\lambda = 0.154$ nm) over a 2θ range of 0.5–10° and 5–60° respectively, and the accelerating voltage and the applied current were 35 kV and 25 mA, respectively. The particle sizes of samples were calculated from XRD data by using the Scherrer equation: $D = K\lambda/(\beta \cos \theta)$, where D is the crystallite size (nm), λ is the wavelength of the X-ray radiation for the Cu target ($\lambda =$ 0.154 nm), β is the peak width at half-maximum height ($2\theta =$ 23.1°) for MEL zeolite (501), θ is the Bragg's angle and K is the Scherrer constant (0.89). Scanning electron microscopy (SEM) was performed on a scanning electron microscope (type HITA-CHI S-4800) with an accelerating voltage of 3 kV. Transmission electron microscopy (TEM) was conducted on a TECNAI G2 F30 operating at 300 kV. To prepare the samples for TEM, a dispersion of the sample in diluted ethanol was dropped onto the TEM sample bronze gridding, dried at room temperature for 1 h. The specific BET surface area (S_{BET}) and other textual properties of the samples were determined by nitrogen adsorption-desorption measurements at 77 K on a nitrogen adsorption apparatus (BELSORP-max). Before the measurements, the samples were outgassed at 300 °C in vacuum for 6 h.

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The pore size distributions were derived from the adsorption branches of the isotherms using the Barrett–Joyner–Halanda (BJH) method. The total pore volume (V_p) was estimated at a relative pressure of 0.99. DR UV-vis spectra were recorded in the 200–600 nm range on a UV-2550 from an aluminum cell with a quartz window. The amounts of Si and Ti in the final zeolite products were quantified by inductively coupled plasma (ICP) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer after dissolving the samples in HF solution. The Solid ²⁹Si MAS NMR measurements were collected on a VARIAN VNMRS-400WB spectrometer. Thermogravimetric analysis (TG) was performed using a PerkinElmer 457 TGA analyzer with a heating rate of 10 °C min⁻¹ under an air flow.

2.3. Catalytic reactions

2.3.1 Hydroxylation of phenol. Catalytic reactions were performed in a glass flask equipped with a reflux condenser and a magnetic stirrer. Typically, 0.1 g of catalyst, 2 g of phenol, 0.8 g of hydrogen peroxide (30 wt% aqueous solution) and 1.6 g of acetone as solvent were introduced in the reactor and heated at the reaction temperature (80 °C) for 6 h under vigorous stirring. The phenol/ H_2O_2 molar ratio was taken to 3.

2.3.2 Epoxidation of cyclohexene. The epoxidation of cyclohexene with anhydrous *tert*-butyl hydroperoxide (TBHP, 5.5 M in decane) was carried out in a 25 mL round-bottomed flask equipped with reflux condenser. In a typical run, 50 mg of the catalyst, 10 mL of acetonitrile, 10 mmol of cyclohexene, and 10 mmol of TBHP were mixed in the flask and stirred vigorously at 60 °C for 2 h.

All products were analyzed on a Shimadzu GC-2014 gas chromatograph equipped with a DM-Wax-30 m column (Dikma Technologies Inc.) and an FID detector.

3. Results and discussion

3.1. Synthesis and characterization of multilayered titanosilicates

Fig. 1 displays the powder XRD patterns of MTS-2 samples synthesized at different temperatures (140–175 $^{\circ}$ C) for 12 days. The wide-angle XRD patterns of all these MTS-2 samples were



Fig. 1 Large-angle powder XRD patterns of MTS-2 synthesized at (a) 140 $^\circ$ C, (b) 150 $^\circ$ C, (c) 165 $^\circ$ C and (d) 175 $^\circ$ C for 12 days.

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almost the same as that of silicalite-2 with MEL structure synthesized using TBAOH as the template, where two intense peaks without shoulders existed in the region of $2\theta = 23-25^{\circ}$ (Fig. 1A). The relative crystallinity of MTS-2 samples increased with increase in crystallization temperature. Although TBAOH has been considered as a typical template for MEL-type molecular sieves, MEL/MFI intergrowths have been reported when using TBA⁺ as the template.^{31,32} Jablonski et al.³³ pointed out that zeolite with MEL structure only shows a single peak at $2\theta =$ 45° while zeolite with MFI structure exhibited a doublet at $2\theta =$ 45° (reflection 10, 0, 0) and $2\theta = 45.5^{\circ}$ (reflection 0, 10, 0) with practically equal intensities. As shown in Fig. 1B, there is only one peak with of a hint of shoulder at $2\theta = 45.5^{\circ}$ for all the MTS-2 samples. Therefore, MTS-2 samples synthesized using CTATos and TBAOH here may be tentatively ascribed to the MEL-type structure, although the formation of MFI/MEL intergrowth could not be excluded. Similarly, Davis and coworkers considered that it was quite difficult to synthesize pure MEL-type molecular sieves using TBA⁺ only.34

These broad XRD peaks for MTS-2 samples, compared with those for bulky MEL structured zeolites, generally could be ascribed to the small dimensions of particles. With the increase of crystallization temperature from 140 °C to 175 °C, the primary particle size increases from 15 nm to 20 nm, calculated according to the Scherrer equation, which could be explained by the fact that the induction period is prolonged at lower temperatures, resulting in more nuclei needed for nucleation and crystal growth,³⁵ and thus minimizing the ultimate crystal sizes.³⁶ It should be noted that quite small primary particles with the size of ~20 nm could be obtained even at a much higher crystallization temperature of 175 °C. The reason should be ascribed to the presence of CTA⁺, which may inhibit the growth of MEL-type zeolite and thus prevent the formation of large crystallites of zeolite MEL.

The morphology observed from SEM images is often the characteristics of crystalline grains and possibly provides some information on the growth mechanism.37,38 Typical SEM images of the as-made samples synthesized at different crystallization temperatures are shown in Fig. 2. MTS-2 samples synthesized at low temperatures of 140 and 150 °C showed the olive-like morphology consisting of thin and sometimes slightly curved nanosheets as shown in Fig. 2b and d, consistent with relatively low crystallinity provided by XRD results. At a low temperature of 140 °C, primary particles were very thin, with the size of ~15 nm. With the crystallization temperature increasing, the zeolite nanosheets became thick and well-shaped, corresponding to a highly crystallized MEL-type structure. Olive-like and microsized aggregates with relatively uniform size were observed for MTS-2 synthesized at the temperature of 160 and 175 °C. Most importantly, neither the amorphous phase nor the faceted bulk crystals of MEL zeolite was detected throughout the entire samples, which is completely different from the physical mixtures of mesoporous materials and zeolites. The other thing to be noted is that nanosheets for MTS-2 synthesized at 165 °C are mostly along one direction as shown in Fig. 2e and f, while some nanosheets for MTS-2 synthesized at 175 °C are arranged perpendicular to each other as shown in Fig. 2h.



Fig. 2 SEM images of MTS-2 synthesized at (a and b) 140 $^\circ C$, (c and d) 150 $^\circ C$, (e and f) 165 $^\circ C$ and (g and h) 175 $^\circ C$ for 12 days.

These results are quite different from that reported by Tsapatsis and coworkers.30 They reported that zeolite nanosheet aggregates with the size of 100-200 nm could be synthesized at a much lower temperature of 115 °C in the presence of ethanol, while in the present work nanosheets of MTS-2 assembled into micro-sized aggregates at a high temperature above 140 °C with the removal of alcohol generated by the hydrolysis of TEOS and additional isopropanol. It is worth mentioning that low reaction temperature and the presence of alcohol are beneficial to obtain dispersed nano-sized zeolite particles due to the formation of a large amount of nuclei needed for nucleation during the long induction period at low temperatures and the proved effect of alcohol on the inhibition from producing zeolite aggregates. However, the TS-2 synthesized at 175 °C using TBAOH as the single structure directing agent with the molar ratio of TBAOH/ $SiO_2 = 0.35$ formed large uniform spherical agglomerates of nano-sized primary particles with the size of 8-14 µm, possessing a low external surface area and volume of mesoporosity, where the alcohol was removed before crystallization. This suggests that the presence of CTATos played an important role in directing the multilayered MEL-type titanosilicate nanosheets.

Moreover, nanosheets reported by Tsapatsis and coworkers could be self-pillared and form a house-of-cards arrangement, however, MTS-2 synthesized at a low temperature of ≤ 160 °C here mostly are along one direction. It indicated that the addition of CTATos may disturb the growth mode of the MEL-type structure and inhibit the repetitive twinning or other intergrowth processes in the crystallization process. Furthermore, the microsized MTS-2 aggregates could be easily recovered by traditional filtration, curtailing the difficulties in separation and recovery.

The TEM images provide complementary information to SEM images. TEM images of MTS-2 synthesized at different crystallization temperatures for 12 days are shown in Fig. 3, which is consistent with SEM images. Low crystallization temperatures of 140 and 150 °C led to thin nanosheets with a thickness less than 5 nm, mostly along one direction. With increase in crystallization temperature, the thickness of zeolite nanosheets increased obviously, and more orthogonally connected nanosheets were observed for the MTS-2 samples synthesized at 175 °C, as shown in Fig. 3g and h.



Fig. 3 TEM images of MTS-2 synthesized at (a and b) 140 $^\circ C$, (c and d) 150 $^\circ C$, (e and f) 165 $^\circ C$ and (g and h) 175 $^\circ C$ for 12 days.

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It is worth nothing that few papers have reported the hydrothermal synthesis of lamellar zeolite using binary templates without any other additives. Very recently, mesoporous ZSM-5 and TS-1 were prepared using CTAB as mesoporogen in the presence of ethanol, but no nanosheets formed in their reports.^{28,39} We believed that the synthesis of MTS-2 in present work took advantage of MEL-type zeolite that tends to form nano-sized primary crystallites preferentially, where the mismatch of nanocrystals and mesophase was minimized due to the decrease in the size of primary zeolite particles, and then the enhanced interactions between zeolite precursors and mesotemplates led to the formation of hierarchical MTS-2 aggregates without phase separation.

Fig. 4 displays the powder XRD patterns of the as-made samples synthesized at 160 °C for different crystallization times of 2 h to 12 days. Sharp small-angle XRD peaks at 2 h show that the sample had an ordered hexagonal mesostructure, similar to MCM-41 materials (Fig. 4A(a)).40,41 These peaks could be indexed to (10), (11), and (20) reflections, corresponding to the two dimensional hexagonal structure. No atomic order was detected at this stage, because of the absence of Bragg reflections in the wide-angle XRD pattern (Fig. 4B(a)). When the synthesis time was increased to 3 days (Fig. 4A(c)), the (11) and (20) reflections in the small-angle region disappeared and the (10) peak was broadened and shifted to lower angle values. This is opposite to the results for the synthesis of mesoporous TS-1 in the presence of [3-(trimethoxysilyl)propyl]-octadecyldimethylammonium chloride (TPOAC), where the reflection at $2-3^{\circ}$ shifted to higher angle values with the crystallization time prolonging.42 No obvious Bragg reflections were noted at this stage in the wide-angle region (Fig. 4B(c)). This result indicates that the initial MCM-41-like mesostructure possibly transformed into a disordered mesostructure and the presence of CTA⁺ strongly inhibited the growth of MEL-type zeolite. At 5 days, some Bragg reflections began to appear in the wide-angle XRD region along with an amorphous halo, indicating the poor crystallinity (Fig. 4A(d)). When the crystallization time was further extended to 7 days (Fig. 4B(e)), most of the intense peaks indexed to MEL structure could be observed, while the small-



Fig. 4 Small-angle (A) and wide-angle (B) powder XRD patterns of asmade samples synthesized at 160 $^{\circ}$ C for (a) 2 h, (b) 1 day, (c) 3 days, (d) 5 days, (e) 7 days and (f) 12 days.

angle peak nearly disappeared (Fig. 4A(e)). The evolution of both meso- and micro-structure demonstrates that the formation of zeolite MTS-2 is accompanied by partial collapse of the MCM-41-like mesostructure during the crystallization process. Nevertheless, complete collapse of the mesostructure did not happen and a broad peak was observed in the small-angle XRD (Fig. 4A(f)), indicating that some disordered mesopores may be retained after hydrothermal crystallization at 160 °C for a duration as long as 12 days. It proves that the mesostructure directed by CTATos is hydrothermally stable to some extent.

The SEM images in Fig. 5 are consistent with the XRD data discussed above. A pure mesophase of MCM-41 without the zeolite morphology was observed in SEM images of Fig. 5a and b during the early stages of the hydrothermal reaction (for 2 h and 1 day). There are some olive-like spheres with the size of 2 μ m randomly dispersed in the amorphous gel obtained for 3 days as shown in Fig. 5c. With the crystallization time increased to 5 days, more irregularly-shaped gel transformed into olive-like spheres. After 12 days, almost all the amorphous gel had disappeared and well crystallized zeolite MTS-2 had formed as olive-like agglomerates composed of primary nanosheets. Therefore, the combined results of XRD and SEM indicate that MTS-2 synthesized at 160 °C for 12 days has a disordered mesostructure and highly crystallized MEL-type zeolite structure, without any obvious macroscopic phase separation. In addition, the transformation from the pure MCM-41 phase to MEL-type zeolite here may follow the solid-solid transformation mechanism suggested by Serrano et al.43 It was reported that



Fig. 5 SEM images of samples in the as-made samples synthesized at 160 $^\circ\text{C}$ for (a) 2 h, (b) 1 day, (c) 3 days, (d) 5 days, (e) 7 days and (f) 12 days.



Fig. 6 N₂ physisorption curves (A) and the corresponding pore size distribution (B) of calcined MTS-2 nanosheets synthesized at various crystallization temperatures for 12 days: (a) 140 °C, (b) 150 °C, (c) 160 °C and (d) 175 °C. (Isotherm: 150/300/450 cm³ g⁻¹ shift.)

small tetraalkylammonium cations, such as TMA⁺ (tetramethylammonium) and TEA⁺ (tetraethylammonium), can easily exchange with the template occluded in the channel of the 2D hexagonal MCM-41 silica,⁴⁴ or enter into the templating micelles in the mesophase by Corma's and Sayari's groups respectively.^{45,46} Here, under the hydrothermal conditions, TBA⁺ molecules may diffuse into the mesoporous channels and then interact with the amorphous pore walls to generate crystallinelike inorganic frameworks, finally transferring the MCM-41 mesophase to the MEL zeolitic structure.

The combination of meso- and micro-porosity was proven by nitrogen physisorption. N2 adsorption-desorption isotherms and pore size distribution (PSD) curves are shown in Fig. 6 and the textual properties are summarized in Table 1. The adsorbed volumes of N₂ for all the calcined MTS-2 are of more than 100 $cm^3 g^{-1}$ at low partial pressure (*P*/*P*₀ < 0.10) (Fig. 6A), indicating that the samples are highly crystallized and contain a considerable amount of zeolitic micropores. In addition, all the MTS-2 samples exhibited clear hysteresis loops at higher pressure P/P_0 > 0.40, which is characteristic of mesoporous and/or macroporous materials, indicating the hierarchical porosity of MTS-2. A broad pore size distribution centered at \sim 12 nm was observed for MTS-2 samples synthesized at low crystallization temperatures (140 °C and 150 °C), while those synthesized at high temperatures of 160 °C and 175 °C showed a more wider pore distribution centered at ~ 28 nm (Fig. 6B). This mesoporosity

may be attributed to intercrystalline mesopores caused by the assemblies of zeolite nanosheets. The relatively larger intercrystalline pores may be related to more consumption of mesopores during the crystallization process and the formation of bigger voids between the larger primary particles (thicker zeolite nanosheets) obtained at high temperature. This is quite different from mesoporous materials mechanically mixed with zeolites. Furthermore, an increase in temperature led to a decrease in both external surface area and mesopore volume accompanied by an increase in the zeolitic micropore volume as listed in Table 1. It was supported by XRD results, where low temperature resulted in relatively low crystallinity and thus small zeolitic micropore volumes. MTS-2 synthesized at 150 °C has the highest BET surface area of 573 m² g⁻¹ here, comparable to that of titanosilicate MFI nanosheets of single-unit cell thickness synthesized with a diquaternary ammonium surfactant (*i.e.*, $C_{16}H_{33}-N^{+}(CH_{3})_{2}-C_{6}H_{12}-N^{+}(CH_{3})_{2}-C_{6}H_{13}$) as the zeolite structure-directing agent (580 m² g⁻¹).⁴⁷ However, MTS-2 synthesized at 150 °C, with the thickness of around 5-10 nm, has a lower external surface area (333 $m^2 g^{-1}$) than these titanosilicate MFI nanosheets with the thickness of \sim 2 nm (425 m² g^{-1}). Similarly, Wang *et al.* reported that multilayered titanosilicate synthesized using a bifunctional surfactant as the structure-directing agent had BET surface area and external surface area of 510 and 357 $\mathrm{m}^2\,\mathrm{g}^{-1}$, respectively,⁴⁸ quite close to those of MTS-2 synthesized at 150 °C. As a reference, TS-2 was synthesized at 175 °C using TBAOH as the single structure directing agent with the molar ratio of TBAOH/SiO₂ = 0.35, in order to show the role of CTATos in directing the formation of nanosheet structures. The reference TS-2 formed large uniform spherical agglomerates of nano-sized primary particles with the size of 8-14 µm, however, it has much lower external surface area (94 m² g⁻¹) and volume of mesoporosity (0.17 cm³ g⁻¹) than MTS-2. Therefore, the active sites in reference TS-2 might be inaccessible to the bulky molecules, the role of CTATos in directing multilayered MEL-type titanosilicate nanosheets was further proved.

In general, the introduction of mesoporosity in hierarchical zeolites is frequently coupled to a lowered micropore volume, which sparkled the definition of the hierarchy factor (HF) to efficiently categorize zeolites by their porosity.⁴⁹ The HF is expressed as the relative mesopore surface area ($S_{\text{meso}}/S_{\text{total}}$) multiplied by a relative microporosity ($V_{\text{micro}}/V_{\text{total}}$). The MTS-2 nanosheets, hydrothermally synthesized using CTATos and

Table 1 Structural data of calcined catalysts										
Samples	$T/^{\circ}\mathbf{C}$	$S_{\rm BET}/{ m m}^2~{ m g}^{-1}$	$S_{\rm ext}/{ m m}^2~{ m g}^{-1}$	$V_{\rm total}/{\rm cm}^3~{\rm g}^{-1}$	$V_{\rm micro}/{\rm cm}^3~{\rm g}^{-1}$	$V_{\rm extra}/{\rm cm}^3~{\rm g}^{-1}$	HF^{a}	$S_{\rm ext}/S_{\rm BET}^{\ \ b}$		
MTS-2	140	539	323	0.77	0.09	0.68	0.07	0.60		
MTS-2	150	573	333	0.76	0.11	0.65	0.08	0.58		
MTS-2	160	517	252	0.63	0.12	0.51	0.09	0.49		
MTS-2	175	506	228	0.57	0.12	0.45	0.09	0.45		
TS-1	175	489	74	0.39	0.18	0.21	0.07	0.15		
TS-2	175	565	117	0.51	0.20	0.31	0.08	0.21		
Ti-MCM-41	175	487	487	0.53	0	0.53	_	1		

^{*a*} Hierarchy factor, $HF = (V_{micro}/V_{total}) \times (S_{ext}/S_{BET})$. ^{*b*} Fraction of external surface area.



Fig. 7 UV-visible spectra of calcined MTS-2 synthesized at various crystallization temperatures for 12 days: (a) 140 $^\circ$ C, (b) 150 $^\circ$ C, (c) 160 $^\circ$ C and (d) 175 $^\circ$ C.

TBAOH as binary templates, showed HF of 0.07–0.09, slightly increased with the temperature increasing. To some extent, it is different from that suggested by Pérez-Ramírez *et al.*, where HF > 0.1 when hierarchical zeolites were fabricated through dealumination or templating methods. Low HF value for MTS-2 samples could be attributed to the formation of quite large total volume and relatively small micropore volume. As the authors did not provide the micropore volume, the HF value of MFI titanosilicate nanosheets with single-unit-cell thickness could not be obtained.⁴⁷

The coordination states of Ti species in MTS-2 were further studied by UV-visible spectroscopy (Fig. 7). All samples synthesized at different temperatures showed a main absorption around 220 nm, the characteristics of tetrahedrally coordinated Ti highly dispersed in the framework.⁵⁰ This could be beneficial for redox reactions that require tetrahedrally coordinated titanium. In addition, no significant absorption at the 260 and 330 nm bands occurred in the UV analysis for MTS-2 crystallized at 140 °C, which indicates extra-framework Ti species are negligible. With increasing crystallization temperature, an absorption at 330 nm attributed to the TiO₂ phase was observed, indicating the formation of extra-framework Ti species at high temperatures despite possessing the same Si/Ti molar ratio in the initial synthetic mixtures. The reason could be that condensation between Si–OH and HO–Si may be much faster than that between Ti–OH and HO–Si in the presence of CTATos at high crystallization temperatures, resulting in the expulsion of Ti species from framework sites. As shown in Table 2, the molar ratio of Si/Ti in the final MTS-2 samples increased with increase in temperature, which confirms that high crystallization temperature disfavors the incorporation of Ti into the framework.

3.2. Catalytic properties of multilayered MTS-2 nanosheets in the hydroxylation of phenol and the epoxidation of cyclohexene

The activity of MTS-2 nanosheets has been compared with that of conventional nano-sized TS-1 and TS-2, as well as that of Ti-MCM-41 with ordered mesopores but amorphous walls. Conventional TS-1 and TS-2 were synthesized with the gel composition of SiO_2 : 0.025TiO₂: 0.18TAAOH: 25H₂O, using TPAOH and TBAOH as structure directing agents, respectively. Ti-MCM-41 was obtained using CTATos as a single template as reported in our previous work.⁵¹ As shown in Fig. 8, TS-1 and TS-2 are nanocrystals with the size of \sim 300 nm, while Ti-MCM-41 exhibits worm-like particles with some larger elongated agglomerates. The textual properties are summarized in Table 1. TS-1 and TS-2 have much lower external surface area and volume of mesoporosity than MTS-2, which might hinder the diffusion of bulky molecules. Ti-MCM-41 has a much higher external surface area and total volume than TS-1 and TS-2, indicating that the active Ti sites in Ti-MCM-41 are highly accessible to the bulky molecules. However, its amorphous structure will not catalyze the reactions contributed to the Ti centers in the zeolitic framework. In addition, such noncrystalline silica frameworks are vulnerable to water environment catalytic reaction conditions, and hence, the catalytic recyclability is lower than the crystalline framework.

It is well known that nano-sized porous materials have a large external surface area and short diffusion path, which significantly improves the mass-transfer rate in the confined space, and thus exhibits high reactivity.⁵² Two test reactions including the hydroxylation of phenol and the epoxidation of cyclohexene were purposely selected. The catalytic activity of TS-1 samples for the hydroxylation of phenol was very sensitive to the crystal size, as the reaction is restricted by pore diffusion limitations.⁵³ As for the epoxidation of cyclohexene, cyclohexene

Table 2Hydroxylation of phenol with H_2O_2 over MTS-2 ^a									
Sample	es	$T/^{\circ}\mathrm{C}$	$d_{ m crysta}/\mu{ m m}$	$\mathrm{Si/Ti}^b$	Conv. ^c /%	$Y_{\rm Ortho}^{\ \ d}/\%$	$Y_{\rm Para}^{e}/\%$	TOF	
MTS-2		140	1	34.5	14.8	7.4	4.9	11.1	
MTS-2		150	1.5	35.9	23.5	12.1	8.0	18.4	
MTS-2		160	1-2	39.9	26.5	13.5	9.0	23.0	
MTS-2		175	1-2	40.2	28.9	14.8	10.6	25.2	
TS-1		175	0.3	47.2	26.0	13.5	8.7	26.5	
TS-2		175	0.3	51.2	23.2	11.7	8.5	15.6	

^{*a*} Reaction conditions: 0.1 g catalyst, 2 g phenol, 0.8 g H_2O_2 (30% aqueous solution), 1.6 g acetone, 80 °C 6 h. ^{*b*} Si/Ti ratio in the product given by ICP data. ^{*c*} Conversion of phenol. ^{*d*} Yield of catechol. ^{*e*} Yield of hydroquinone. ^{*f*} Turnover frequency in mol mol⁻¹ h⁻¹.



Fig. 8 SEM images of reference samples: (a) TS-1, (b) TS-2 and (c) Ti-MCM-41.

molecules are too large to diffuse into the 10-MR pores of both MFI and MEL structure, and thus the epoxidation of cyclohexene mostly occurred on the external surface of zeolites.⁵⁴

3.2.1 Hydroxylation of phenol with H₂O₂. Titanium silicalite-1 (TS-1) with MFI structure was proved to be an active catalyst in the hydroxylation of phenol,55,56 which has been commercialized by Enichem.57 As a member of the pentasil family of zeolites, TS-2 also shows considerable catalytic performances in the hydroxylation of phenol.⁵⁸ Meanwhile, it was reported that the framework structure differences do not perturb the catalytic performances by comparing catalytic behaviors of TS-1 and TS-2 with similar Si/Ti ratios and crystal sizes.58 This is not surprising, as TS-2 and TS-1 framework structures are very similar. However, it was demonstrated that the catalytic activity was very sensitive to the crystal size.53 When the crystal size of TS-1 is beyond 1 µm, the diffusion of products and reactants is quite difficult and the auto-decomposition of H_2O_2 may be the prevailing reaction. Therefore, not only low activities but also very low H₂O₂ efficiencies are observed. As a result, nano-sized TS-1 or TS-2 (<300 nm) were used for the hydroxylation of phenol, making severe difficulties in the separation and recovery. In this case, TS-1 and TS-2 with the size of ~ 300 nm were synthesized as a reference. The phenol conversion for three MTS-2 samples synthesized at \geq 150 °C for 12 days is comparable to that over nano-sized TS-1 and TS-2 (Table 2), while MTS-2 crystallized at 140 °C was less active due to its poor crystallinity (small micropore volume). Moreover, MTS-2 samples show larger TOF than that of nano-sized TS-2, implying the more effective catalytic activity of Ti incorporated into the framework of MTS-2 nanosheets. It indicated that an increase in the size of MTS-2 aggregates up to 1-2 µm did not exacerbate the diffusion limitation of reactants and products

here, taking advantage of hierarchical porosity and thin nanosheets of MTS-2 samples. Furthermore, nanosized TS-1 and TS-2 have severe difficulties in the recovery during their synthesis and applications due to their colloidal properties. However, micro-sized MTS-2 samples could be easily recovered by conventional filtration. In summary, the formation of microsized aggregates not only keeps well the advantages of catalytic activity and shape selectivity of nanosized TS-2, but also curtails the difficulties in separation and recovery. The reference TS-2 was synthesized at 175 °C using TBAOH as the single structure directing agent with the molar ratio of TBAOH/SiO₂ = 0.35 showed the similar catalytic activity with nanosized TS-1 on the hydroxylation of phenol (conv._{phenol} = 24.1%) due to its comparable external surface area (94 m² g⁻¹) with nano-sized TS-1 and well crystallized zeolitic structure.

3.2.2 Epoxidation of cyclohexene with TBHP. The catalytic activity of MTS-2 has been further investigated by the epoxidation of cyclohexene using TBHP as oxidant. The epoxidation of cyclohexene was carried out in acetonitrile following the report by Na et al.47 In the epoxidation of cyclohexene with TBHP (5.5 M in decane), cyclohexene oxide (CHO) was almost the sole product, irrespective of the type of titanosilicate (Table 3). Nanosized TS-1 and TS-2 possess a small external surface area and volume of mesoporosity (Table 1) leading to low conversion of cyclohexene because the 10-MR of the MFI structure provided a significant hindrance for the bulky molecules of cyclohexene and TBHP (Table 3). As MEL structure zeolite tends to form nano-sized primary crystallites preferentially, nano-sized TS-2 had slightly larger external surface area and volume of mesoporosity than TS-1 (Table 1), thus showed higher conversion than that of nano-sized TS-1 due to the better accessibility of active sites to bulky molecules (Table 3). Notably, the conversion

Table 3 Epoxidation of cyclohexene with TBHP over MTS-2 ^a									
Samples	$T/^{\circ}\mathrm{C}$	$d_{ m crystal}/\mu{ m m}$	Si/Ti ^b	Si/Ti ^c	Conv. ^d /%	CHO _{sel} ^e /%	TOF		
MTS-2	140	1	40	34.5	17.5	99.0	37.7		
MTS-2	150	1.5	40	35.9	14.1	98.9	31.5		
MTS-2	160	1-2	40	39.9	7.6	97.0	18.8		
MTS-2	175	1-2	40	40.2	6.7	96.7	16.7		
TS-1	175	0.3	40	47.2	1.2	99.0	3.5		
TS-2	175	0.3	40	51.2	6.1	99.0	19.3		
Ti-MCM-41	175	>2	40	32.3	19.6	96.9	39.6		

^{*a*} Reaction conditions: 0.05 g catalyst, 10 mL CH₃CN, 10 mmol cyclohexene, 10 mmol TBHP, 60 °C 2 h. ^{*b*} Si/Ti ratio in gel. ^{*c*} Si/Ti ratio in the product given by ICP data. ^{*d*} Conversion of cyclohexene. ^{*e*} Selectivity of cyclohexene oxide (CHO). ^{*f*} Turnover frequency in mol mol⁻¹ h⁻¹.

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of cyclohexene on MTS-2 synthesized at 140 °C was much higher than that on nano-sized TS-1, and its TOF reached the same level as that of Ti-MCM-41. Since the bulky cyclohexene tested here were too big to approach the internal Ti sites, the high catalytic activity indicates that the Ti sites on the external surface of the nanosheets are sufficiently active to convert the bulky cyclohexene to its epoxide counterparts. It is deduced that the active Ti sites in MTS-2 were highly accessible to the bulky molecules because of the presence of inter-crystalline mesoporosity. The catalytic activity decreased with the crystallization temperature increasing from 140 °C to 175 °C, which might be explained by the reduced mesoporosity and external surface area due to the formation of thicker nanosheets and more extraframework Ti species at high temperatures. Nevertheless, the MTS-2 synthesized at 175 °C still showed higher conversion than that of nanosized TS-1.

The reference TS-2 was synthesized at 175 °C using TBAOH as the single structure directing agent with the molar ratio of TBAOH/SiO₂ = 0.35 and it showed much lower catalytic activity than MTS-2 on the epoxidation of cyclohexene (conv._{cyclohexene} = 3.5%) due to its small external surface area and volume of mesoporosity, illustrating that the formation of multilayered MTS-2 by the addition of CTATos is important for reactions which occur on the external surface.

Interestingly, MTS-2 samples synthesized at different temperatures show an opposite trend in these two reactions, where MTS-2 sample synthesized at 140 °C showed highest activity for the epoxidation of cyclohexene, while this sample had the lowest activity for the hydroxylation of phenol. This probably was attributed to the fact that the epoxidation of cyclohexene could only occur on the external surface of titanosilicate, while the activity for hydroxylation of phenol was mostly contributed to the Ti centers in the zeolitic framework. Among others, the MTS-2 sample synthesized at 140 °C has the largest fraction of external surface area, but smallest micropore volume. Therefore, its different behavior in these two reactions could be easily understood.

3.2.3 Post fluoride treatment of as-made MTS-2 samples. The MTS-2 samples have been proved to possess numerous active sites on the external surface area and extremely thin diffusion pathway, exhibiting high catalytic activity for the hydroxylation of phenol and the epoxidation of cyclohexene. Nevertheless, the external surface of multilayered MTS-2 might be terminated with a large number of silanol groups, and the hydration of silanol groups could cause poor accessibility of hydrophobic olefin to the Ti sites. Although this problem can be significantly resolved by blocking the silanols *via* silylation,^{59,60} such treatment has obscured the wide catalytic use of titanosilicate with hydrophilic surface.

In the previous studies, the fluoride anions were considered to be detrimental to the catalytic activity of titanosilicate catalysts in epoxidation reactions.^{61,62} Recently, Fang *et al.* found that the introduction of Si–F groups into Ti–MWW through post-acid treatment in the presence of NH₄F could greatly enhance the catalytic activity in liquid-phase oxidation reactions.⁶³ However, the direct treatment of calcined titanosilicate nanosheets with NH₄F still led to the collapse of the structure and decreased catalytic activity. Only fluoride treatment of asmade TS-1 nanosheets could reduce the silanols and enhance the hydrophobicity and catalytic activity.⁴⁷ Noticeably, fluorine atoms did not exist on the nanosheet sample after fluoride treatment.

In the present study, we also used the post fluoride treatment to decrease the concentration of silanols on the as-made MTS-2 samples, in order to increase the surface hydrophobicity and thus the catalytic activity. As shown in Table 4, the relative Q^4/Q^3 ratios for all the MTS-2 samples, calculated from the areas of Q^4 (-113 ppm) and Q^3 (-102 ppm) in ²⁹Si MAS NMR spectra, increased after the fluoride treatment. It was suggested that the decrease of silanols was attributed to the formation of siloxane bridges [*i.e.*, (SiO)₃Si-O-Si(OSi)₃] by condensation between neighboring silanols.47 All MTS-2 samples after fluoride treatment had a slightly high relative crystallinity, as listed in Table 4. Possibly, NH₄F treatment might remove some amorphous titano-silica/silica species, or insert silica species into framework defects, and thus induce a recrystallization process on the nanosheet surface under present post-treatment conditions, since the fluoride anions could be used as a mineralizing agent. In contrast to the results of nanosheet F-TS-1 (the molar ratio of Si/Ti slightly decreased from 57 to 54 after the fluoride treatment),47 MTS-2 samples synthesized at 160 and 175 °C obviously showed an increased Si/Ti ratio after the NH4F treatment, as listed in Table 5, while MTS-2 samples synthesized at 140 and 150 °C showed quite closer molar ratios of Si/Ti. This may be attributed to different amounts of templates occluded in the MTS-2 samples synthesized at varied temperatures. As shown in Fig. 9, MTS-2 samples synthesized at 140 and 150 °C showed much higher weight loss in the range of 200-600 °C than those

Table 4	Relativ	ve crysta	allinity a	and amou	unt of sil	anol gro	oups of	MTS-2
Samples	140 ^{<i>a</i>}	150	160	175	F-140 ^b	F-150	F-160	F-175
R.C. ^c Q^4/Q^3	75 5.9	85 6.38	98 10.04	103 10.20	79 9.98	87 10.19	99 11.17	108 11.77

 a MTS-2 synthesized at different temperatures for 12 days. b MTS-2 post treated with NH₄F. c Relative crystallinity using conventional TS-2 as the standard.

Table 5 Epoxidation of cyclohexene with TBHP over fluoride-treated MTS- 2^a

$T/^{\circ}C$	$d_{\mathrm{crystal}}/\mu\mathrm{m}$	Si/Ti ^b	Si/Ti ^c	Conv. ^d /%	CHO _{sel} ^e /%	TOF
140	1	34.5	34.3	24.0	98.0	51.4
150	1.5	35.9	36.2	22.4	98.9	50.6
160	1-2	39.9	44.4	14.9	97.6	40.9
175	1-2	40.2	52.2	12.6	97.9	40.5

^{*a*} Reaction conditions: 0.05 g catalyst, 10 mL CH₃CN, 10 mmol cyclohexene, 10 mmol TBHP, 60 °C 2 h. ^{*b*} Si/Ti ratio in MTS-2 samples given by ICP data before the fluoride treatment. ^{*c*} Si/Ti ratio in fluoride-treated samples given by ICP data. ^{*d*} Conversion of cyclohexene. ^{*e*} Selectivity of cyclohexene oxide (CHO). ^{*f*} Turnover frequency in mol mol⁻¹ h⁻¹.



Fig. 9 TG–DTG curves of as-made MTS-2 synthesized at various crystallization temperatures for 12 days: (a) 140 $^{\circ}$ C, (b) 150 $^{\circ}$ C, (c) 160 $^{\circ}$ C and (d) 175 $^{\circ}$ C.

synthesized at 160 and 175 °C. The occluded templates included both TBA⁺ and CTA⁺, where high crystallization temperature may decompose the CTA⁺ via Hoffman elimination and/or expel the CTA⁺ out of zeolite particles. Therefore, obviously fewer templates were occluded in the as-made MTS-2 samples synthesized at high temperatures of 160 and 175 °C. These occluded organic templates could prevent Ti active centers from attack by fluorides and thus inhibit the detrimental effect of fluorides. As for MTS-2 samples synthesized at 140 and 150 °C, more TBA⁺ and CTA⁺ cations prevent the leaching of Ti species during the fluoride treatment, while some Ti species on the external surface of those synthesized at 160 and 175 °C could be attacked by fluoride and then leached due to less protection of occluded templates. The variation of Ti centers could also be proved by UV-vis spectra as shown in Fig. 10. For MTS-2 samples synthesized at 140 and 150 °C, there is only very minor variation for Ti chemical environment



Fig. 10 UV-visible spectra of fluoride-treated MTS-2 synthesized at various crystallization temperatures for 12 days: (a) 140 $^{\circ}$ C, (b) 150 $^{\circ}$ C, (c) 160 $^{\circ}$ C and (d) 175 $^{\circ}$ C.

after fluoride treatment, which further confirmed the protection effect of occluded templates. Quite differently, the contribution of the adsorption at 330 nm decreased obviously after the fluoride treatment for those synthesized at 160 and 175 °C, which suggested that some extra-framework TiO₂ species were removed. This is consistent with the report by Guo *et al.*, where some extra-framework titanium species could be removed from the as-made TS-1 sample by the treatment with $NH_4F-H_2O_2$.⁶⁴

Epoxidation of cyclohexene with TBHP was used to test fluoride-treated MTS-2 nanosheets. As shown in Table 5, the conversion of cyclohexene increased after fluoride treatment in all the cases. The positive effect of fluoride treatment can be explained in terms of the decrease in the silanol concentration. Since the external surface of the MTS-2 nanosheets becomes less hydrophilic by decreasing the silanol concentration *via* fluoride treatment, which favors to increase cyclohexene accessibility to the active Ti sites and, consequently, increase the reaction rate. Therefore, fluoride treatment distinctly improved the catalytic capacity of MTS-2 samples. Especially, MTS-2 samples synthesized at 140 and 150 °C showed higher conversion and TOF than MCM-41 material, as listed in Table 5.

4. Conclusion

In summary, multilayered MEL-type titanosilicate nanosheets (MTS-2) were directly synthesized using binary templates of cetyltrimethylammonium tosylate (CTATos) and tetrabutylammonium hydroxide (TBAOH). Taking advantage of MEL structure zeolite that tends to form nano-sized primary crystallites preferentially, the mismatch of nanocrystals and mesophase was minimized and thus phase separation was prevented. The titanosilicate nanosheets possess large inter-sheet mesopore volume and exhibit improved catalytic activities for the hydroxylation of phenol and the epoxidation of cyclohexene compared with mesoporous MCM-41, conventional TS-1 and TS-2. Furthermore, the catalytic activity of the external Ti sites for the epoxidation of cyclohexene could be enhanced remarkably by reducing the amount of silanols *via* post fluoride treatment.

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