# Controlling the Morphology and Titanium Coordination States of TS-1 Zeolites by Crystal Growth Modifier

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and elongated platelet TS-1 crystals enriched in tetrahedral framework Ti sites (TiO<sub>4</sub>) or mononuclear octahedrally coordinated Ti species (TiO<sub>6</sub>). Both samples showed significant improvement in catalytic activity for the  $H_2O_2$ -mediated epoxidation of alkenes. In particular, the elongated platelet TS-1 enriched in "TiO<sub>6</sub>" species afforded the highest activity in 1-hexene epoxidation, with a turnover frequency (TOF) of up to 131 h<sup>-1</sup>, which is approximately twice as high as that of the conventional TS-1 zeolite (TOF: 65 h<sup>-1</sup>) and even higher than those of the literature-reported TiO<sub>6</sub>-containting TS-1 catalysts derived from the hydrothermal post-treatment of TS-1 zeolites. This work demonstrates that the morphologies and the titanium coordination states of TS-1 zeolites can be effectively tuned by directly introducing suitable crystal growth modifiers, thus providing new opportunities for developing highly efficient titanosilicate zeolite catalysts for important catalytic applications.

## INTRODUCTION

Zeolites have been extensively used as efficient heterogeneous catalysts in the petrochemical and fine chemical industries owning to their unique features, such as uniform micropores, tunable acidities and redox properties, and high thermal and hydrothermal stability.<sup>1</sup> Modulation of the morphologies and active sites of zeolites plays a key role in enhancing their catalytic properties.<sup>2-5</sup> Diverse strategies have been implemented to alter the morphology and microstructure of zeolites, such as adjusting synthesis conditions, adding seeds, introducing additives, employing microwave irradiation, and adopting various post-treatment methods.<sup>6–15</sup> One of the most effective methods for zeolite crystal engineering is the introduction of crystal growth modifiers, a special type of additives in the zeolite synthetic system. Growth modifiers commonly refer to the molecules that can interact with the specific facets of zeolite crystals or associate with amorphous precursors to regulate nucleation and growth kinetics, thus altering the crystal size and morphology.<sup>16,17</sup> So far, some macromolecules like polymers, proteins, and peptides and small organic molecules like lactams and amino acids have

could afford the generation of perfect hexagonal plate TS-1 crystals

been utilized as crystal growth modifiers, which can effectively afford the morphology control of zeolite crystals.<sup>18–23</sup>

Several easily available and inexpensive amino acids and their derivatives such as lysine, L-carnitine, and arginine have shown great advantages in modifying the morphology and microstructure of zeolite crystals like NaA (LTA), Y (FAU), and ZSM-5 (MFI).<sup>24–30</sup> For instance, Hong's group reported that introducing lysine, L-carnitine, or their salt derivatives could generate disordered mesopores within single-crystalline LTA zeolites; the resultant zeolites exhibited improved adsorption capacity for catalase enzyme.<sup>25</sup> In 2017, the successful synthesis of a core—shell zeolite Y containing an ant-nest-like hollow interior was achieved by the same group through introducing L-carnitine; the obtained zeolite exhibited

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Table 1. Compositions and Texture	l Parameters of Various TS-1 Zeolites
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sample	Si/Ti <sup>a</sup>	$S_{\rm BET} (m^2/g)^b$	$S_{\rm micro} ({\rm m}^2/{\rm g})^c$	$S_{\rm ext} ({\rm m}^2/{\rm g})^c$	$V_{\rm micro}  ({\rm cm}^3/{\rm g})^c$	$V_{\rm meso}  ({\rm cm}^3/{\rm g})^d$	RC % <sup>e</sup>
TS-1#con	34.3	410	275	135	0.13	0.09	100
TS-1#A_15Et:0.4LC	35.2	384	272	111	0.12	0.10	97
TS-1#B_15Et:0.6LC	38.3	349	265	84	0.12	0.12	97
TS-1#C_0Et:0.6LC	41.1	387	286	100	0.13	0.06	73
		1.					

<sup>*a*</sup>Measured by inductively coupled plasma (ICP). <sup>*b*</sup>S<sub>BET</sub> (total surface area) calculated using the BET method. <sup>*c*</sup>S<sub>micro</sub> (micropore area), S<sub>ext</sub> (external surface area), and  $V_{micro}$  (micropore volume) calculated using the *t*-plot method. <sup>*d*</sup>V<sub>meso</sub> (mesopore volume) calculated using the BJH method (from adsorption). <sup>*e*</sup>RC: Relative crystallinity is calculated through comparing the total intensity of the three characteristic peaks of the samples.

enhanced catalytic activity for the Friedel–Crafts reaction.<sup>27</sup> In 2019, Qin et al. reported that the crystal morphology of silicalite-1 (**MFI**) could be tuned in a certain range by using arginine as the growth modifier.<sup>28</sup> The authors found that the introduced arginine could induce a reduction in the crystal size through impeding the nanoparticle addition. Our recent work also suggested that L-lysine could be used as a crystal growth modifier to generate nanosized zeolite single crystals or defect-free hierarchical ZSM-5 nanocrystals through kinetic-modulated crystallization.<sup>29</sup> These results have demonstrated that amino acids may act as effective crystal growth modifiers in zeolite synthesis owing to their proximal binding moieties (i.e., amino and carboxyl groups) that can strongly interact with the amorphous precursors or the specific crystal surface of zeolites.

As one of the most important heteroatom-containing zeolite catalysts, titanosilicate zeolite TS-1 (MFI) has been widely applied in the green synthesis of some nitrogen- and oxygencontaining organic intermediates with  $H_2O_2$  as the oxidant.<sup>31-33</sup> To enhance the catalytic properties of the TS-1 zeolites, great efforts have been devoted to modulating the morphology and crystal size, generating hierarchical pores, and adjusting the coordination states of Ti species.<sup>34-39</sup> For instance, Xiao and coworkers reported that TS-1 crystals with sheet-like morphology could be synthesized by the addition of urea to the starting gels; the resultant zeolites showed very high catalytic activity in the Beckmann rearrangement of cyclohexanone oxime.<sup>34</sup> They proposed that the sheet-like TS-1 crystals with a short *b*-axis length (along the straight channels of the MFI network) are more favorable for the diffusion and conversion of cyclohexanone oxime. It was believed that the generation of highly active Ti species is the most important factor for improving the catalytic performance of TS-1. Ideally, one perfect TS-1 zeolite crystal should have the isolated tetrahedral framework Ti species (TiO<sub>4</sub>) as much as possible and, meanwhile, avoid the formation of extra-framework Ti species, such as oligomeric six-coordinated Ti species or the anatase phase.<sup>40</sup> Notably, several recent literature works revealed that the mononuclear six-coordinated Ti species  $(TiO_6)$ , obtained by hydrothermally post-treating conventional TS-1 with basic agents like tetrapropyl ammonium hydroxide/ NaOH solutions, possessed very high catalytic oxidation activity, in some cases, even higher than that of the framework "TiO<sub>4</sub>" species.<sup>41-43</sup> In fact, such a hydrothermal posttreatment method has been widely used to adjust the morphology, porosity, and coordination states of Ti species of the TS-1 zeolites to improve their catalytic activity and selectivity.<sup>11,41</sup> However, the basic solution etching process results in a considerable weight loss of the parent zeolite crystals and, in some cases, may also form some undesirable defect sites, thus decreasing the structure stability and catalytic activity of the TS-1 zeolites.<sup>42</sup> Therefore, it remains a

significant subject to develop a more simple and effective strategy for the synthesis of TS-1 zeolites with preferential crystal morphology and abundant mononuclear  $TiO_6$  species.

Very recently, our group developed an effective method for the one-step fast synthesis of zeolites TS-1 with highly active Ti species through seed-assisted microwave irradiation.<sup>44</sup> The addition of active seeds coupled to microwave irradiation can produce plenty of highly coordinated Ti precursors that play an important role in creating more active "TiO<sub>6</sub>" species (besides "TiO<sub>4</sub>" species) in the zeolite framework. The resultant TS-1 zeolites showed enhanced catalytic activity for 1-hexene epoxidation, confirming the higher activity of "TiO<sub>6</sub>" species than that of "TiO<sub>4</sub>" species. This progress suggests that highly active "TiO<sub>6</sub>" species may be directly created in the zeolite framework of TS-1 zeolites by optimizing the hydrothermal synthesis method and conditions.

In this work, taking advantage of the unique features of Lcarnitine such as the high structure stability, solubility, and diverse functional moieties (i.e., ammonio, carboxyl, and hydroxyl groups), we utilized L-carnitine as a crystal growth modifier to control the synthesis of TS-1 zeolites with desirable morphologies and Ti coordination states. By altering the amounts of L-carnitine and ethanol (cosolvent with water), a series of TS-1 crystals with different morphologies and titanium coordination states were hydrothermally synthesized. Significantly, elongated platelet TS-1 crystals with a high aspect ratio were obtained through optimizing the synthesis parameter, which contains abundant mononuclear "TiO<sub>6</sub>" species. The resultant TS-1 zeolites were characterized by combining a variety of characterization means, including powder X-ray diffraction (XRD), N<sub>2</sub> adsorption/desorption measurements, scanning electron microscopy (SEM), UVvisible diffuse reflectance spectroscopy (UV-vis), UV Raman spectroscopy, and X-ray absorption spectroscopy (XAS). As expected, the elongated platelet TS-1 crystals enriched in "TiO<sub>6</sub>" species showed superior catalytic activity and stability for the epoxidation of alkenes with  $H_2O_2$  as the oxidant.

#### EXPERIMENTAL SECTION

**Chemicals and Materials.** Tetraethylorthosilicate (TEOS), ethanol (Et), and methanol were purchased from Beijing Chemical Works. L-Carnitine (LC: 3-hydroxy-4-(trimethylammonio)butanoate) was purchased from Tokyo Chemical Industry in Shanghai. Tetrabutyltitanate (TBOT) and tetrapropylammonium hydroxide (25 wt %) were purchased from Sinopharm. Allyl chloride (98%), 1-hexene (98%), 1-heptene (98%), cyclopentene (96%), and 1-octene (98%) were purchased from Aladdin. All reagents were of analytical grade and used as received.

**Synthesis of TS-1 Zeolites with L-Carnitine as the Modifier.** TS-1 zeolites were hydrothermally synthesized from the starting gels with the optimized molar composition of SiO<sub>2</sub>:0.033TiO<sub>2</sub>:0.3TPAOH:124H<sub>2</sub>O:xC<sub>2</sub>H<sub>5</sub>OH:yLC. (x and y rep-

resent ethanol/SiO<sub>2</sub> and LC/SiO<sub>2</sub> ratios in the synthesis gel, respectively; x refers to the initially introduced ethanol without considering that part of ethanol generated by the hydrolysis of TEOS.) Typically, TPAOH (25 wt %) and deionized water were first mixed completely (solution A), while certain amounts of TEOS and TBOT were dissolved in the ethanol to form solution B. Solution B was added dropwise to the solution A under stirring. After that, a certain amount of LC was dropped into the solution under stirring. After 3 h, the initial gel was transferred to a Teflon-lined stainless-steel autoclave and crystallized in a conventional oven at 180 °C for 48 h. The as-synthesized TS-1 zeolites were centrifuged and fully washed with water and ethanol and dried overnight at 80 °C in an oven. After calcination at 550 °C for 8 h, the resulting products were obtained, which are denoted as TS-1#A\_15Et:0.4LC, TS-1#B\_15Et:0.6LC, and TS-1#C 0Et:0.6LC, as shown in Table 1. Besides, two other samples with Si/Ti ratios of 74 and 58, named TS-1#B-58 15Et:0.6LC and TS-1#B-74 15Et:0.6LC, respectively, were also synthesized by using the same conditions as those of TS-1#B 15Et:0.6LC (Si/Ti = 33) for the purpose of making the comparison of the catalytic properties with the related literature.

The conventional TS-1 zeolite (TS-1#con) was synthesized according to a literature preparation procedure.<sup>37</sup> The molar composition of the initial gel was as follows:  $SiO_2:0.033TiO_2:0.3TPAOH:124H_2O$ , and the synthesis condition was similar to that of the previously mentioned TS-1 zeolites, just without the addition of ethanol and L-carnitine.

Characterization. Powder XRD patterns were recorded on a Shimadzu XRD-6000 diffractometer (40 kV, 30 mA), using Ni-filtered Cu K $\alpha$  radiation to characterize the crystallinity and phase purity of the as-synthesized TS-1 zeolites. SEM was used to characterize the crystal size and morphology of TS-1 zeolites by using a JSM-6700F (JEOL) electron microscope. Nitrogen adsorption-desorption measurements were carried out on a Micromeritics 2020 analyzer at 77 K. Prior to the analysis,  $\sim$ 50 mg samples were degassed at 350 °C under vacuum overnight. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet AVATAR 370 DTGS spectrometer in the 4000-500 cm<sup>-1</sup> range. X-ray absorption near-edge structure (XANES) spectra at the Ti K-edge were performed using the Sector 20-BM beamline of the Advanced Photon Source at Argonne National Laboratory (Argonne, IL). The beamline was equipped with a doublecrystal Si(111) monochromator. A 12-element Ge fluorescence detector was used to collect the spectra of the Ti K-edge. The energy was calibrated according to the absorption edge of a pure Ti foil as a reference. The acquired data were processed according to standard procedures using the ATHENA module. The UV-vis spectra were recorded on a Shimadzu UV-2400PC spectrophotometer using a BaSO<sub>4</sub> plate as a reference. Inductively coupled plasma/optical emission spectroscopy (ICP/OES) was used to detect the chemical compositions of samples on a PerkinElmer Optima 3300 DV ICP instrument. UV Raman spectra with an excitation line at 260 nm were recorded on a UV Raman spectrograph using a Jobin-Yvon T6400 triple-stage spectrograph with a spectral resolution of  $2 \text{ cm}^{-1}$ . The line at 260 nm was from the double-frequency of a DPSS 532 model 200 apparatus. The power of the 260 nm line of the samples was <1.0 mW.

**Catalytic Epoxidation of Alkenes with H<sub>2</sub>O<sub>2</sub> as the Oxidant.** The catalytic epoxidation of alkenes was carried out in a 25 mL round-bottomed flask equipped with a reflux condenser. The whole device was immersed in a thermostated oil bath at the previously designed temperature under vigorous stirring. Typically, 50 mg of catalyst, alkene (10 mmol), and CH<sub>3</sub>OH (10 mL) were added to the round-bottomed flask. The catalytic reaction was initiated by adding 10 mmol H<sub>2</sub>O<sub>2</sub> to the mixture at 60 °C. The quantitative analyses of the reagents and products were carried out by a GC-9790II gas chromatograph with an HP-5 capillary column. The conversion of alkenes and the selectivity of products were calculated on a C-atom basis, and carbon balances were within 100  $\pm$  5% in all tests.

#### RESULTS AND DISCUSSION

Three representative TS-1 zeolites, TS-1#A\_15Et:0.4LC, TS-1#B\_15Et:0.6LC, and TS-1#C\_0Et:0.6LC, were hydrothermally synthesized by using TPAOH as the microporous template and L-carnitine as the crystal growth modifier in the presence/absence of a certain amount of ethanol. The XRD patterns of the resultant TS-1 zeolites exhibit the characteristic peaks of the MFI structure at  $2\theta$  of 7.8, 8.8, 23.0, 23.9, and 24.4°, confirming the phase purity of the samples (Figure 1).



Figure 1. XRD patterns of various TS-1 samples and the simulated pattern of MFI zeolite.

Compared with the samples of TS-1#con and TS-1#A\_15Et:0.4LC, the relative intensity of the [020] reflection  $(8.8^{\circ})$  of TS-1#B\_15Et:0.6LC and TS-1#C\_0Et:0.6LC becomes stronger, indicating the presence of a preferential *ac* plane in the crystals.<sup>45,46</sup> As shown in Table 1, TS-1#A\_15Et:0.4LC and TS-1#B\_15Et:0.6LC have a relative crystallinity (RC) of 97%, quite near that of the conventional TS-1#Con (100%), whereas TS-1#C\_0Et:0.6LC shows a relatively low RC of 73%. These results suggest that introducing a suitable amount of L-carnitine and ethanol may retain the high crystallinity for TS-1 zeolites.

Figure 2 displays the SEM images of various TS-1 zeolites. TS-1#con shows regular hexagonal prism morphology with an average size of 0.7  $\mu$ m and a uniform thickness of ~0.5  $\mu$ m (Figure 2a). When a certain amount of LC or ethanol is introduced into the sol-gel system, the thickness of the TS-1 crystals (along the b axis) obviously decreases to ~0.3  $\mu$ m (Figure 2b-d). TS-1#A 15Et:0.4LC and TS-1#C 0Et:0.6LC crystals show hexagonal plate-like morphology with a size of about 0.8 and 0.9  $\mu$ m, respectively (Figure 2b,d). A significant difference could be observed for TS-1#B 15Et:0.6LC, which exhibits an interesting crystal shape of elongated platelet morphology with well-developed ac planes and a short dimension along the b axis (Figure 2c). The crystals of TS-1#B 15Et:0.6LC are uniform in the size of about  $0.9 \times 0.3 \times$ 3.0  $\mu$ m ( $a \times b \times c$ ); significantly, it has an average c/b aspect ratio of 10, which is one of the largest aspect ratios among the reported values for TS-1 crystals.<sup>46</sup> As is known, there are two channel systems in MFI-type zeolite: a straight 10-membered ring channel (0.53\*0.56 nm) parallel to the *b* axis, and a sinusoidal channel (0.51\*0.55 nm) parallel to the *a* axis. It is



**Figure 2.** SEM images of (a) TS-1#con, (b) TS-1#A\_15Et:0.4LC, (c) TS-1#B\_15Et:0.6LC, and (d) TS-1#C\_0Et:0.6LC.

highly desirable to synthesize **MFI** zeolites with a very short *b* axis, which could provide a short path along the straight 10membered ring channels for mass transfer, thus being beneficial for increasing the diffusional flux of sorbate molecules during a catalytic reaction process.<sup>34</sup>

The  $N_2$  adsorption/desorption isotherms of the TS-1 samples are given in Figure 3. All of the samples display the



Figure 3.  $N_2$  adsorption/desorption isotherms of TS-1#con, TS-1#A\_15Et:0.4LC, TS-1#B\_15Et:0.6LC, and TS-1#C\_0Et:0.6LC.

type-I isotherms in the partial pressure range of 0.1 to 0.9 ( $P/P_0$ ), indicating the microporous characteristics of these zeolites. The appearance of a weak uptake in the 0.9 to 1.0 range should be a hint of a small number of meso- or macropores present in the samples, which usually originate from the particle-piled pores. The textural parameters of various TS-1 zeolites are summarized in Table 1.

The FT-IR spectra of various TS-1 samples are shown in Figure 4. The weak absorption band at 965 cm<sup>-1</sup> is commonly attributed to the stretching vibration of Si–O–Ti or Si–O perturbed by a Ti atom in the framework of TS-1.<sup>37</sup> The bands at 1225 and 550 cm<sup>-1</sup> are ascribed to the asymmetric stretching and double-ring tetrahedral vibration of SiO<sub>4</sub> and TiO<sub>4</sub> tetrahedrals, respectively.<sup>47</sup>



Figure 4. FT-IR spectra of TS-1#con, TS-1#A\_15Et:0.4LC, TS-1#B\_15Et:0.6LC, and TS-1#C\_0Et:0.6LC.

UV-vis DRS spectra of various TS-1 zeolites are shown in Figure 5. All of the samples display a strong absorption peak at



Figure 5. UV-vis DRS spectra of TS-1#con, TS-1#A\_15Et:0.4LC, TS-1#B\_15Et:0.6LC, and TS-1#C\_0Et:0.6LC.

~207 nm, which is attributed to the isolated tetrahedral framework Ti species (TiO<sub>4</sub>), originating from the charge transfer of the  $p\pi$ – $p\pi$  transitions between O<sup>2–</sup> and Ti<sup>4+</sup> in the framework of TS-1 zeolites.<sup>42,43</sup> An obvious absorption peak at ~330 nm can be observed in the TS-1#con and TS-1#C\_0Et:0.6LC, which could be related to the formation of extra-framework bulk TiO<sub>2</sub>. For TS-1#A\_15Et:0.4LC, no obvious absorption peak could be detected at 330 nm or other positions, suggesting that the isolated TiO<sub>4</sub> species are dominant in this material. Notably, for the sample of TS-1#B\_15Et:0.6LC, another wide and strong absorption band center at ~270 nm could be detected. The assignment of the electronic transition in this region is quite complicated because it might be related to different kinds of Ti species, like pentacoordinated and hexacoordinated Ti species either in isolated form or in oligomeric form.<sup>48</sup>

UV-Raman resonance spectroscopy with an excitation line at 260 nm was used to get further insights into the coordinative states of Ti species in the TS-1 zeolites. As shown in Figure 6, the typical bands at 380 and 800 cm<sup>-1</sup> detected in the four samples are the characteristic signals of siliceous zeolites (like silicalite-1) with a MFI structure.<sup>49</sup> For the samples of TS-1#con, TS-1#A 15Et:0.4LC, and TS-1#C 0Et:0.6LC, the



**Figure 6.** UV-Raman spectra of various TS-1 samples excited at 260 nm: (a) TS-1#con, (b) TS-1#A\_15Et:0.4LC, (c) TS-1#B\_15Et:0.6LC, and (d) TS-1#C\_0Et:0.6LC.

bands at 490, 530, 956, and 1125  $\text{cm}^{-1}$  in the spectra could be attributed to the asymmetric stretching and symmetric stretching vibration of the framework TiO4 and Ti-O-Si species.<sup>4</sup> These four bands are very weak for TS-1#B 15Et:0.6LC, suggesting that the content of TiO<sub>4</sub> species in this sample should be quite low. Notably, an obvious band at 695 cm<sup>-1</sup> could be observed in the samples TS-1#B\_15Et:0.6LC and TS-1#C\_0Et:0.6LC. This signal has recently been recognized as the characteristic of a mononuclear hexacoordinated Ti species  $(TiO_6)$ , which is partially coordinated with hydroxyl groups and H<sub>2</sub>O, shown as  $Ti(OSi)_2(OH)_2(H_2O)_2$ .<sup>40</sup> Observably, the Raman band at 695 cm<sup>-1</sup> is the dominating signal in the spectrum of TS-1#B 15Et:0.6LC; it could be directly associated with the Ti species that feature a strong adsorption band at  $\sim$ 270 nm in the UV-vis spectrum. These results suggest that such special mononuclear TiO<sub>6</sub> species are prominent in the sample of TS-1#B 15Et:0.6LC. It should be pointed out that TS-1#C 0Et:0.6LC did not give an obvious peak at 270 nm (UV-vis spectrum), although it gave a clear UV-Raman band of 695 cm<sup>-1</sup>. This might be an indication that the content of the TiO<sub>6</sub> species in this sample is not very high, whereas the appearance of a relatively strong band of 695 cm<sup>-1</sup> should be assigned to the resonance effect that can selectively enhance the Raman band associated with framework titanium atoms.<sup>49</sup>

To further investigate the nature of the Ti species, X-ray adsorption spectroscopy measurements were performed, and the normalized Ti K-edge XANES spectra of various TS-1 zeolites are shown in Figure 7, together with Ti foil and anatase TiO<sub>2</sub> for references. All TS-1 zeolites exhibit a sharp pre-edge peak at ~4968 eV caused by the  $1s \rightarrow 3pd$  electronic transition of Ti.48,50 It was proposed that the pre-edge peak intensity strongly depends on the symmetry around the Ti species. Compared with the tetrahedrally coordinated Ti(IV) species, the octahedrally coordinated Ti(IV) species are characterized by a much lower intensity due to the small p-d hybridization that occurs in octahedral symmetry. In the present case, TS-1#A 15Et:0.4LC shows the strongest pre-edge peak, reflecting the highest content of TiO<sub>4</sub> species. The lowest peak intensity of TS-1#B\_15Et:0.6LC suggests that the content of TiO<sub>4</sub> is rather low, implying that the six-coordinated Ti species should be dominant in this sample. The fact that no obvious spectral



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Figure 7. Normalized Ti K-edge XANES spectra for various TS-1 samples.

components are ascribable to the fraction of other Ti species (e.g., bulk TiO<sub>2</sub> and polymeric TiO<sub>x</sub> species) suggests that mononuclear hexacoordinated TiO<sub>6</sub> species should be prevalent in TS-1#B\_15Et:0.6LC. Moreover, the Fourier-transformed extended X-ray absorption fine-structure spectrum (FT-EXAFS) of TS-1#B\_15Et:0.6LC shows only a major signal of the Ti–O bond, whereas the signals of the Ti–O–Ti bond are nearly negligible (Figure S1). These results provide clear evidence that the dominating Ti species in TS-1#B\_15Et:0.4LC and TS-1#B\_15Et:0.6LC are isolated TiO<sub>4</sub> and mononuclear TiO<sub>6</sub> species, respectively.

The above results demonstrate that TS-1 crystals with different morphologies and titanium coordination states could be directly hydrothermally synthesized by introducing Lcarnitine as a crystal growth modifier and ethanol as a cosolvent. The amount of L-carnitine and ethanol in the synthetic gel greatly affects the crystal growth and the Ti insertion into the MFI framework. In the case without the addition of ethanol, the introduced L-carnitine may also influence the morphology and the Ti coordination states of the zeolites to a certain extent to generate hexagonal plate-like TS-1 crystals containing both TiO<sub>4</sub> and TiO<sub>6</sub> species (TS-1#C\_0Et:0.6LC), whereas without L-carnitine, the addition of a certain amount of ethanol does not have an obvious effect on the morphology and the crystal size of the TS-1 zeolites in comparison with the conventional TS-1#con (Figure S2). It should be mentioned that even without additional EtOH, a certain amount of EtOH and BuOH could also be formed by the hydrolysis of TEOS and TBOT during the hydrothermal synthesis process, which may also influence the crystallization process and the morphology of the resultant TS-1 zeolites to a certain extent. In general, the insertion rate of Ti into the zeolite framework must match well with the formation rate of the zeolite to generate isolated TiO<sub>4</sub> species and inhibit the formation of an unfavorable anatase phase.<sup>39</sup> Our results further demonstrate that the generation of a mononuclear TiO<sub>6</sub> species could also be effectively achieved by introducing a growth modifier of L-carnitine and a cosolvent of ethanol. Notice that controlling the ratio of ethanol and L-carnitine (e.g., 15Et:0.6LC) is a critical factor for affording the formation of the elongated platelet morphology and the generation of abundant TiO<sub>6</sub> species.

To gain insight into the growth process of the elongated platelet TS-1#B\_15Et:0.6LC zeolite, time-resolved samples were collected at different crystallization stages (6-48 h). The XRD patterns of the extracted solids from the early crystallization stage (6 and 12 h) exhibit amorphous features (Figure 8). Obvious diffraction peaks characteristic of the MFI



Figure 8. XRD patterns of TS-1#B\_15Et:0.6LC samples with different crystallization times.

structure start to appear in samples crystallized after 24 h, with a gradual increase in intensity with time. As seen from SEM images, extracted solids with a rough surface are observed after crystallization for 12 h, whereas a large number of sheet-like crystals covered with abundant small nanoparticles appear at 24 h (Figure 9a,b). With further increasing the crystallization



Figure 9. SEM images of TS-1#B\_15Et:0.6LC samples at different crystallization stages of (a) 12, (b) 24, (c) 30, and (d) 48 h.

time, the surface-deposited nanoparticles gradually disappear, and perfect crystals with a smooth surface and a uniform elongated platelet shape are observed after 48 h (Figure 9c,d). These results clearly reveal that amorphous nanoparticle precursors rapidly form in the initial growth stage; then, these metastable species can act as Si and Ti sources for TS-1 crystal growth through a dissolution–recrystallization process.<sup>19</sup> Notably, the coordination states of the Ti species remain constant throughout the synthesis period of 24 to 48 h, with TiO<sub>6</sub> as the dominant species, as shown in the UV–vis DRS

spectra (Figure S3). Although, experimentally, it is difficult to determine how the modifier of L-carnitine impacts the nucleation and crystal growth processes of TS-1 zeolites at the molecular level owing to the complexity of zeolite crystallization, our current results could still provide evidence that modifier-precursor interactions should be present, as the morphology and Ti coordination states of the zeolites obviously changed after L-carnitine was introduced. Previously, it has been proposed that the coordinative actions of Lcarnitine onto the aluminosilicate framework may finally result in the formation of a core-shell zeolite Y with an ant-nest-like hollow interior.<sup>27</sup> In the present case, the existence of coordinative interactions between L-carnitine and Ti atoms should also play a crucial role in generating mononuclear sixcoordination Ti species in the framework of TS-1 zeolites. Hence our results suggest that L-carnitine can not only functionalize as a common morphology modifier by attaching to specific surface sites of the crystal and by inhibiting the nucleation during the hydrothermal synthesis process but also act as a suitable ligand to adjust the coordination environment of Ti species by building suitable coordination action with Ti species throughout the entire crystal growth process. Although additional work is still required to reveal the concrete coordination interaction between Ti<sup>IV</sup> and L-carnitine in the zeolitic synthesis system, the rapid formation of Ti-O bonds between the amino acid and Ti<sup>IV</sup> in the presence of aqueous alcohol has already been revealed in the literature work.<sup>51</sup> In the present case, the oxygen-containing groups in L-carnitine should easily interact with the Ti species by forming Ti-O bonds, which seems to be beneficial for affording the Ti species in the state of mononuclear hexa-coordination, while simultaneously modulating the incorporation rate of Ti to match well with that of Si with the assistance of a certain amount of ethanol cosolvent and, finally, resulting in the formation of uniformed TiO<sub>6</sub> species in the elongated platelet TS-1 zeolites.

By comparing the thermogravimetric (TG) profile and the FT-IR spectrum of the as-synthesized TS-1#B\_15Et:0.6LC (without calcination) with that of LC (Figures S4 and S5), it can be concluded that no detectable L-carnitine modifiers are present in the as-synthesized TS-1#B\_15Et:0.6LC crystals. These results suggest that the L-carnitine does not distribute inside the channels of the as-synthesized zeolites, further confirming that the introduced L-carnitine should mainly act as a morphology modifier for the formation of the TS-1 zeolite rather than a template for the formation of zeolite framework. On the basis of the above information, the role of L-carnitine in the formation of the elongated platelet TS-1 crystals containing abundant TiO<sub>6</sub> species is schematically illustrated in Scheme 1. In short, the soluble silicon/titanium monomer or oligomers in the initial synthesis gel starts to agglomerate into small amorphous nanoparticles upon heating; then, TS-1 crystals gradually grow under the direction of the TPAOH template through the molecule addition of soluble species (classical path) or through the direct addition of amorphous nanoparticles on the crystal faces (nonclassical path). During this process, the introduced L-carnitine could build coordinative action with the monomer Si and Ti species as well as the amorphous nanoparticles, and it may also act as an adsorbate that can cover the preferential face of the crystal (i.e., the ac face). In these cases, the crystal growth along the b orientation may be considerably inhibited, thus finally resulting in the



formation of the elongated platelet TS-1 zeolite crystals with dominant  ${\rm TiO}_6$  species.

The catalytic properties of various TS-1 zeolites were first investigated for the 1-hexene epoxidation with H<sub>2</sub>O<sub>2</sub> as an oxidant, as shown in Table 2. TS-1#con and TS-1#C 0Et:0.6LC had relatively low catalytic activities, with 30 and 25% conversion after 2 h of reaction, respectively, which are consistent with the literature-reported TS-1 catalysts synthesized by conventional hydrothermal methods.<sup>38</sup> The conversion of 1-hexene increased to 42% upon using TS-1#A 15Et:0.4LC as a catalyst, whereas the highest activity was obtained over the catalyst of TS-1#B 15Et:0.6LC, with 55% 1hexene conversion and 96% epoxide selectivity, respectively. The TOF over TS-1#B 15Et:0.6LC catalyst could reach 131  $h^{-1}$  under the test conditions, which was around two times as high as that of the conventional TS-1#con zeolite (with TOF of 65  $h^{-1}$ ). On the basis of the above characterization results, it can be proposed here that the presence of abundant "TiO<sub>6</sub>" active sites in TS-1#B 15Et:0.6LC should be mainly responsible for its superior catalytic activity. The sheet-like morphology of this catalyst may expose more geometric surface area and catalytically active sites in the direction of the (010), owing to the larger c/b aspect ratio of 10, and may also provide a shorter diffusion path for reactants along the straight channel of the MFI network, thus being another favorite factor for improving its catalytic property.

In addition, the two other TS-1#B\_15Et:0.6LC catalysts with higher Si/Ti ratios of 74 and 58, which also possess elongated platelet morphology and isolated  $TiO_4$  and  $TiO_6$  species, respectively (Figures S6–S8), were also quite active

for the epoxidation of 1-hexene (Table S1). Their catalytic activities were higher than those of the literature-reported  $\text{TiO}_6$ -containting TS-1 catalysts (with similar Ti contents), which were derived from the hydrothermal post-treatment of conventional TS-1 with organic amine agents.<sup>41,42</sup> Notably, under similar operation conditions, the TS-1#B\_15Et:0.6LC catalyst could give a much higher 1-hexene conversion and  $H_2O_2$  utilization rate (see Table 2) than the previous reported TS-1 zeolites synthesized through an active seed-assisted microwave irradiation strategy (TS-1-AM), which also contain a certain amount of "TiO<sub>6</sub>" species besides the "TiO<sub>4</sub>" species.<sup>44</sup> This might be due to the fact that TS-1#B\_15Et:0.6LC contains a greater concentration of highly active "TiO<sub>6</sub>" species than does TS-1-AM.

Moreover, the catalytic properties of various TS-1 zeolites were also studied for the oxidation of other alkenes, such as allyl chloride, cyclopentene, and 1-heptene (Table S2 and Figure S9). It was found that TS-1#B 15Et:0.6LC also showed excellent catalytic activity for the epoxidation of allyl chloride and cyclopentene. The relatively low selectivity for cyclopentene epoxide (or high selectivity for glutaraldehyde) should mainly be related to the presence of more acidic Ti-OH groups in TiO<sub>6</sub> species of TS-1#B 15Et:0.6LC zeolites, which can lead to the side reaction of the ring opening of the cyclopentene epoxide.<sup>40</sup> The formation of the side product glutaraldehyde could be significantly inhibited when the weak basic acetonitrile is used as the solvent, although an obvious decrease in the catalytic activity of TS-1#B 15Et:0.6LC catalysts was observed (entry 4 in Table S2). As for the epoxidation of 1-heptene, all of the TS-1 zeolites including TS-1#B 15Et:0.6LC exhibited relatively low catalytic activity, which provides indirect evidence that the active TiO<sub>6</sub> species should mainly distribute on the inner surface (or in the framework) of TS-1 zeolites, similar to the TiO<sub>4</sub> species.

The recycling experiments suggested that the TS-1#B\_15Et:0.6LC catalyst can be easily recycled after simple filtration, and its catalytic activity remained good after five cycles (Figure 10). Additional characterization results based on XRD, TEM, and UV-vis DRS spectra demonstrate that the morphology, structure, and coordination states of the Ti species of the used TS-1#B\_15Et:0.6LC zeolite are well remaining in comparison with the fresh one (Figure S10–S12). According to the related literature,<sup>42,43</sup> it was known that the mononuclear TiO<sub>6</sub> species like Ti(OSi)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(OH)<sub>2</sub>, which are generally derived from the hydrothermal post-treatment of conventional TS-1 with basic agents, might be easily converted into condensed Ti species or anatase TiO<sub>2</sub> with the neighboring defect sites of Si–OH or Ti–OH species

Table 2. C	atalytic	Results of	1-Hexene	Epoxidation	with H <sub>2</sub>	$0_2$ as	• Oxidant	over	Different	TS-1	Samples'
	,										

catalyst	conversion (%)	epoxides	others <sup>b</sup>	TOF $(h^{-1})^c$	$H_2O_2$ efficiency $(\%)^d$
TS-1#con	30	95	5	65	28
TS-1#A_15Et:0.4LC	42	96	4	95	40
TS-1#B_15Et:0.6LC	55	96	4	131	53
TS-1#B-58_15Et:0.6LC	48	95	5	150	46
TS-1#B-74_15Et:0.6LC	35	97	3	145	34
TS-1#C_0Et:0.6LC	25	94	6	65	24

<sup>*a*</sup>Reaction conditions: catalyst 50 mg, 1-hexene 10 mmol,  $H_2O_2$  10 mmol,  $CH_3OH$  10 mL, temperature 333 K, time 2 h. <sup>*b*</sup>2-Methoxyhexan-1-ol, 1methoxyhexan-2-ol, and 1,2-hexanediol. <sup>*c*</sup>Turn over frequency (TOF) was calculated on the basis of the conversion of olefin per hour divided by the amount of Ti species in the TS-1 zeolite. <sup>*d*</sup>Efficiency of  $H_2O_2$  for epoxides = (amount of epoxides/amount of  $H_2O_2$  consumed)\*100%



**Figure 10.** Recycling experiments of 1-hexene epoxidation catalyzed by TS-1#B\_15Et:0.6LC with  $H_2O_2$  as the oxidant. Reaction conditions: catalyst 50 mg, alkene 10 mmol,  $H_2O_2$  10 mmol, CH<sub>3</sub>OH 10 mL, temperature 60 °C. Others: 1-methoxyhexan-2-ol, 2-methoxyhexan-1-ol, 1,2-hexanediol.

(caused by an etching process). In the present work, the high stability of TS-1#B\_15Et:0.6LC could be mainly attributed to the uniform distribution of the framework  $TiO_6$  species in the perfect zeolites with high crystallinity.

Above all, the catalytic epoxidation properties of the TS-1 zeolites are highly dependent on the coordinative states of the Ti species and the morphology of the zeolites. Compared with TS-1#con zeolites, the hexagonal plate TS-1#A 15Et:0.4LC and elongated platelet TS-1#B 15Et:0.6LC have higher catalytic activities for alkene epoxidation, which could be mainly due to the well-defined surface environments, such as the short path along the (010) plane and the optimal active TiO4 and TiO6 species. It was found that the efficiency of H<sub>2</sub>O<sub>2</sub> for epoxides could reach 53% when TS-1#B\_15Et:0.6LC was used as the catalyst, which is much higher than that of other catalysts under the test conditions (Table 2). These results suggest that the elongated platelet-like TS-1#B 15Et:0.6LC with a higher concentration of active TiO<sub>6</sub> species could efficiently activate and utilize H2O2 for the epoxidation reaction. The relatively high utilization efficiency of H<sub>2</sub>O<sub>2</sub> over this catalyst might be at least partly assigned to the absence of unfavorable Ti species like anatase TiO<sub>2</sub>, which is responsible for the inefficient decomposition of  $H_2O_2$ . Notably, it seems unreasonable to find that the sample of TS-1#C 0Et:0.6LC, which contains both catalytically active TiO<sub>4</sub> and TiO<sub>6</sub> species, showed lower catalytic activity than TS-1#A 15Et:0.4LC and TS-1#B 15Et:0.6LC, even lower than the conventional TS-1#con. This might be explained by the presence of a portion of anatase TiO<sub>2</sub> in TS-1#C 0Et:0.6LC, which can accelerate the decomposition of H<sub>2</sub>O<sub>2</sub>, thus decreasing the conversion of alkene. Concerning the fact that both TS-1#A\_15Et:0.4LC and TS-1#B\_15Et:0.6LC catalysts have similar common features in morphology and composition, such as a high degree of crystallinity, similar Si/Ti ratios, and well-developed (010) faces and approximate *b*-axis thickness (~300 nm), the relatively high catalytic activity of TS-1#B 15Et:0.6LC zeolite may suggest that TiO<sub>6</sub> species are more active than TiO<sub>4</sub> species for alkene epoxidation.

## CONCLUSIONS

In summary, TS-1 zeolites with different morphologies and coordinative states of Ti species have been hydrothermally synthesized by using L-carnitine as a crystal growth modifier and ethanol as a cosolvent. The zeolite morphology and the coordinative states of Ti species could be effectively modulated by controlling the amount of the growth modifier L-carnitine and the cosolvent ethanol. The resultant hexagonal plate-like TS-1#A 15Et:0.4LC and the elongated platelet TS-1#B 15Et:0.6LC zeolites contain abundant mononuclear  $TiO_4$  and  $TiO_6$  species, respectively, which can be identified by combining a variety of characterization means, including UV-vis, UV Raman, and X-ray absorption spectroscopies. Our results suggest that L-carnitine can act as a modifier to modulate the morphology of the zeolite TS-1 by mediating the growth pathways of the crystals and to adjust the coordinative environment of the Ti species in the zeolite framework by building a suitable interaction with the precursor of the Ti species during the hydrothermal synthesis process. Catalytic tests demonstrate the superior catalytic activity and structural stability of TS-1#B 15Et:0.6LC zeolites for the epoxidation of alkene, which are attributed to the enriched mononuclear TiO<sub>6</sub> species and the perfect crystal morphology. This work offers a useful strategy to effectively synthesize TS-1 zeolites with desirable crystal morphology, Ti coordination states, and excellent catalytic performance, which may bring new opportunities to develop more efficient titanosilicate zeolites for catalytic applications.

## ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01518.

Fourier transform Ti K-edge EXAFS fitting curve, SEM images, UV-vis DRS spectra, TG profiles, FT-IR spectra, PXRD patterns, and catalytic results (PDF)

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#### Notes

The authors declare no competing financial interest.

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#### REFERENCES

(1) Li, Y.; Yu, J. H. New stories of zeolite structures: their descriptions, determinations, predictions, and evaluations. *Chem. Rev.* **2014**, *114*, 7268–7316.

(2) Lupulescu, A. I.; Kumar, M.; Rimer, J. D. A facile strategy to design zeolite L crystals with tunable morphology and surface architecture. *J. Am. Chem. Soc.* **2013**, *135*, 6608–6617.

(3) Serrano, D. P.; Escola, J. M.; Pizarro, P. Synthesis strategies in the search for hierarchical zeolites. *Chem. Soc. Rev.* **2013**, *42*, 4004–4035.

(4) Perego, C.; Millini, R. Porous materials in catalysis: challenges for mesoporous materials. *Chem. Soc. Rev.* 2013, 42, 3956–3976.

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

(6) Deng, X. J.; Wang, Y. N.; Shen, L.; Wu, H. H.; Liu, Y. M.; He, M. Y. Low cost synthesis of Titanium Silicalite-1 (TS-1) with highly catalytic oxidation performance through a controlled hydrolysis process. *Ind. Eng. Chem. Res.* **2013**, *52*, 1190–1196.

(7) Li, H.; Jin, J.; Wu, W.; Chen, C.; Li, L.; Li, Y.; Zhao, W.; Gu, J.; Chen, G.; Shi, J. L. Synthesis of a hierarchically macro-/mesoporous zeolite based on a micro-emulsion mechanism. *J. Mater. Chem.* **2011**, *21*, 19395.

(8) Xin, H.; Zhao, J.; Xu, S.; Li, J.; Zhang, W.; Guo, X.; Hensen, E.; Yang, Q.; Li, C. Enhanced catalytic oxidation by hierarchically structured TS-1 zeolite. *J. Phys. Chem. C* **2010**, *114*, 6553–6559.

(9) Fang, Y. M.; Hu, H. Q.; Chen, G. H. In situ assembly of zeolite nanocrystals into mesoporous aggregate with single crystal like morphology without secondary template. *Chem. Mater.* **2008**, *20*, 1670–1672.

(10) Dai, C.; Zhang, A.; Li, L.; Hou, K.; Ding, F.; Li, J.; Mu, D.; Song, C.; Liu, M.; Guo, X. Synthesis of hollow nanocubes and macroporous monoliths of silicalite-1 by alkaline treatment. *Chem. Mater.* **2013**, *25*, 4197–4205. (11) Jiao, Y.; Adedigba, A. L.; He, Q.; Miedziak, P.; Brett, G.; Dummer, N. F.; Perdjon, M.; Liu, J.; Hutchings, G. J. Inter-connected and open pore hierarchical TS-1 with controlled framework titanium for catalytic cyclohexene epoxidation. *Catal. Sci. Technol.* **2018**, *8*, 2211–2217.

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

(13) Jiao, Y.; Forster, L.; Xu, S.; Chen, H.; Han, J.; Liu, X.; Zhou, Y.; Liu, J.; Zhang, J.; Yu, J.; D'Agostino, C.; Fan, X. Creation of Al-Enriched mesoporous ZSM-5 nanoboxes with high catalytic activity: converting tetrahedral extra-framework Al into framework sites via post treatment. *Angew. Chem., Int. Ed.* **2020**, *59*, 2–11.

(14) Zhang, R.; Zhong, P.; Arandiyan, H.; Guan, Y.; Liu, J.; Wang, N.; Jiao, Y.; Fan, X. Using ultrasound to improve the sequential postsynthesis modification method for making mesoporous Y zeolites. *Front. Chem. Sci. Eng.* **2020**, *14*, 275–287.

(15) Abdulridha, S.; Jiao, Y.; Xu, S.; Zhang, R.; Garforth, A.; Fan, X. Mesoporous zeolitic materials (MZMs) derived from zeolite Y using a microwave method for catalysis. *Front. Chem.* **2020**, No. 482.

(16) Jones, F.; Ogden, M. Controlling crystal growth with modifiers. *CrystEngComm* **2010**, *12*, 1016–1023.

(17) Ma, W.; Lutsko, J.; Rimer, J.; Vekilov, P. Antagonistic cooperativity between crystal growth modifiers. *Nature* **2020**, *577*, 497–515.

(18) Liu, Z.; Dong, X.; Zhu, Y.; Emwas, A. H.; Zhang, D.; Tian, Q.; Han, Y. Investigating the influence of mesoporosity in zeolite beta on its catalytic performance for the conversion of methanol to hydrocarbons. *ACS Catal.* **2015**, *5*, 5837–5845.

(19) Lv, G.; Deng, S.; Zhai, Y.; Zhu, Y.; Li, H.; Wang, F.; Zhang, X. P123 lamellar micelle assisted construction of hierarchical TS-1 stacked nanoplates with constrained mesopores for enhanced oxidative desulfurization. *Appl. Catal., A* **2018**, *567*, 28–35.

(20) Li, R.; Smolyakova, A.; Maayan, G.; Rimer, J. D. Designed peptoids as tunable modifiers of zeolite crystallization. *Chem. Mater.* **2017**, *29*, 9536–9546.

(21) Davis, T. M.; Snyder, M. A.; Krohn, J. E.; Tsapatsis, M. Nanoparticles in lysine-silica sols. *Chem. Mater.* **2006**, *18*, 5814–5816.

(22) Zhao, D.; Wang, Y.; Chu, W.; Wang, X.; Zhu, X.; Li, X.; Xie, S.; Wang, H.; Liu, S.; Xu, L. Direct synthesis of hollow single-crystalline zeolite Beta using a small organic lactam as a recyclable hollow-directing agent. J. Mater. Chem. A 2019, 7, 10795–10804.

(23) Chen, C.; Zhai, D.; Dong, L.; Wang, Y.; Zhang, J.; Liu, Y.; Chen, Z.; Wang, Y.; Qian, W.; Hong, M. Organic anion facilitates in situ synthesis of mesoporous LTA zeolites. *Chem. Mater.* **2019**, *31*, 1528–1536.

(24) Watanabe, R.; Yokoi, T.; Tatsumi, T. Synthesis and application of colloidal nanocrystals of the MFI-type zeolites. *J. Colloid Interface Sci.* **2011**, 356, 434–441.

(25) Chen, Z.; Zhang, J.; Yu, B.; Zheng, G.; Zhao, J.; Hong, M. Amino acid mediated mesopore formation in LTA zeolites. *J. Mater. Chem. A* **2016**, *4*, 2305–2313.

(26) Zhang, J.; Chen, Z.; Wang, Y.; Zheng, G.; Zheng, H.; Cai, F.; Hong, M. Influence of the nature of amino acids on the formation of mesoporous LTA-type zeolite. *Microporous Mesoporous Mater.* **2017**, 252, 79–89.

(27) Zhang, J.; Bai, S.; Chen, Z.; Wang, Y.; Dong, L.; Zheng, H.; Cai, F.; Hong, M. Core-shell zeolite Y with antnest like hollow interior constructed by amino acids and enhanced catalytic activity. *J. Mater. Chem. A* 2017, *5*, 20757–20764.

(28) Qin, W.; Agarwal, A.; Choudhary, M. K.; Palmer, J. C.; Rimer, J. D. Molecular modifiers suppress nonclassical pathways of zeolite crystallization. *Chem. Mater.* **2019**, *31*, 3228–3238.

(29) Zhang, Q.; Mayoral, A.; Terasaki, O.; Zhang, Q.; Ma, B.; Zhao, C.; Yang, G.; Yu, J. H. Amino Acid assisted construction of singlecrystalline hierarchical nanozeolites via oriented aggregation and intraparticle ripening. J. Am. Chem. Soc. **2019**, 141, 3772–3776.

(30) Zhang, Q.; Chen, G.; Wang, Y.; Chen, M.; Guo, G.; Shi, J.; Luo, J.; Yu, J. H. High-quality single-crystalline MFI-Type nanozeolites: A

facile synthetic strategy and MTP catalytic studies. *Chem. Mater.* 2018, 30, 2750–2758.

(31) Přech, J. Catalytic performance of advanced titanosilicate selective oxidation catalysts – a review. *Catal. Rev.: Sci. Eng.* **2018**, *60*, 71–131.

(32) Bregante, D. T.; Flaherty, D. W. Periodic trends in olefin epoxidation over group IV and V framework substituted zeolite catalysts: A kinetic and spectroscopic study. *J. Am. Chem. Soc.* 2017, 139, 6888–6898.

(33) Jin, S.; Wang, Z.; Tao, G.; Zhang, S.; Liu, W.; Fu, W.; Zhang, B.; Sun, H.; Wang, Y.; Yang, W. UV resonance raman spectroscopic insight into titanium species and structure-performance relationship in boron-free Ti-MWW zeolite. *J. Catal.* **2017**, *353*, 305–314.

(34) Shan, Z.; Wang, H.; Meng, X.; Liu, S.; Wang, L.; Wang, C.; Li, F.; Lewis, J. P.; Xiao, F. S. Designed synthesis of TS-1 crystals with controllable b-oriented length. *Chem. Commun.* **2011**, *47*, 1048–1050. (35) Deng, Z.; Yang, Y.; Lu, X.; Ding, J.; He, M.; Wu, P. Studies on the epoxidation of methallyl chloride over TS-1 microsphere catalysts in a continuous slurry reactor. *Catal. Sci. Technol.* **2016**, *6*, 2605–2615.

(36) Du, S.; Li, F.; Sun, Q.; Wang, N.; Jia, M.; Yu, J. H. A green surfactant-assisted synthesis of hierarchical TS-1 zeolites with excellent catalytic properties for oxidative desulfurization. *Chem. Commun.* **2016**, *52*, 3368–3371.

(37) Du, S.; Sun, Q.; Wang, N.; Chen, X.; Jia, M.; Yu, J. H. Synthesis of hierarchical TS-1 zeolites with abundant and uniform intracrystalline mesopores and their highly efficient catalytic performance for oxidation desulfurization. *J. Mater. Chem. A* **201***7, 5,* 7992–7998.

(38) Bai, R.; Sun, Q.; Song, Y.; Wang, N.; Zhang, T.; Wang, F.; Zou, Y.; Feng, Z.; Miao, S.; Yu, J. Intermediate-crystallization promoted catalytic activity of titanosilicate zeolites. *J. Mater. Chem. A* **2018**, *6*, 8757–8762.

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

(40) Guo, Q.; Sun, K.; Feng, Z.; Li, G.; Guo, M.; Fan, F.; Li, C. A thorough investigation of the active titanium species in TS-1 zeolite by in situ UV resonance raman spectroscopy. *Chem. - Eur. J.* **2012**, *18*, 13854–13860.

(41) Wu, L.; Tang, Z.; Yu, Y.; Yao, X.; Liu, W.; Li, L.; Yan, B.; Liu, Y.; He, M. Facile synthesis of a high-performance titanosilicate catalyst with controllable defective Ti(OSi)<sub>3</sub>OH sites. *Chem. Commun.* **2018**, *54*, 6384–6387.

(42) Wu, L.; Deng, X.; Zhao, S.; Yin, H.; Zhuo, Z.; Fang, X.; Liu, Y.; He, M. Synthesis of a highly active oxidation catalyst with improved distribution of titanium coordination states. *Chem. Commun.* **2016**, *52*, 8679–8682.

(43) Xu, L.; Huang, D. D.; Li, C. G.; Ji, X.; Jin, S.; Feng, Z.; Xia, F.; Li, X.; Fan, F.; Li, C.; Wu, P. Construction of unique six-coordinated titanium species with an organic amine ligand in titanosilicate and their unprecedented high efficiency for alkene epoxidation. *Chem. Commun.* **2015**, *51*, 9010–9013.

(44) Xu, W.; Zhang, T.; Bai, R.; Zhang, P.; Yu, J. A one-step rapid synthesis of TS-1 zeolites with highly catalytically active mononuclear  $TiO_6$  species. J. Mater. Chem. A **2020**, 8, 9677–9683.

(45) Fan, W.; Fan, B.; Shen, X.; Li, J.; Wu, P.; Kubota, Y.; Tatsumi, T. Effect of ammonium salts on the synthesis and catalytic properties of TS-1. *Microporous Mesoporous Mater.* **2009**, *122*, 301–308.

(46) Liu, M.; Chang, Z.; Wei, H.; Li, B.; Wang, X.; Wen, Y. Low-cost synthesis of size controlled TS-1 by using suspended seeds: from screening to scale-up. *Appl. Catal., A* **2016**, 525, 59–67.

(47) Du, Q.; Guo, Y.; Wu, P.; Liu, H. Synthesis of hierarchically porous TS-1 zeolite with excellent deep desulfurization performance under mild conditions. *Microporous Mesoporous Mater.* **2018**, *264*, 272–280.

(48) Signorile, M.; Crocellà, V.; Damin, A.; Rossi, B.; Lamberti, C.; Bonino, F.; Bordiga, S. Effect of Ti speciation on catalytic performance of TS-1 in the hydrogen peroxide to propylene oxide reaction. J. Phys. Chem. C 2018, 122, 9021–9034.

(49) Li, C.; Xiong, G.; Xin, Q.; Liu, J.-k.; Ying, P.-l.; Feng, Z.-c.; Li, J.; Yang, W.-b.; Wang, Y.-z.; et al. UV resonance raman spectroscopic identification of titanium atoms in the framework of TS-1 zeolite. *Angew. Chem.*, *Int. Ed.* **1999**, *38*, 2220–2222.

(50) Dong, J.; Zhu, H.; Xiang, Y.; Wang, Y.; An, P.; Gong, Y.; Liang, Y.; Qiu, L.; Zheng, A.; Peng, X.; Lin, M.; Xu, G.; Guo, Z.; Chen, D. Toward a unified identification of Ti location in the MFI framework of high-Ti-loaded TS-1: combined EXAFS, XANES, and DFT study. *J. Phys. Chem. C* **2016**, *120*, 20114–20124.

(51) Chrissanthopoulos, A.; Klouras, N.; Ntala, Ch.; Sevastos, D.; Dalas, E. Inhibition of hydroxyapatite formation in the presence of titanocene–aminoacid complexes: an experimental and computational study. *J. Mater. Sci.: Mater. Med.* **2015**, 15.