RESEARCH ARTICLE

Controllable synthesis of a large TS-1 catalyst for clean epoxidation of a C=C double bond under mild conditions

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Abstract Development of a titanium silicalite-1 (TS-1) catalyst with good crystallinity and a four-coordinate Ti framework is critical for efficient catalytic oxidation reaction under mild conditions. Herein, a size-controlled TS-1 zeolite (TS-1#0.1ACh (acetylcholine)) was synthesized via steam-assisted crystallization by introducing acetylcholine as a crystal growth modifier in the preparation process, and TS-1#0.1ACh was also employed in epoxidations of different substrates containing C=C double bonds. The crystalline sizes of the as-synthesized TS-1#0.1ACh catalysts were controlled with the acetylcholine content, and characterization results showed that the particle sizes of highly crystalline TS-1#0.1ACh zeolite reached 3.0 µm with a good Ti framework. Throughout the synthetic process, the growth rate of the crystals was accelerated by electrostatic interactions between the connected hydroxyl groups of the acetylcholine modifier and the negatively charged skeleton of the pre-zeolites. Furthermore, the TS-1#0.1ACh catalyst demonstrated maximum catalytic activity, good selectivity and high stability during epoxidation of allyl chloride. Importantly, the TS-1#0.1ACh catalyst was also highly versatile and effective with different unsaturated substrates. These findings may provide novel, easily separable and large TS-1 catalysts for efficient and clean industrial epoxidations of C=C double bonds.

Keywords size-controlled TS-1, crystal modifier, steam-assisted crystallization, epoxidation

1 Introduction

Zeolite catalytic technologies are efficient and heterogeneous processes used in the syntheses of petrochemical

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and fine chemical products, owing to their unique features of weak diffusion, shape selectivity, catalyst recyclability, and adjustable active centres [1-4]. Consequently, porous zeolites play crucial parts in various catalytic reaction systems, such as catalytic co-aromatization by USY zeolite [5], catalytic alkylation with H-mordenite zeolite [6] and catalytic oxidation by HZSM-5 zeolite [7]. Among porous zeolites, MFI type zeolites (e.g., silicalite-1, ZSM-5) are among the most widely studied materials. In particular, titanium silicalite-1 (TS-1), first synthesized by Taramass in 1983 [8], has attracted great attention from many researchers, due to its excellent catalytic activity in the epoxidation of alkenes, ammoxidation of cyclohexanone, oxidation of alcohols, and hydroxylation of aromatics [9–11]. For example, Gordon et al. [12] showed that TS-1 showed high efficiency in epoxidation of propylene with H₂O₂, which was due to binuclear sites rather than isolated four-coordinate titanium centres. Nevertheless, conventional microporous TS-1 also has defects, including small crystallite sizes, few tetrahedrally coordinated Ti atoms, and narrow pore channels (approximately 0.55 nm), which limit its catalytic application in industry [13–15].

To overcome the above drawbacks of TS-1 zeolites, various features of the zeolite are required for commercial application, including (1) strengthening the mechanical properties to enhance catalytic stability; (2) reducing the resistance to product flow between zeolites to separate and easily recycle the zeolites; (3) simplifying the synthetic processes to reduce the cost. Interestingly, during the preparation of large TS-1 particles, increasing the particle size and mechanical strength is a great way to meet the stringent requirements, including simple separation, and good catalytic activity. For example, Yang et al. [16] prepared X zeolites with different particle sizes (0.9, 3.2, and 15.0 µm) and applied them to alkylation reactions in a continuous flow slurry reactor, and the results showed that 3.2 µm X zeolites exhibited better stability than the other two samples. As a result, syntheses of high-performance and bulky TS-1 zeolites are meaningful and also enormously challenging.

Fortunately, many researchers have proposed multiple strategies to modulate zeolite surfaces, microstructures, and crystal sizes, such as employing new preparation methods, changing synthetic processes, and introducing additives [17,18]. Crystal growth modifiers are often added for zeolite crystal engineering due to the ease of operation and cost of manufacturing. Growth modifiers contain macromolecular compounds (e.g., polymers and peptides) and small molecule compounds (e.g., lactams and amino acids) [19,20], which interact with zeolite facets and combine with amorphous precursors to change the nucleation and growth rates, which alters the morphologies and sizes of crystals [21,22]. Considering the easily available processes and low synthetic cost, cheap lactam derivatives such as L-carnitine and acetylcholine (ACh) have exhibited significant merit in modifying morphology and structure [23]. For instance, Yu's group [24] developed a large hexagonal and flat TS-1 with a rich framework for the Ti⁴⁺ species by using Lcarnitine as a crystalline modifier, and the TS-1 zeolites exhibited better catalytic activity in the alkene epoxidation reaction. Additionally, Zhang et al. [25] successfully designed and synthesized novel core-shell zeolite Y with hollow interiors by introducing L-carnitine. As a result, the zeolite Y exhibited excellent catalytic performance in the Friedel-Crafts process. In 2019, the authors synthesized the perfectly hierarchical ZSM-5 zeolite via introduction of L-lysine as a modifier [26]. Recently, Yang et al. [27] reported that beta zeolites with different particle sizes and similar Si/Al ratios were prepared by adding imidazole as a crystal modifier during the synthetic process, and the products were used for liquidphase transalkylation of diethylbenzene and benzene. Based on these results, it is reasonable to expect small molecule modifiers containing proximal binding moieties, such as amino and carboxyl groups, may affect the morphologies and sizes of zeolites during the synthetic process, which is attributable to the strong interactions between these binding groups and amorphous precursors or the crystalline surfaces.

In previous work, conventional microporous TS-1 was mainly prepared by hydrothermal crystallization with long crystallization times [28]. To further reduce the synthetic cost of the zeolite, multiple approaches have been implemented to simplify crystallization and shorten the time required, such as solid phase crystallization, addition of seeds, syntheses involving microwave irradiation, and vapour-assisted syntheses [29,30]. Liu et al. [31] proposed a synthetic method for production of sizecontrolled TS-1 involving the addition of seed crystals in a nanosized S-1 suspension, and TS-1 synthesis was successfully scaled up and the TS-1 applied in epoxidation of propylene. The yield of propylene oxide based on propylene and H_2O_2 reached 64.3% and 96.5%, respectively. In 2020, Xu et al. [32] reported a one-step rapid synthesis of TS-1 zeolites by using microwave irradiation, and the resultant catalysts contained highly active Ti species and exhibited excellent activity in epoxidation of 1-hexene. Very recently, we proposed a rapid approach to preparing a highly efficient TS-1 zeolite with high crystallinity and active Ti species through steam-assisted crystallization [33]. Therefore, it is important to synthesize inexpensive and high-performance TS-1 zeolites for catalytic reactions through rapid synthetic methods involving crystal growth modifiers (small molecules) added during zeolite preparation.

ACh amino groups may affect amorphous zeolite precursors via hydrogen bonding and electrostatic interactions. We report for the first time a size-controlled and rapid synthesis of TS-1 (TS-1#xACh) zeolite through steamassisted crystallization by introducing ACh as a growth modifier. The resulting samples were analyzed with various characterization techniques to study their morphologies, titanium coordination states and zeolite growth mechanisms. Furthermore, the resultant TS-1#0.1ACh catalysts provided good catalytic performance for epoxidation of allyl chloride (ACH) and were readily separated and recovered easily for catalyst recycling. Additionally, the TS-1#0.1ACh catalyst also exhibited good broad substrate compatibility in epoxidation reactions. These features have great scientific and practical significance for development of efficient and low-cost heterogeneous Ti-containing catalysts for catalytic epoxidation reactions.

2 Experimental

2.1 Materials

Tetrapropyl ammonium hydroxide (TPAOH) was purchased from Kente Catalysts Technologies Co., Ltd., China. Tetraethyl orthosilicate (TEOS), hydrogen peroxide (30 wt %), ACH, 1-hexene, 1-octene, 1-decene, 1-tetradecene and methyl oleate were purchased from Aladdin Chemistry Co. Ltd., China. Tetrabutyl titanate (TBOT) was purchased from Tianjin Kemiou Chemical Co., Ltd., China. Isopropanol (IPA), methanol and acetonitrile were purchased from Xilong Science Co., Ltd., China. ACh was purchased from Wuhan Dongkang Source Technology Co., Ltd., China.

2.2 Preparation of the catalyst

The small TS-1 (TS-1-s) zeolite was synthesized by water vapour-assisted crystallization according to prior literature [33]. In an example, TPAOH and distilled water were placed in a round-bottomed flask and vigorously stirred for 10 min, and then a mixture of TEOS, IPA and TBOT was slowly added to the above solution at ambient temperature and stirred for 2 h to obtain mixed

solution A. The resulting mixed solution had molar ratios of TEOS:0.025 TBOT:0.24 TPAOH:1.74 IPA:7.35 H_2O . Then, mixed solution A was dried at 70 °C for 24 h to obtain a dry gel and then milled into a powder. The obtained powder was placed in a 10 mL polytetrafluoroethylene (PTEF) beaker and crystallized at 170 °C for 18 h in a stainless-steel autoclave with distilled water at the bottom (mass ratio of powder to distilled water = 1:10). After the crystallized samples were washed with deionized water to neutrality, the solid product was dried at 120 °C overnight and calcined at 550 °C for 5 h to obtain TS-1-s.

Furthermore, the large spherical TS-1 zeolite was synthesized via introduction of ACh in the crystallization process. Typically, ACh (TEOS:ACh = 1:x, molar ratio) was added to mixed solution A and then transferred to a PTEF beaker and crystallized at 170 °C in a stainlesssteel autoclave with distilled water at the bottom (mass ratio of powder to distilled water = 1:10) for 18 h. The obtained solid sample was named TS-1#xACh-unwashed. Afterwards, the unwashed TS-1#xACh was washed with deionized water to the neutral point and dried at 120 °C for 12 h, then designated TS-1#xACh-washed. Finally, some TS-1#xACh-washed catalysts were calcined at 550 °C (5 h) and denoted TS-1#xACh (x = 0.05, 0.075, 0.1, 0.2, 0.4).

2.3 Catalyst characterization

X-ray diffraction (XRD) patterns for the zeolite were obtained on a BRUKER D8 ADVANCE diffractometer with a Cu-K α radiation source and scanning steps of 0.02° over the range 5° to 80°. Fourier transform infrared (FTIR) spectra of the zeolite were recorded on a Thermo Nicolet iS5 FTIR spectrometer over the spectral range of 400–4000 cm⁻¹ with KBr pellets. Nitrogen physisorption (N₂ adsorption) was surveyed at -196 °C with a Micromeritics ASPS 2020 M apparatus. Surface textural information of the catalysts was calculated with the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda models. Ultraviolet-visible diffuse reflectance spectra (UV-vis) were recorded from 190 to 600 nm on a PE950 spectrometer with BaSO₄ as the reference. A Varian 720 inductively coupled plasma optical emission spectrometer was used to analyse sample elements. Scanning electron microscopy (SEM) was performed on a Zeiss Sigma 500 microscope, and transmission electron microscopy (TEM) was performed on an FEI Tecnai G2 F20 s-twin field emission transmission electron microscope operated at 200 kV. The energy dispersive X-ray spectrometer of the TEM instrument was used to record element maps. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo K-Alpha+ spectrometer with Al-K α radiation (1486.8 eV). NH₃-temperature program desorption (NH₃-TPD) was performed with an ASAP 2920 Micromeritics instrument.

2.4 Catalytic examination

The catalyst activity was tested with a heating system equipped with a magnetic stirrer and a condensation circulating pump. For a typical epoxidation reaction, 1.53 g of ACH and 0.1 g of catalyst were added to a 25 mL two-necked round-bottom flask, then 20 mL of solvent was added, and finally, 3.4 g of H_2O_2 ($n_{C=C}:n_{H_2O_2} = 2:3$) was added to the reactor. The mixed solvent system was maintained at 60 °C for 4 h. After the reaction, the catalyst and the mixed solvent system were separated by centrifugation at 10000 r min⁻¹, and the resulting upper liquid was analyzed with a 7890B Agilent gas chromatography (GC) system with a flame ionization detector and FFAP capillary column (0.32 mm pillar \times 0.5 µm). The GC injector port temperature was 220 °C, and it was run with splitless injections, the flame ionization detector temperature was 240 °C and the column oven temperature program increased the temperature from 150 to 230 °C at a heating rate of 20 °C·min⁻¹ and held that temperature for 15 min. The concentration of unreacted H₂O₂ was obtained by iodometric titration [34]. Conversion of the C=C double bond $(X_{c=c})$ and H_2O_2 $(X_{H_2O_2})$ and the selectivity for the epoxidation product (S_{epo}) were calculated as follows:

$$X_{\rm c=c}(\%) = \frac{n_{\rm c=c}^0 - n_{\rm c=c}}{n_{\rm c=c}^0} \times 100\%,$$
 (1)

$$X_{\rm H_2O_2}(\%) = \frac{n_{\rm H_2O_2}^0 - n_{\rm H_2O_2}}{n_{\rm H_2O_2}^0} \times 100\%,$$
 (2)

$$S_{\rm epo}(\%) = \frac{n_{\rm epo}}{n_{\rm c=c}^0 - n_{\rm c=c}} \times 100\%,$$
 (3)

where $n_{e=c}^{0}$ is the initial molar content and $n_{c=c}$ is the measured molar content of the substrate at a particular time. $n_{H_2O_2}^{0}$ is the initial molar content, and $n_{H_2O_2}$ is the measured molar content of H_2O_2 . n_{epo} denotes the molar content of epoxidized product.

2.5 Reusability and regeneration testing of catalysts

Reusability and regeneration are important properties of heterogeneous catalysts. Hence, the TS-1#0.1ACh catalyst was used for ACH epoxidation under ideal circumstances. Generally, 1.53 g of propylene chloride, 0.1 g of catalyst, 20 mL of methanol and 3.4 g of H_2O_2 were put into a two-necked round-bottomed flask and heated to 60 °C in an oil bath for a certain reaction time. After the reaction, the catalyst was separated and washed with nonpolar solvent several times and dried overnight at above 100 °C. The obtained catalyst was used in the next run. Moreover, the spent TS-1#0.1ACh catalyst was washed, dried and calcined at 550 °C in air, and then the regenerated catalyst was collected and designated TS-1#0.1ACh-Re.

3 Results and discussion

3.1 Characterization of catalysts

The crystalline structures of the TS-1 and TS-1#xACh samples were characterized by XRD and the results are displayed in Fig. 1. All of the samples showed five characteristic peaks typical of pure TS-1 zeolite (2θ = 7.9°, 8.8°, 23.1°, 23.9°, and 24.4°) except for the TS-1#0.4ACh sample [35,36], which proved that the MFI structure was successfully synthesized and that the structure was not destroyed by introducing ACh. Notably, a single diffraction peak at 24.4° was important evidence for the transition from monoclinic symmetry to orthogonal symmetry [37]. Instead, the TS-1 structure was not formed in the TS-1#0.4ACh sample. Furthermore, the crystallinities of the TS-1-based samples were calculated and are listed in Table 1. The results showed that the crystallinity increased first and then decreased with the increases in n_{ACh} : n_{TEOS} within the range 0–0.4, and the TS-1#0.1ACh sample had the highest crystallinity (155%). This may be because the carboxyl and hydroxyl groups of the ACh compound interacted strongly with the many silanol groups on the surface in the amorphous precursor [24,38].

Figure S1 (Electronic Supplementary Material, ESM) illustrates the FTIR spectra of the TS-1 and TS-1#xACh catalysts. The broad and strong absorption peak at 3340 cm⁻¹ was attributed to the stretching vibration of the hydroxyl groups (–OH), and the band at 1621 cm⁻¹ was

attributed to the bending vibrations of -OH, which may have been caused by small amounts of waters of crystallization or the Si-OH and Ti-OH hydroxyl groups of the TS-1 zeolite. For the TS-1-s, TS-1#0.05ACh, TS-1#0.075ACh and TS-1#0.1ACh samples, the five main absorption peaks at 1229, 1101, 802, 550 and 450 cm^{-1} were due to the typical MFI structure [39]. However, the five characteristic peaks of the TS-1#0.2ACh and TS-1#0.4ACh samples were significantly weaker. The band at 1229 cm⁻¹ was the characteristic absorption peak for Si-O or Ti-O bond stretching vibrations. The bands at approximately 1101 and 802 cm⁻¹ were caused by asymmetric and symmetric stretching vibrations of $[SiO_4]$ tetrahedra, respectively. The bands at 550 and 450 cm^{-1} are considered to be the stretching and bending vibrations of the Si-O-Ti structure in TS-1, respectively [40]. In particular, the significant characteristic band at approximately 960 cm⁻¹ is widely attributed to tetrahedrally coordinated Ti in TS-1, which is indicative of Ti insertion into the TS-1 zeolite framework; the IR band is due to tensile vibrations of SiO4 tetrahedra and Ti atoms [9,37,41].

The morphologies and grain sizes of the TS-1-s and TS-1#xACh catalysts were characterized by SEM. As shown in Fig. 2, TS-1-s displayed ellipsoidal shapes with particle diameters of approximately 120 nm (Fig. 2(a)). After introducing a certain amount of ACh into the crystallization system, the particle sizes of TS-1#xACh increased significantly with increasing ACh content over the range 0.05–0.1 (in Figs. 2(b–f)), and the uniform



Fig. 1 XRD diffraction patterns of the TS-1-s and TS-1#xACh: (a) $2\theta = 5^{\circ}-80^{\circ}$; (b) $2\theta = 20^{\circ}-25^{\circ}$.

Table 1 Specific surface areas, crystallinities and crystal size of all samples

Sample	$S_{\rm BET}/({\rm m}^2\cdot{\rm g}^{-1})$	$S_{\text{Ext}}/(\text{m}^2 \cdot \text{g}^{-1})$	$V_{\text{Mesopore}}/(\text{cm}^3 \cdot \text{g}^{-1})$	$V_{\text{Micropore}}/(\text{cm}^3 \cdot \text{g}^{-1})$	Crystallinity/%	Ti/(wt %)
TS-1-s	494	170	0.26	0.13	100	1.18
TS-1#0.05ACh	467	136	0.10	0.13	141	1.50
TS-1#0.075ACh	435	135	0.08	0.12	147	1.69
TS-1#0.1ACh	474	135	0.07	0.14	155	1.73
TS-1#0.2ACh	50	25	0.12	0.01	42	1.72
TS-1#0.4ACh	186	84	0.23	0.04	-	1.84

sizes of the TS-1#0.05ACh, TS-1#0.075ACh and TS-1#0.1ACh samples are listed in Table 1. In contrast, as shown in Figs. 2(g) and 2(h), with the further increases in ACh content, TS-1#0.2ACh and TS-1#0.4ACh exhibited small crystal sizes of approximately 30 nm. Interestingly, the TS-1#0.1ACh sample exhibited crystals with a spherical layered morphology, which differed from the morphologies of the other samples (Figs. 2(d) and 2(e)). The crystal diameters of TS-1#0.1ACh were the largest and reached \sim 3 µm. The XRD data show that the TS-1#0.2ACh sample exhibited the MFI structure and low crystallinity due to insufficient crystallization; in particular, TS-1#0.4ACh did not show the MFI topology in the presence of excess ACh. TEM studies were also adopted to reveal the structures of the TS-1-s and TS-1#0.1ACh catalysts, and the results are shown in Fig. 3. The high resolution TEM images clearly confirmed that the grains of TS-1#0.1ACh were larger than those of TS-1-s, which is attributed to the ACh added during the process of TS-1#0.1ACh zeolite crystallization, which is consistent with the SEM results.

Figures 3(c) and 3(d) show lattice fringes of 0.35 with consistent single-crystalline features of the MFI zeolite. Additionally, the element distributions of the catalyst were analyzed by high angle angular dark field-scanning transmission electron microscopy (HAADF-STEM) and mapping. Figures 3(e–h) show that O, Si and Ti were uniformly dispersed in TS-1#0.1ACh.

The N₂-adsorption, UV-vis and XPS characterization analysis results of the sample are shown in Fig. 4. All of the samples presented typical microporous structures indicated by the type-I isotherms seen at partial pressures $(P/P_0 = 0.1-0.9)$ (Fig. 4(a)) [42]. The appearance of H3 hysteresis loops at $P/P_0 = 0.9-1.0$ indicated the presence of small amounts of particle-piled mesoporous structures in the small-sized samples, such as TS-1-s, TS-1#0.2ACh and TS-1#0.4ACh [43]. Nevertheless, the hysteresis loops of the large samples (TS-1#0.05ACh, TS-1#0.075ACh and TS-1#0.1ACh) did not appear, since the gaps between large particles were small and did not exhibit obvious intercrystalline adsorption. In addition, as shown in Fig. S2 (cf. ESM), the TS-1-s and TS-1#xACh samples



Fig. 2 SEM images of (a) TS-1-s, (b) TS-1#0.05ACh, (c) TS-1#0.075ACh, (d-f) TS-1#0.1ACh, (g) TS-1#0.2ACh and (h) TS-1#0.4ACh.



Fig. 3 TEM images of (a) TS-1-s, (b-d) TS-1#0.1ACh; (e) HAADF-STEM image of TS-1#0.1ACh, and (f-h) elemental maps for O, Si and Ti in TS-1#0.1ACh.



Fig. 4 (a) Nitrogen physisorption curves and (b) UV–vis spectra for TS-1-s and TS-1#xACh; XPS (c) Ti 2p spectra of TS-1#0.1ACh and (d) O 1s spectra of TS-1#0.1ACh.

had homologous pore size distribution curves with micropore sizes less than 2 nm.

The UV-vis spectra of the TS-1-s and TS-1#xACh samples are shown in Fig. 4(b), which indicate the Ti coordination. A distinct peak at approximately 210 nm was attributed to the framework Ti⁴⁺, which originated from $p\pi - p\pi$ charge transfer transitions between O²⁻ and isolated tetrahedral Ti species in the TS-1 zeolite framework [33]. For the TS-1#0.2ACh and TS-1#0.4ACh samples, the characteristic band at 260 nm indicated formation of Ti species with different coordination geometries, such as pentacoordinated and hexacoordinated [44]. Notably, for the TS-1#0.05ACh sample, another obvious absorption peak at approximately 330 nm was detected, which was attributed to extra-framework bulk TiO₂ [34,45]. However, generation of the extra-framework TiO₂ was avoided as much as possible with the TS-1 catalyst and was due to undesired decomposition of the H₂O₂ solution. Therefore, isolated framework Ti species were dominant in the TS-1-s, TS-1#0.075ACh and TS-1#0.1ACh samples, especially in TS-1#0.1ACh, and can be considered the catalytic active centers in these epoxidation reactions. The surface element electronic states of the TS-1#0.1ACh sample were further characterized with XPS measurements. As shown in Fig. 4(c), the Ti 2p XPS data contained two strong characteristic peaks at 460.0 and 464.8 eV, which were assigned to the binding

energies of the $2p_{3/2}$ and $2p_{1/2}$ states for Ti⁴⁺ species in the TS-1#0.1ACh sample, respectively [46]. Additionally, peaks at approximately 103.5 and 532.8 eV were observed in the Si 2p (Fig. S3, cf. ESM) and O 1s (Fig. 4(d)) spectra, respectively. The acid properties of the catalyst surface were also determined by NH₃-TPD, and the results are presented in Fig. S4 (cf. ESM). There were three desorption peaks located at approximately 160, 300 and 480 °C, and these corresponded to weak acid sites, medium acid sites and strong acid sites, respectively [28]. Clearly, the NH₂-TPD results showed that the amount of acid in the TS-1#0.1ACh sample, which contained weak acid and medium acid sites, was slightly higher than that of the TS-1-s sample, but neither sample showed obvious strong acid sites. Therefore, the TS-1#0.1ACh catalyst may promote more acid-catalyzed side reactions than the TS-1-s catalyst.

The textural parameters and the chemical compositions of all zeolites are summarized in Table 1. When the molar ratio of ACh/SiO₂ did not exceed 0.1, the S_{BET} and S_{Ext} of the TS-1#xACh samples decreased slightly from 494 to 474 m²·g⁻¹ with increasing ACh addition. However, the molar ratio was further increased to above 0.1, and the surface areas of both TS-1#0.2ACh and TS-1#0.4ACh rapidly decreased by 50 and 186 m²·g⁻¹, respectively. Significantly, TS-1#0.4ACh showed no MFI topology and an amorphous structure (see Fig. 1).

3.2 Possible synthetic mechanism for the TS-1#0.1ACh catalyst

To explore the growth process of the large TS-1#0.1ACh zeolite, samples were collected after different crystallization periods (4–18 h). As shown in Fig. 5, the XRD pattern for the solid sample from the initial crystallization stage (4 h) showed an amorphous structure. Instead, the typical MFI topology structure began to appear at a crystallization time of 8 h, and the crystallinity of the sample increased with time and reached maximum crystallinity at 13 h. Furthermore, the surface morphologies and structural variations of the samples at different crystallization times were also monitored by SEM. Figure 6 shows that amorphous solids were observed after crystallization for 4 h, while ellipsoidal crystals with sizes of approximately 1.2 µm appeared at 8 h (Figs. 6(a) and 6(b)). As the crystallization time was extended, the surfaces of perfect crystals with layered structures and



Fig. 5 XRD patterns for the TS-1#0.1ACh crystallized at 170 °C for different times.



Fig. 6 SEM images of TS-1#0.1ACh crystallized at 170 $^{\circ}$ C for different times: (a) 4 h, (b) 8 h, (c) 13 h, and (d) 18 h.

particle sizes of 3.0 µm were observed after 18 h (Fig. 6(d); these results were consistent with the XRD results. This may be attributed to the presence of a large amount of ACh modifier in the initial solid-phase mixed gel, which significantly accelerated the growth rate of the zeolite during the crystallization period. In addition, evolution of the surface groups on the TS-1#xAChsamples with different treatment methods, such as with or without washing after crystallization and with or without calcination after drying at 120 °C, was detected by FTIR spectroscopy. The characteristic adsorption bands seen at 1602 and 1382 cm⁻¹ in Fig. S5 (cf. ESM) were attributed to carboxylic acid groups (COO⁻) and were obvious in the TS-1#0.1ACh-unwashed, TS-1#0.1ACh-washed and TS-1#0.4ACh-unwashed samples, which was mainly due to formation of carboxylic acids from the ester groups in ACh via hydrolysis under the alkaline conditions [38]. The weaker characteristic bands at 3275 and 1479 cm⁻¹ were ascribed to C-H stretching vibrations and the quaternary ammonium groups (C₄N⁺) in ACh, respectively [47]. However, the adsorption bands at 1479 and 1382 cm⁻¹ were not observed for the TS-1-s and TS-1#0.1ACh-calcined catalysts because ACh adsorbed on the surface of samples was removed during the multiple washes and high-temperature calcination processes. Consequently, a moderate amount of the crystal growth modifier (such as carboxylic acid and ammonium groups) in the zeolite crystallization system can accelerate crystal growth and generate large TS-1#0.1ACh particles (see Fig. 6(d)). In contrast, excess modifier could cover grain surfaces and result in poor accessibility of the silicon/ titanium monomer, which would inhibit the growth of zeolite grains such as in the TS-1#0.4ACh sample (Fig. 2(h)). Therefore, it is understandable that the sizes of crystals in the TS-1#xACh samples decreased with reductions in the amount of ACh added up to 0.1 ($x \leq$ 0.1) (see Figs. 2(a-c)).

Based on the above characterization data and several literature reports [24,48], a possible mechanism for the synthesis of TS-1 zeolites with large particles sizes and high crystallinity was developed and is illustrated in Scheme 1. The main processes were as follows: first, small amorphous TS-1 nanoparticles were formed through agglomeration of the soluble silicon/titanium monomer or oligomers in the initial synthetic system; second, under structural control by the template, the TS-1 crystals rapidly assembled and grew by introducing the modifier to the soluble species in the steam-assisted crystallization system, assuming that ACh molecules coordinated with the monomeric Si/Ti and amorphous nanoparticles covered the faces of the TS-1 crystals by uniform adsorption; finally, crystal growth was considerably accelerated, especially during the early stages of zeolite crystallization; thus, the large TS-1 zeolites with good framework Ti were formed successfully.



Scheme 1 Proposed synthetic process for large TS-1 zeolites via introduction of an acetylcholine modifier into the steam-assisted crystallization system.

3.3 Catalyst evaluation

To estimate the catalytic activities of the catalyst samples, ACH epoxidation was employed as a probe reaction. As shown in Fig. 7, TS-1-s displayed ACH conversion and epichlorohydrin (ECH) selectivity of 71.98% and 87.48%, respectively. In contrast, TS-1#0.05ACh, TS-1#0.075ACh and TS-1#0.1ACh exhibited better catalytic activities, in which TS-1#0.1ACh showed more favourable activity with increased ACH conversion of 92.3% and ECH selectivity of 86.07%. By comparison with the TS-1-s sample, therefore, TS-1#xACh (x < 0.1) showed a clear advantage in catalytic activity, which was attributed to the highly tetrahedral Ti frameworks (see Fig. 4(b)) and high crystallinities (see Table 1). Moreover, TS-1#0.2ACh showed weak catalytic activity in ACH epoxidation with an ACH conversion of 30.13% and ECH selectivity of 81.12%. This may be because TS-1#0.2ACh had a low specific surface area and poor crystallinity (Table 1), although it exhibited a typical MFI topology. In particular, TS-1#0.4ACh exhibited no catalytic activity for epoxidation of ACH owing to the lack of an MFI structure. In addition, the H₂O₂ conversion was directly proportional to the ACH conversion. The H₂O₂ conversion of TS-1#0.075ACh (62.47%) was slightly higher than that of TS-1#0.1ACh (61.98%) because undesired decomposition of H2O2 was caused by a small amount of extra-framework TiO₂ in TS-1#0.075ACh (see Fig. 4(b) [34]. According to a literature report [33], TS-1-based zeolite had almost no obvious acidity, which was consistent with the NH₃-TPD results for the TS-1#xACh catalysts (see Fig. S4). Thus, the acidcatalysed side reactions and formation of byproducts was avoided during epoxidation of ACH. As expected, all catalysts except the TS-1#0.4ACh catalyst showed similar ECH selectivities of approximately 85%. In summary, the optimal TS-1#0.1ACh catalyst was selected and used in the following reactions for additional performance investigation. Our previous work [9] showed that the conversion rates of ACH were 82.3% and 99.3% in epoxidation reactions catalyzed by the traditional TS-1 and TS-1 treated with TPAOH, respectively. In this work, the conversion rate for propene chloride reached 92.3% in the epoxidation reaction catalyzed by TS-1#0.1ACh, and TS-1#0.1ACh did not need further treatment.



Fig. 7 ACH conversion, H_2O_2 conversion and ECH selectivity of TS-1-s and TS-1#xACh catalysts (reaction conditions: C=C:H₂O₂ = 2:3 (molar ratio), 3.4 g of H₂O₂, 0.1 g of catalyst, 20 mL of methanol, 60 °C, 4 h).

3.4 Catalyst reusability and regeneration

Reusability and regeneration of solid catalysts is crucial for heterogeneous catalytic systems used in industrial applications. To develop a high-efficiency TS-1-based zeolite for epoxidation reactions, the stability and regeneration of the TS-1#0.1ACh catalyst after epoxidation of ACH were studied carefully (in Fig. 8). The used catalyst was separated from the liquid mixture by centrifugal and drying methods, simply washed with solvent and then used in the next process. As shown in Fig. 8, the ACH and H₂O₂ conversion of the fresh TS-1#0.1ACh catalyst were 92.30% and 61.98%, respectively, and the ECH selectivity was 86.07%. Nevertheless, the activity of the catalyst decreased slightly after it was recycled twice, while the ACH conversion decreased to 78.96%, and the selectivity for ECH increased slightly. This is largely explained by the fact that a small amount of product was adsorbed on the inner surfaces of the catalyst, blocked the pores during epoxidation and could not be removed completely by simple washing [34,49]. At the same time, the acidity of the catalyst surface was reduced (Si-OH sites on the inner and outer surfaces of the catalyst were covered), which inhibited side reactions and increased the

content of ECH produced [50,51]. Compared with the fresh TS-1#0.1ACh catalyst, the ACH conversion dropped by approximately 20% for the fifth recovery of the catalyst, and the stability of the catalyst was considered acceptable for practical application. Furthermore, to investigate the possibility of reusing the solid catalyst for the epoxidation reaction, regeneration of the TS-1#0.1ACh catalyst was also studied. The spent TS-1#0.1ACh catalyst was processed by calcination at 550 °C for 5 h. The catalytic activity of the regenerated TS-1#0.1ACh catalyst was recovered and was close to that of the fresh TS-1#0.1ACh catalyst, and the ACH conversion and ECH selectivity were completely recovered to 93.08% and 87.50%, respectively. These results showed that the spent catalyst was regenerated and recycled efficiently so as to save production costs, which will lay a great foundation for industrial application of the TS-1-based catalyst.

3.5 Range of substrates

The scope of the epoxidation catalyzed by the TS-1-based



Fig. 8 Recycling and regeneration of TS-1#0.1ACh in ACH epoxidation (reaction conditions: $C=C:H_2O_2 = 2:3$ (molar ratio), 3.4 g of H_2O_2 , 0.1 g of catalyst, 20 mL of methanol, 60 °C, 4 h).

catalyst was examined. Epoxidations of different alkenes and methyl oleate with clean H₂O₂ as the oxidant and TS-1#0.1ACh as the catalyst were evaluated under the same conditions, and the results are listed in Table 2. Under the present reaction conditions (0.1 g of TS-1#0.1ACh, $n_{\text{substrate}}$: $n_{\text{H}_2\text{O}_2}$ = 2:3, 20 mL of acetonitrile, 70 °C, 4 h), the substrates, including C3-C10 alkenes and methyl oleate, were transformed into the corresponding epoxides, and the amounts of byproducts produced by hydrolysis were ignored. Although substrate conversion decreased with increasing alkene carbon chain length, the selectivity for the epoxide product remained nearly constant. The relative conversions for the various alkenes decreased in the order ACH > 1-hexene > 1-octene \approx 1-decene > 1-tetradecene > methyl oleate. This could be because the active Ti-OOH species generated via reaction of TS-1#0.1ACh with H_2O_2 was embedded in the catalyst; thus, the C=C double bond had difficulty approaching the active site owing to steric hindrance [52], and the steric hindrance between the active site of the catalyst and the long chain alkenes was higher in the reaction system. For example, ACH conversion over the TS-1#0.1ACh catalyst exhibited the highest value and reached 92.30% owing to utilization of the inner and outer surfaces of the catalyst for ACH epoxidation. Instead, the conversions for macromolecules (such as 1-tetradecene and methyl oleate) were less than 6%, indicating that severe diffusion and mass transfer resistance appeared for the microporous TS-1#0.1ACh and limited the epoxidation process to the outer surfaces of the catalyst only. In addition, the selectivity to target products is obtained by epoxidation of some substrates with H₂O₂. The selectivities for all alkenes were more than 86%, but the selectivity for epoxidation of methyl oleate (EMO) was lower than the others, which may be because the EMO-containing ester groups were prone to hydrolysis reactions in the reaction system containing water, which generated the corresponding byproducts [53].

 Table 2
 Epoxidation of various monoalkenes and methyl oleate catalyzed by TS-1#0.1ACh

	$C = C + H_2O_2$	$\frac{\text{TS-1#0.1ACh}}{\text{Solvent, 60-70 °C}} \xrightarrow{O}_{C-C} + \text{H}_2\text{C}$)	
Entry	Substrate	Product	Conversion/%	Selectivity/%
1 ^{a)}	✓ ^{CI}	CI	92.30	86.07
2	~~~	°~~~	37.59	98.12
3	~~~~	0	19.94	95.56
4	~~~~~	0	20.86	93.37
5	~~~~~~	0	5.48	90.05
6			3.15	69.64

Reaction conditions: $C=C:H_2O_2 = 2:3$ (molar ratio, 3.4 g of H_2O_2), 0.1 g of catalyst, 20 mL of acetonitrile, 70 °C, 4 h; a) reaction conditions: $C=C:H_2O_2 = 2:3$ (molar ratio, 3.4 g of H_2O_2), 0.1 g of catalyst, 20 mL of methanol, 60 °C, 4 h.

4 Conclusions

In summary, we have developed a facile strategy for synthesis of the TS-1 zeolite with controlled particle sizes, good framework Ti and high crystallinity. This novel TS-1 was prepared via introduction of the modifier ACh into the synthetic process using steam-assisted crystallization. The structural characterization results showed that the particle sizes of TS-1#xACh increased gradually with increasing ACh amount up to 0.1 but decreased significantly with excessive ACh, which was attributed to accelerated crystallization of the ACh modifier. Notably, TS-1#0.1ACh presented optimal particle sizes of 3 µm, and XRD and UV-vis data revealed that it exhibited high crystallinity and tetrahedrally coordinated framework Ti. More excitingly, TS-1#0.1ACh showed the highest catalytic activity (conversion of 92.3% and selectivity of 86.07%) for epoxidation of ACH. Moreover, the TS-1#0.1ACh catalyst was proven to be very stable and easily regenerated via calcination at high temperature. Importantly, it also showed excellent range for epoxidations of various monoalkenes. This work provides a valuable approach for synthesizing TS-1 with controlled particles sizes and good framework Ti, high crystallinity, and good catalytic activity, which could expand the range of catalytic applications in industry.

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