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Synthesis of Titanosilicates

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1.1 Introduction

Zeolites are microporous crystals that are constructed by tetrahedral SiO_4 and AlO_4 species interlinked by sharing O atoms, and they demonstrate remarkable application prospects in adsorption, separation, ion exchange, and heterogeneous solid-acid catalysis [1]. Typically, a part of the framework of Si and Al atoms can be replaced by heteroatoms, such as Ti, Sn, Ge, Zr, B, P, V, and Ga, via isomorphous substitution, resulting in heteroatomic zeolites or metallosilicates [2–4]. Among these heteroatomic zeolites, titanosilicate is the most representative one, and it can catalyze diverse selective oxidation reactions, such as alkene epoxidation, aldehyde or ketone ammoxidation, benzene or phenol hydroxylation, 1,4-dioxane oxidation, selective oxidation of pyridine derivatives, and oxidation desulfurization [5–9], as well as acid-catalyzed reactions, such as ring-opening reactions of epoxides [10–12], ethylenediamine condensation [13], and Beckmann rearrangement of oxime [14] (as shown in Figure 1.1). Moreover, the discovery of titanosilicates has expanded the application scope of zeolites, as heterogeneous catalysts, from acid catalysis to the redox field. Several reviews and monographs have proposed opportunities and challenges for titanosilicates in synthetic and catalytic applications [3–9, 15–18]. As depicted in Figure 1.2, the number of annual publications related to titanosilicates has rapidly increased from 1983 to 2023, and this number has remained at approximately 200–350 over the last decade.

Notably, titanosilicates can be divided into microporous, mesoporous, and hierarchical types based on their textural properties and pore sizes. Among these, microporous titanosilicates, with isolated tetrahedral Ti species, possess pores that are <2 nm in size, and these include small- and medium-pore titanosilicate zeolites with 8- or 10-membered ring (MR), 12-MR large-pore zeolites, and extra-large-pore zeolites with ≥ 14 MRs. Among the 255 ordered zeolite framework structures with three-letter codes and the partially disordered zeolite structures recognized by the International Zeolite Association Structure Commission (IZA), 28 structures

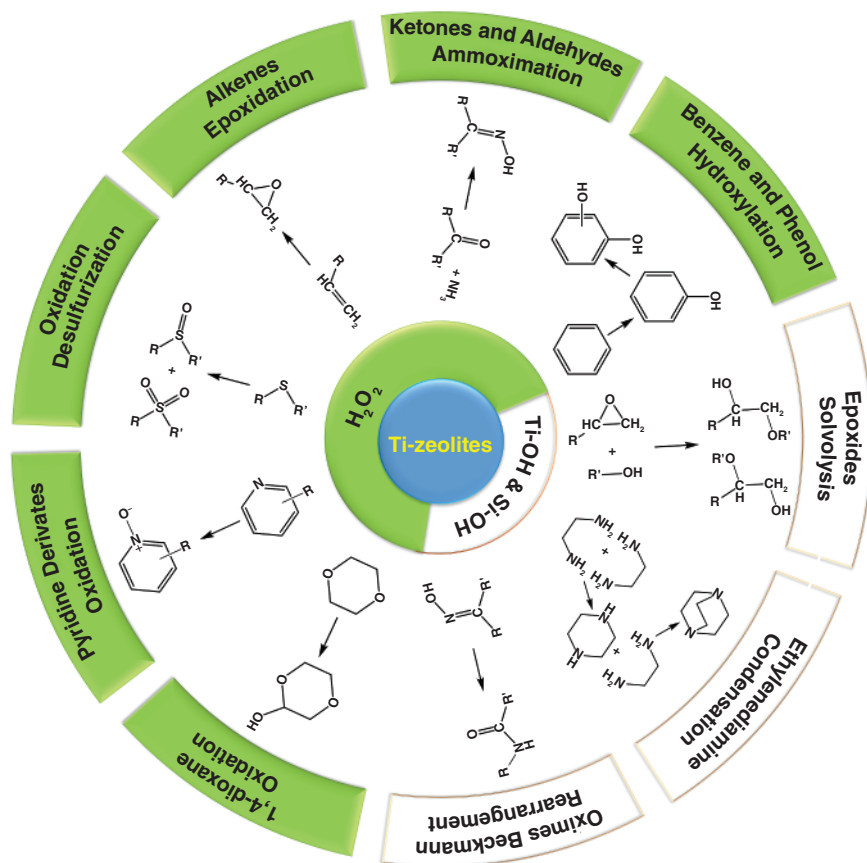


Figure 1.1 Reactions catalyzed by titanosilicates.

can be synthesized as microporous titanosilicates. Owing to their unique porosity and hydrophobicity, microporous titanosilicates can activate H_2O_2 molecules and catalyze selective oxidation reactions. Titanosilicalite-1 (TS-1), with MFI topology, was the first microporous titanosilicate to be employed as a commercial catalyst. For example, the application of TS-1 in the liquid-phase epoxidation of propylene to propylene oxide using H_2O_2 as the oxidant was first reported by EniChem in 1983 [19] and was implemented on a commercial scale by Evonik and SKC in South Korea in 2008. Mesoporous titanosilicates, such as Ti-MCM-41, Ti-MCM-48, Ti-KIT-5, Ti-SBA-15, and Ti-SBA-16, possess pores that are $>2\text{ nm}$ in size and amorphous pore walls [5]. They are more active than microporous materials in the oxidation of bulky substrates with cumene hydroperoxide or *tert*-butyl hydroperoxide (TBHP) as the oxidant. However, they are much less active in oxidation reactions using hydrogen peroxide as the oxidant owing to their extremely high hydrophilicity derived from abundant surface silanols on their amorphous pore walls [20]. Hierarchical titanosilicates contain both micropores and mesopores and exhibit better catalytic properties than their microporous counterparts, particularly

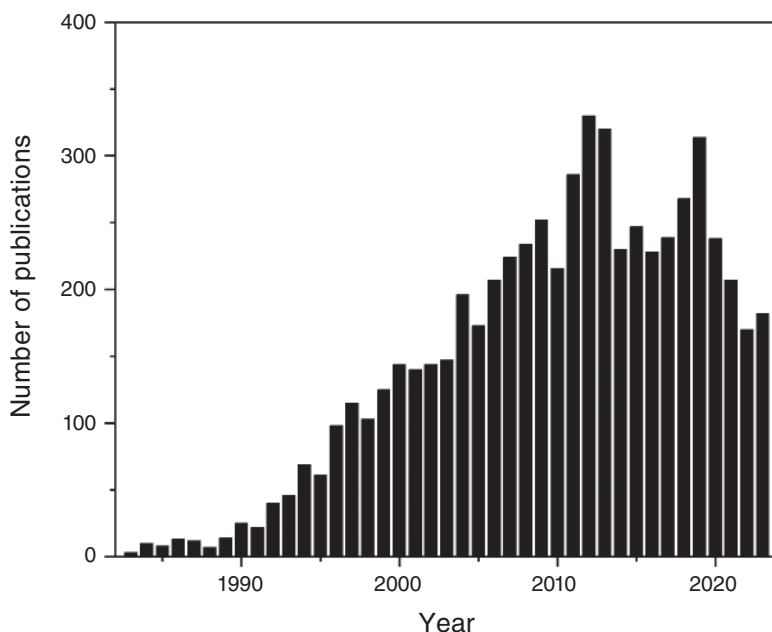


Figure 1.2 Change trend of annual publication number for titanosilicates. Source: SciFinder.

in catalytic reactions involving bulky substrates and/or organic hydroperoxide oxidants [5, 18].

Titanosilicates are primarily synthesized via hydrothermal synthesis (HTS), dry-gel conversion (DGC), fluoride-assisted synthesis, and post-synthesis methods (see Figure 1.3). Among these, HTS has been the most widely adopted approach for zeolite synthesis. This is because the contents and distributions of Ti species, crystal sizes, morphologies, and other physicochemical properties of titanosilicates can be tailored by adjusting the composition of synthetic gels and the crystallization conditions [15]. Particularly, the formation of anatase TiO_2 via the oligomerization of Ti monomers in a HTS process is generally easy owing to the faster hydrolysis rate of the Ti precursor compared to that of the Si precursor. However, the formation of anatase TiO_2 results in low activity and selectivity in catalytic reactions. Consequently, several strategies have been proposed to inhibit the generation of the anatase phase by using additional additives, such as H_2O_2 , isopropanol, Triton X-100, Tween-20, and $(\text{NH}_4)_2\text{CO}_3$, as well as by accurately adjusting the feeding rate [21–27]. These methods generally slow the hydrolysis of Ti precursors to match that of the Si precursors, thereby lowering the anatase content. As an example, Lin et al. [28] proposed a reversed-oligomerization synthesis strategy to address the mismatched hydrolysis rates between Si and Ti precursors, which was implemented by the fast oligomerization of Ti monomers and subsequent de-oligomerization to Ti monomers with the aid of hydroxyl free radicals ($\cdot\text{OH}$) generated in situ by ultraviolet (UV) irradiation.

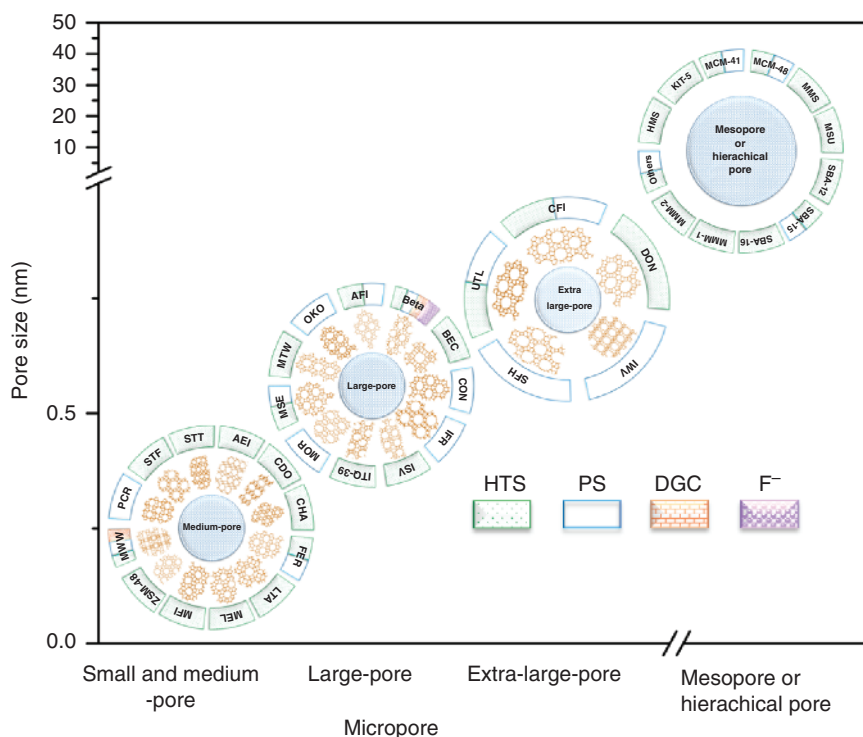


Figure 1.3 Overview of the synthesis methods of titanosilicates with different structures. HTS indicates hydrothermal synthesis, PS indicates post-synthesis, DGC indicates dry-gel conversion, F^- indicates fluoride-assisted method. Small and medium-pore stands for 8-MR and 10-MR titanosilicates, large-pore for 12-MR and extra-large pore for ≥ 14 -MR.

The DGC method can be classified into vapor-phase transport (VPT) and steam-assisted crystallization (SAC) based on the volatility of structure-directing agents (SDAs) [9]. The VPT approach is applicable to volatile SDAs, where SDAs and water are not present in dried synthetic gels but are transferred to them via the vapor phase. The SAC approach can be realized by adding non-volatile SDAs to the dried synthetic gels with water placed below them; subsequently, the synthetic gels can be crystallized using steam. Compared with traditional HTS methods, the DGC method presents several advantages, such as lower SDA consumption, higher product yield, and shorter crystallization time. The crystal sizes obtained by DGC methods can differ from those obtained by direct HTS. For instance, for Ti-Beta synthesized through the DGC method, the crystal size is much smaller than that obtained by the HTS method [29], whereas the opposite is true for MWW-type titanosilicates [30]. In addition, DGC can be used to prepare hierarchical titanosilicate zeolites [31–33].

In fluoride-assisted synthesis, the presence of F^- can accelerate the crystallization process; however, titanosilicate crystals are usually larger than those obtained via HTS [34]. In contrast to aluminosilicates, the concentrations of alkali metal ions

(such as Na^+ and K^+) in synthetic gels should be limited to obtain titanosilicates with high activities. Notably, MOR- and MSE-type zeolites barely crystallize in siliceous gels in the absence of Al^{3+} and alkali metal ions. Thus, the post-synthesis method is another available approach for titanosilicates. The post-synthesis method can proceed in the gas–solid [35], liquid–solid [36], or solid–solid phase [37], depending on the phase of the Ti source. In this chapter, we highlight the most remarkable achievements in the synthesis of titanosilicates with different pore topologies, including medium-pore, large-pore, extra-large-pore, mesopore, and Engelhard Ti silicates (ETS).

1.2 Synthesis of Medium-Pore Titanosilicates

1.2.1 TS-1 Synthesis

TS-1 (MFI topology), which possesses a three-dimensional (3D) medium-pore system (10-MR, ~ 0.55 nm), is one of the most studied titanosilicates and has been applied in many industrial processes, such as propylene epoxidation [19], phenol hydroxylation [38], and cyclohexanone ammoximation [39]. The first discovery of a TS-1 zeolite can be dated back to the patent disclosed by Taramasso et al. in 1983 [19], which was based on the matching hydrolysis of tetraethylorthosilicate (TEOS) and tetraethylorthotitanate (TEOT) using tetrapropylammonium hydroxide (TPAOH) as the SDA.

Extra-framework Ti species tend to form in TS-1 in the presence of Na^+ and K^+ from commercial aqueous TPAOH solutions as impurities [40, 41]. The diffraction peaks ascribed to the extra-framework anatase TiO_2 can even be detected in the X-ray diffraction patterns of TS-1 zeolites once the Na^+ concentration in the synthetic gel reaches a very high level. Moreover, residual alkali metal cations in the synthesized titanosilicates are detrimental to their reactivity in selective catalytic oxidation reactions [42].

In addition to alkali metal cations, the Ti content in synthetic gels and crystallization temperature were also found to be key factors for TS-1 synthesis [43]. The Ti content of the TS-1 samples is always lower than that of synthetic gels, implying that the Ti atoms in the synthetic gels could not be completely introduced into the MFI framework. Excess Ti in the synthetic gel increases the risk of forming extra-framework anatase TiO_2 as an impurity. Hence, several attempts have been made to maximize the amount of tetrahedrally incorporated Ti species in the framework to achieve a higher activity. It has been found that TPAOH should be slowly added into the synthetic gels at low temperatures under vigorous stirring to inhibit the formation of extra-framework Ti species [44]. In other words, it is necessary to match the hydrolysis rates between the Si and Ti precursors to obtain abundant silanol groups for condensation with the monomeric Ti species generated by hydrolysis. Fan et al. proposed that the Si/Ti molar ratio in the framework of the TS-1 zeolite can be decreased to 34 using $(\text{NH}_4)_2\text{CO}_3$ as a crystallization-mediating agent to match the hydrolysis rate of the Ti precursor with that of the Si precursor

and the crystallization rate [23]. In contrast, the Si/Ti ratio was 58 in the absence of $(\text{NH}_4)_2\text{CO}_3$.

Recent research on the synthesis of TS-1 has mainly focused on (a) enhancing the accessibility of the framework Ti species by constructing hierarchical TS-1 zeolites by tuning the particle size and morphology and (b) developing alternative SDAs to replace expensive TPAOH for practical applications. Representative approaches for constructing hierarchical TS-1, such as mesopore-directed methods, mesopore-free methods (kinetic-regulated or DGC methods), and demetallization methods, have been reviewed previously [2, 5, 18]. On the other hand, the high cost of TPAOH has stimulated many researchers to concentrate on reducing its dosage or finding an alternative SDA. TS-1 can be prepared using a cheaper SDA of tetrapropylammonium bromide (TPABr); however, the large zeolite crystals ($15 \times 8 \times 1.5 \mu\text{m}$) obtained in earlier studies are undesirable [45]. Zuo et al. reported the synthesis of TS-1 with a crystal size of 200 nm using TPABr as the SDA, where seeding played a crucial role in reducing the crystal size [46].

TS-1 zeolites with novel morphologies have also been reported. In contrast to the raspberry morphology of traditional TS-1 zeolites, a lamellar TS-1 zeolite with oriented growth and sheet-like morphology ($0.5\text{--}1.0 \mu\text{m}$ length and 20–50 nm thickness) was synthesized with a bifunctional surfactant as the SDA [47]. Due to its hierarchical structure, layered TS-1 showed a higher activity than conventional TS-1, Ti-MWW, Ti-Beta, or even mesoporous titanosilicate Ti-MCM-41 in cyclohexene epoxidation with TBHP as the oxidant. Wang et al. [48] reported the one-pot synthesis of TS-1 microspheres that were approximately $10 \mu\text{m}$ using a triblock copolymer (F127) as the supporting additive through a temperature-programmed self-assembly strategy. The TS-1 microspheres were self-assembled from TS-1 nanoparticles (50–100 nm) and possessed more intercrystal mesopores than traditional TS-1 zeolite, resulting in higher activities during the oxidation of bulky substrates, such as 3-picoline and cyclohexene. Moreover, these TS-1 microspheres exhibited high mechanical stability under harsh thermal and hydrothermal conditions. Thus, because of their high reactivity and mechanical strength, TS-1 microspheres have potential applications in slurry reactors [49].

1.2.2 Ti-MWW Synthesis

Ti-MWW is another medium-pore titanosilicate with a two-dimensional (2D) pore system consisting of intralayer 10-MR sinusoidal pore channels and an interlayer 10-MR pore channel linked to intracrystalline 12-MR supercages [50]. Direct HTS of Ti-MWW is challenging [51]. A key breakthrough was achieved by introducing H_3BO_3 as a structure-supporting agent for the synthesis of Ti-MWW zeolites with high activity, inspired by the HTS of the borosilicate MWW-type zeolite ERB-1. Nevertheless, a higher B content in the synthetic gel is required for Ti-MWW zeolite than for ERB-1 because the introduction of Ti^{4+} ions considerably hinders the crystallization of the MWW framework [52]. The UV–visible spectra of the as-synthesized Ti-MWW had an adsorption band at ca. 220 nm, attributed to the tetrahedrally coordinated framework Ti species, together with another band

at 260 nm, related to the extra-framework octahedral Ti species on the external surface of the Ti-MWW zeolites [52]. Irrespective of the Ti content in the synthetic gel, a band at approximately 330 nm was not observed in the UV–visible spectra of Ti-MWW, implying that the generation of the anatase TiO_2 phase was effectively inhibited.

Hexamethyleneimine (HMI) and piperidine (PI) can be employed as SDAs for Ti-MWW synthesis, and the obtained samples are denoted as Ti-MWW(HMI) and Ti-MWW(PI), respectively. The two Ti-MWW zeolites have similar specific surface areas but significantly different Ti^{4+} distributions owing to their different particle sizes. Irrespective of the Si/Ti molar ratio in the zeolites, the Ti-MWW(PI) zeolite showed the main adsorption band at approximately 260 nm, together with a band at approximately 220 nm, indicating more extra-framework Ti species (Figure 1.4). In contrast, the main absorption band in the UV–visible spectrum of Ti-MWW(HMI)

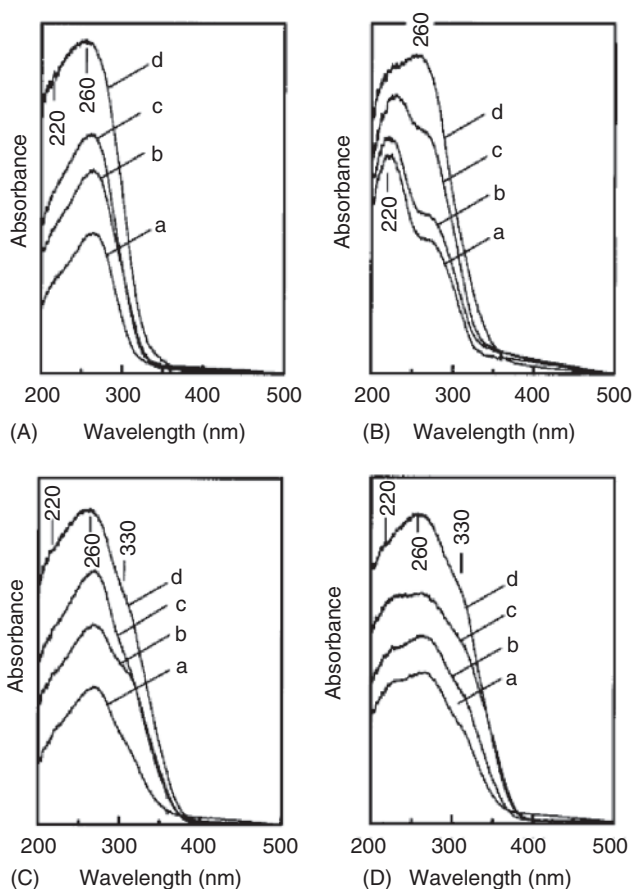


Figure 1.4 UV-visible spectra of as-synthesized (A) and calcined Ti-MWW(PI) (C), and as-synthesized (B) and calcined Ti-MWW(HMI) (D) with the Si/Ti molar ratios of 100 (a), 50 (b), 30 (c), and 10 (d). Source: Reprinted with permission from Wu et al. [52]. Copyright American Chemical Society (2001).

shifted from 260 to 220 nm with increasing Si/Ti molar ratio, indicating that the incorporation of Ti species preferentially occurred in the framework. After calcination of the as-synthesized Ti-MWW zeolites, a new band at approximately 330 nm, attributed to the anatase TiO_2 phase, emerged in the UV-visible spectra for both Ti-MWW(HMI) and Ti-MWW(PI), signifying that the neighboring external surface Ti species partially condensed and aggregated upon calcination. The formed anatase TiO_2 in the calcined Ti-MWW zeolite was barely removed by acid treatment. Therefore, acid treatment is usually performed on as-synthesized Ti-MWW zeolites rather than on calcined zeolites to remove the extra-framework Ti species on the surface, accompanied by a small amount of framework Ti species.

The B content in the Ti-MWW zeolite framework was far below that of the synthetic gel, implying that most of the B species were not involved in building the MWW structure. Additionally, owing to the weak acidity and increased electronegativity of the zeolite framework, the presence of residual framework boron is detrimental to selective oxidation reactions, although most of the framework boron atoms are extracted from the MWW framework by acid treatment. Hence, many other methods, such as the fluoride-assisted method [9] and DGC method [30], have been developed to synthesize Ti-MWW zeolites with reduced boron content in synthetic gels. Wu et al. developed a post-synthesis method to prepare boron-free Ti-MWW by incorporating Ti species into the framework of deboronated MWW via PI-assisted reversible 3D–2D–3D structure conversion [53]. However, boron-free Ti-MWW synthesized via the gas-phase atom planting strategy showed relatively low reactivity in oxidation reactions because of the presence of extra-framework octahedral Ti species and the anatase TiO_2 phase [54]. Lu et al. [36] recently reported the boron-free synthesis of Ti-MWW by introducing framework Ti species into an acidic medium, and the obtained Ti-MWW zeolites showed outstanding catalytic properties for 1-hexene epoxidation. In addition to post-synthesis methods, boron-free Ti-MWW can be one-pot hydrothermally synthesized using HMI and *N,N,N*-trimethyl-1-adamantanmonium hydroxide (1-TMAdOH) as dual-SDAs with a small amount of K^+ [55]. This method was inspired by the synthesis of a highly siliceous MWW zeolite (ITQ-1). After the detrimental K^+ was removed by mild acid treatment, the obtained Ti-MWW catalyst showed high activity in epoxidation reactions.

1.2.3 TS-2 Synthesis

TS-2 with its MEL topology of two intersecting 10-MR pore channels shows a catalytic performance similar to that of the TS-1 zeolite because of the similar secondary building units. In contrast to the abundant literature on TS-1 synthesis, studies on TS-2 synthesis are limited. The synthesis of TS-2 was first reported by Reddy et al. via the crystallization of synthetic gels containing TEOS, tetrabutyl orthotitanate (TBOT), and tetrabutylammonium hydroxide (TBAOH) [56, 57]. Moreover, the crystallization process can be accelerated by microwave-assisted heating [58]. Tuel et al. [59] found that tetrabutylphosphonium hydroxide was an alternative SDA for TS-2 synthesis. In addition to HTS, DGC [60] and F^- -assisted

methods [61] have also been applied to TS-2 synthesis. Moreover, TS-2 can be prepared by the solid–gas reaction of the borosilicate MEL-type zeolite B-ZSM-11 with saturated TiCl_4 vapor; however, it shows poor catalytic reactivity in epoxidation reactions owing to the presence of anatase TiO_2 [62]. Xu et al. recently reported an intergrowth-triggered TS-2 microsphere formed by adjusting the synthetic parameters [63]. The initially formed microspheres were well preserved during the crystallization process because of the special intergrowth stacking style occurred in the synthetic gels with high alkalinity.

1.2.4 Synthesis of Other Medium-Pore Titanosilicates

Ti-FER zeolites with 2D-intersecting 10×8 -MR pore channels can be synthesized using HF/pyridine as the mineralizing agent with [64] or without seeds [65]. FER zeolites can also be synthesized as 2D-layered zeolites, on which structural modifications are applicable to construct Ti-FER zeolites with larger pore systems. The structural diversity of layered Ti-FER zeolites is available in Chapter 2. Ti-ZSM-48, with non-interpenetrating linear 10-MR pore channels (5.3×5.6 Å in diameter) and Si/Ti molar ratios ≥ 30 , can be hydrothermally synthesized using diaminoctane, hexamethonium hydroxide, or trimethylpropylammonium hydroxide as SDAs [66–68]. However, Ti-ZSM-48, which has a partially disordered structure, is inactive for phenol hydroxylation with H_2O_2 because of diffusional limitations or subtle differences in the Ti microenvironment compared to TS-1 and TS-2 [68, 69]. In addition, small- and medium-pore titanosilicates with other topologies, such as STF [70], CHA [71–74], LTA [75, 76], CDO [77], AEI [78], STT [79], and PCR [80, 81], have also been successfully synthesized, but were inactive or showed less attractive activity in catalytic reactions because of mass transfer limitations.

1.3 Synthesis of Large-Pore Titanosilicates

1.3.1 Ti-Beta Synthesis

Titanoaluminosilicate Ti-Al-Beta, with 3D 12-MR pore channels, was first prepared by a HTS method via the isomorphous substitution of Si^{4+} by Ti^{4+} in the aluminosilicate Al-Beta. It showed higher activity than TS-1 in the selective oxidation of cycloalkanes with H_2O_2 as the oxidant [22], indicating that titanosilicates with relatively large pores are more efficient for oxidation reactions involving bulky substrates. Further study on the synthesis and characterization of Ti-Al-Beta was conducted to illustrate the influence of synthetic parameters on the Ti-coordinated states and catalytic properties in selective oxidation reactions [82, 83]. The Ti species introduced in Ti-Al-Beta tends to adopt extra-framework octahedral coordination rather than framework tetrahedral coordination. Moreover, the acidity derived from the framework tetrahedral Al in Ti-Al-Beta easily accelerates the ring opening of epoxides, decreasing epoxide selectivity in alkene epoxidation [83].

Thus, the amount of Al in Ti-Al-Beta should be decreased to eliminate the adverse effects of Al on catalytic performance. Al-free Ti-Beta titanosilicate has been successfully synthesized with tetraethylammonium hydroxide (TEAOH) and dealuminated Beta as the SDA and seed, respectively, as reported by Corma et al. [84]. However, Al-free Ti-Beta obtained by the above seeding methodology still showed very low-epoxide selectivity in alkene epoxidation. A similar phenomenon was observed for an Al-free Ti-Beta zeolite prepared by a solid–gas phase reaction between borosilicate B-Beta and saturated TiCl_4 vapor [85]. This phenomenon can be illustrated by the presence of numerous internal Si–OH groups (framework defects) in the Al-free Ti-Beta (Ti-Beta(OH)) obtained in OH^- media. Some Si–OH groups are formed after the elimination of TEA^+ and are balanced by SiO^- groups upon calcination [84]. Corma et al. found that TEA^+ can be neutralized by F^- instead of SiO^- for synthesis in an F^- medium, resulting in the formation of defect-less Ti-Beta zeolites (Ti-Beta(F)) with high crystallinity, hydrophobicity, and hydrothermal stability [34, 86]. Because of its hydrophobicity, Ti-Beta(F) is superior to Ti-Beta(OH) in unsaturated fatty oil epoxidation reactions in terms of reactivity and epoxide selectivity [34, 87]. Additionally, several other approaches, such as the DGC method, interzeolite transformation, and dissolution–recrystallization methods, have also been reported for the synthesis of Ti-Beta zeolites [29, 88–90]. Inspired by the DGC method for preparing high-silica Beta zeolite [91], large-pore Ti-Beta with high hydrophobicity has been prepared by the DGC method, even in the presence of alkali metal cations [29, 88]. The hydrophobic Ti-Beta obtained by the DGC method showed higher catalytic reactivity and selectivity to epoxides than the hydrophilic Ti-Beta(OH) in selective oxidation reactions [29, 92], which is in accordance with previous conclusions related to the effects of zeolite polarity on the catalytic properties in selective oxidation reactions [34, 86]. Zhu et al. [89] reported the interzeolite transformation of Ti-MWW zeolite into Ti-Beta zeolite (as shown in Figure 1.5), which showed excellent catalytic properties for cyclohexene epoxidation with H_2O_2 as the oxidant. The framework structure similarity between MWW and Beta zeolites and the addition of Beta seeds play crucial roles in the crystallization of Ti-Beta. The interzeolite transformation of Ti-MWW (10×10 -MR pore channels) to large-pore Ti-Beta ($12 \times 12 \times 12$ -MR pore channels) breaks the traditional interzeolite transformation concept (spontaneous transformation toward a denser zeolite framework) of zeolite synthesis [93–95]. The dissolution–recrystallization of dealuminated-Beta zeolite in a mixture of a tetraethylammonium aqueous solution and a Ti precursor produced Ti-Beta with nanosized crystals, high Ti content, and intercrystal mesoporosity, which showed outstanding catalytic properties in cyclohexene epoxidation with hydrogen peroxide or TBHP as the oxidant [90].

1.3.2 Ti-MOR Synthesis

Ti-MOR, which contains 12-MR pore channels, has shown unique catalytic properties both in the hydroxylation of toluene and ammoximation of ketones [96, 97]. Until now, MOR structures have not been crystallized in siliceous gels without

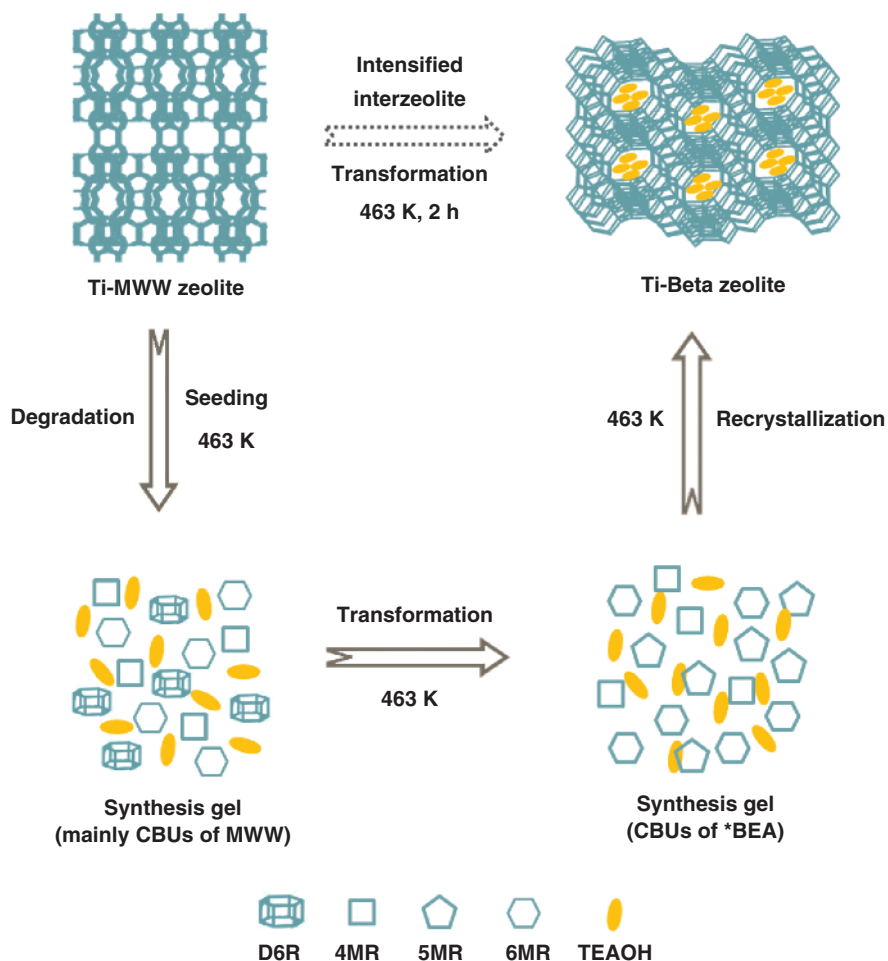


Figure 1.5 Flow Diagram for the interzeolite transformation of Ti-MWW zeolites into Ti-Beta zeolites. Source: Reprinted with permission from Zhu et al. [89]. Copyright Royal Society of Chemistry (2019).

the assistance of Al^{3+} [98]. Thus, a highly active Ti-MOR can only be prepared by dealumination of the aluminosilicate zeolite Al-MOR and the subsequent gas–solid reaction between TiCl_4 vapor and the dealuminated MOR at elevated temperature [99]. The transport of TiCl_4 molecules and reactants is strongly related to the length of the 12-MR pore channel along the *c*-axis. In this sense, Yang et al. investigated Ti-MOR zeolites with different crystal lengths along the *c*-axis to understand the role of the 12-MR pore channel length on the catalytic performance (Figure 1.6) [100]. The crystal length along the *c*-axis plays a critical role in the diffusion of framework Al species out of the 12-MR pore channels and the diffusion of Ti species into the 12-MR pore channels, which affects the amount of Ti inserted and the catalytic activity.

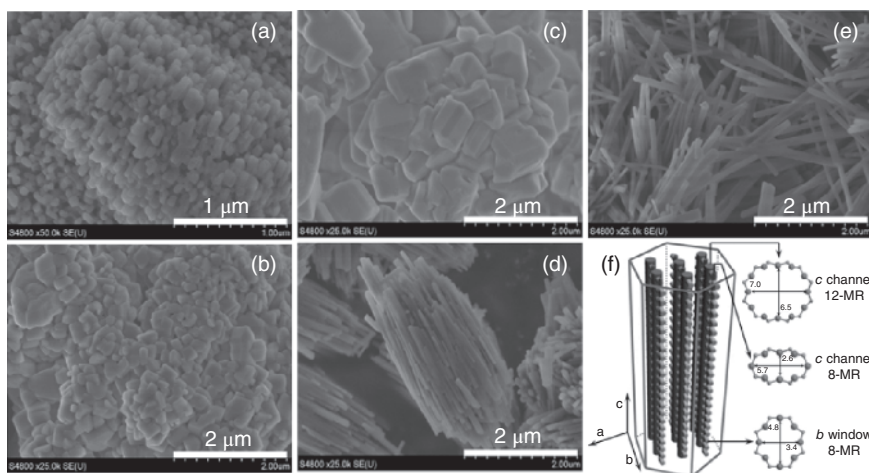


Figure 1.6 The SEM images of MOR zeolites with different crystal lengths of 110 nm (a), 230 nm (b), 630 nm (c), 2450 nm (d), 5160 nm (e) and the pore channels of MOR zeolite (f). Source: Yang et.al. [100]/Reproduced with permission from Elsevier.

1.3.3 Ti-MSE Synthesis

The Ti-containing MSE zeolite is another large-pore titanosilicate with 3D $12 \times 10 \times 10$ -MR pore channels and an 18×12 -MR supercage linked to the 10-MR pore channel. Similar to the MOR, the MSE structure cannot be obtained via hydrothermal crystallization without the assistance of Al^{3+} . Kubota et al. attempted to synthesize Ti-MSE by introducing a Ti tetrabutoxide and H_2O_2 aqueous solution into an aluminosilicate gel with *N,N,N',N'*-tetraethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium diiodide ($\text{TEBOP}^{2+}(\text{I}^-)_2$) as the SDA [101]. Most framework Al atoms were extracted from the zeolite framework via acid treatment. However, titanoaluminosilicates show low phenol hydroxylation activity after acid treatment, possibly because of their hydrophilic nature. Thus, highly active Ti-MSE zeolites can only be synthesized using the post-atom planting method. Ti-MSEs are known as Ti-MCM-68 [101–105], Ti-UZM-35 [106], and Ti-YNU-2 [107] according to the parent materials used for Ti planting. Ti-MCM-68 was first synthesized by dealumination of Al-MCM-68 (HTS using $\text{TEBOP}^{2+}(\text{I}^-)_2$ as the SDA) and a subsequent gas–solid reaction between TiCl_4 vapor and dealuminated MCM-68 [104]. The obtained Ti-MCM-68 showed superior catalytic performance compared to that of TS-1 for phenol hydroxylation with hydrogen peroxide in terms of reactivity and para-product selectivity. However, the HTS of Al-MCM-68 requires an extremely long crystallization period (>14 days) using $\text{TEBOP}^{2+}(\text{I}^-)_2$ as the SDA. Peng et al. [105] found that Al-MCM-68 could be rapidly crystallized in only one day via the inter-zeolite transformation method using siliceous Beta zeolite as the silica source. The corresponding Ti-MCM-68 showed high catalytic activity for anisole hydroxylation. In addition, another MSE titanosilicate, Ti-UZM-35, synthesized by the combination of the dealumination of Al-UZM-35 (synthesized

using dimethyldipropylammonium hydroxide (DMDPAOH) as the SDA) and a subsequent gas–solid reaction [106] showed comparable reactivity and product selectivity to the Ti-MCM-68 zeolite in the hydroxylation of phenol. Ti-YNU-2 exhibited remarkably enhanced catalytic properties compared to Ti-MCM-68 although the preparation process was relatively complex [107]. To prepare Ti-YNU-2, an all-silica YNU-2P precursor with abundant internal defects was stabilized by steam treatment and subsequently treated with TiCl_4 vapor. Kubota et al. claimed that new five- or six-coordinated Ti species were present in Ti-YNU-2, which accounted for the enhanced catalytic reactivity and para-selectivity in phenol hydroxylation. In addition to the gas-phase Ti source, Ti-MCM-68, which has a high catalytic reactivity and para-selectivity for phenol hydroxylation, has been prepared using a liquid-phase source [102].

1.3.4 Synthesis of Other Large-Pore Titanosilicates

Other large-pore titanosilicates, such as Ti-ZSM-12 (unidimensional 12-MR pore channel) [108], Ti-ITQ-39 (3D $12 \times 12 \times 10$ -MR pore channel) [109], Ti-ITQ-7 (3D $12 \times 12 \times 12$ -MR pore channel) [110, 111], Ti-SSZ-33 (3D $12 \times 12 \times 10$ -MR pore channel) [112], Ti-IPC-2 (2D 12×10 -MR pore channel) [80, 113], Ti-SSZ-42 (unidimensional 12-MR pore channel) [114], Ti-SAPO-5 (unidimensional 12-MR pore channel) [115], and Ti-ITQ-17 (3D $12 \times 12 \times 12$ -MR pore channel) [116], have also been successfully synthesized. Ti-ZSM-12 has been prepared using hexamethylene bis(diethylmethylammonium) hydroxide as the SDA via HTS [108]. However, the catalytic activities of Ti-ZSM-12 in cyclohexene epoxidation with H_2O_2 and TBHP were both much lower than those of Ti-Beta, possibly due to its smaller unidimensional micropore channels ($5.6 \times 6.0 \text{ \AA}$) compared to Beta. Ti-ITQ-39, with its combination of medium- and large-pore channels, was synthesized using the HTS method [109]. Ti-ITQ-39 was highly active in linear and cyclic alkene epoxidation with H_2O_2 , showing unique epoxide selectivities compared to TS-1 (medium-pore) and Ti-Beta (large-pore). Ti-SSZ-33 and Ti-SSZ-42, with topologies of CON [112] and IFR [114], respectively, were post-synthesized by the insertion of Ti species into the corresponding borosilicates and were active for cycloalkene epoxidation. Similar to the Beta zeolite, ITQ-7 possesses 3D 12-MR pore channels with one sinusoidal 12-MR pore channel along the *c*-axis and two straight 12-MR pore channels along the *a*- and *b*-axes [117]. Ti-ITQ-7 was synthesized using 1,3,3-trimethyl-6-azonium-tricyclo[3.2.1.4_{6,6}]dodecane as the SDA in F^- media [111] and showed catalytic properties comparable to those of Ti-Beta(F) owing to the similar secondary building units in the two zeolite structures. The crystallization time was reduced from 12 days to 12 hours, and the Ti incorporation efficiency was increased from 17.2% to 51% by introducing Ge atoms into the synthetic gels because of the enhanced structural stability of the Ge atoms located in the double-four ring cages [110, 118]. With a higher Ti content, Ti-Ge-ITQ-7 showed superior activity in the epoxidation of various alkenes compared to Ti-ITQ-7. ITQ-17, with the BEC topology, has a 3D 12-MR pore channel system ($6.3 \times 7.5 \text{ \AA}$ and $6.0 \times 6.9 \text{ \AA}$). However, the titanogermanium

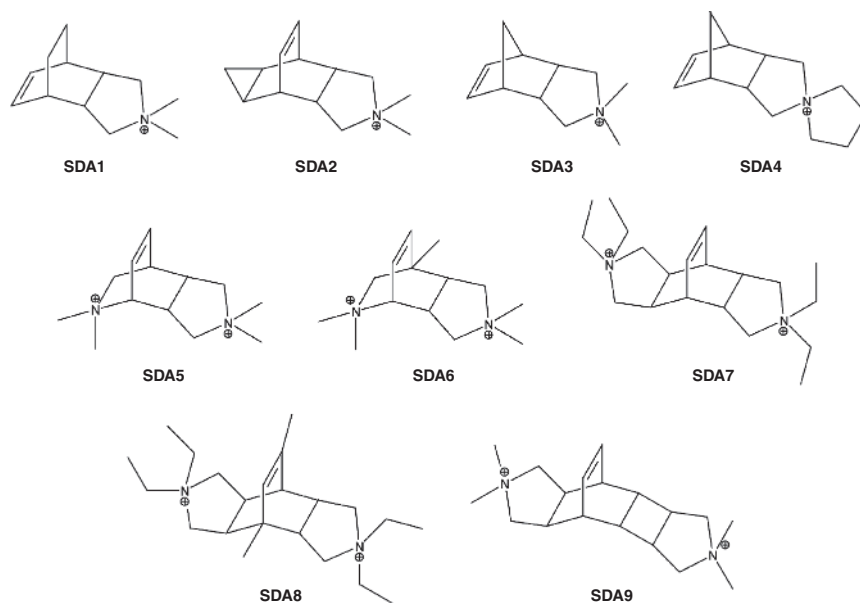


Figure 1.7 Different SDAs used for the synthesis of Ti-ITQ-17. Source: Reprinted with permission from Moliner et al. [116]. Copyright American Chemical Society (2008).

silicate ITQ-17 shows very low hydrothermal stability [116], and ITQ-17 with its stable zeolite structure can only be in the form of germanate [119] or silicogermanate [120]. Nevertheless, it was expected that Ge-free Ti-ITQ-17 should exhibit a superior catalytic behavior to Ti-Beta because the former has a larger pore opening compared to Ti-Beta ($6.6 \times 6.7 \text{ \AA}$ and $5.6 \times 5.6 \text{ \AA}$). All-silica ITQ-17 was first synthesized using 4,4-dimethyl-4-azonia-tricyclo[5.2.2.0^{2,6}]undec-8-ene Iodide as the SDA in buffered media containing hexafluorosilicate species and K^+ [121]. After the successful synthesis of all-silica ITQ-17, Ti-ITQ-17 was synthesized under similar conditions. However, the incorporation of Ti species into the zeolite framework was inhibited by K^+ [116]. Thus, further theoretical molecular modeling using different organic molecules as the SDA was performed to find a suitable SDA for Ti-ITQ-17 synthesis that would allow crystallization in the absence of K^+ . Among the nine designed SDAs, SDA9 showed an optimum directing ability for the crystallization of Ti-ITQ-17 (see Figure 1.7) [116]. The obtained Ti-ITQ-17 exhibited higher reactivity and epoxide selectivity than Ti-Beta for the epoxidation of bulky cycloalkenes.

1.4 Synthesis of Extra-Large-Pore Titanosilicates

The synthesis of extra-large-pore Ti-zeolites with 14-MR or larger is desirable because of the combination of high hydrothermal stability and accessibility to bulky molecules [122]. In recent years, many extra-large-pore titanosilicates have been obtained by crystallization in highly concentrated gels in the presence of Ge

atoms and F^- or by post-synthesis methods. Ti-DON [123] and Ti-CFI [124] with unidimensional 14-MR pore channels were synthesized using bis(pentamethylcyclopentadienyl) cobalt(III) hydroxide and *N*-methylsparteinium hydroxide as SDAs, respectively. However, the isomorphous incorporation of Ti atoms into the frameworks of DON and CFI is more difficult than that of TS-1. Moreover, extra-framework Ti species were found in both the Ti-DON and Ti-CFI samples. Recently, Ti-UTL, with a 2D intersecting 14-MR and 12-MR pore channels, was successfully synthesized in the form of titanogermanosilicate [80]. In addition, other extra-large-pore titanosilicates, such as Ti-ECNU-9 (2D 14×12 -MR pore channels) [125] and Ti-IWV (2D 12×10 -MR pore channels) [126], were successfully synthesized using post-synthesis methods, which will be further described in Chapter 2.

1.5 Synthesis of Mesoporous Titanosilicates

Ordered mesoporous molecular sieves with amorphous pore walls and uniform mesopore sizes up to 43 nm were first developed by Mobil in 1992 [127]. Corma et al. reported the first Ti-containing mesoporous molecular sieve, MCM-41 (Ti-MCM-41), which was active in selective epoxidation reactions involving bulky substrates [128]. Subsequently, a similar mesoporous titanosilicate Ti-HMS (hexagonal mesoporous silica) with higher activity than Ti-MCM-41 was developed by Tanev et al. [129]. Tatsumi et al. synthesized cubic Ti-MCM-48 with a 3D pore channel system [130] and Ti-SBA-15 with uniform tubular main channels varying from 5 to 30 nm and linked to micropores [131]. Ti-SBA-15 exhibited not only high hydrothermal stability but also excellent resistance to Ti leaching compared to Ti-MCM-41. Other mesoporous titanosilicates, such as hexagonal Ti-SBA-12 [132], cubic Ti-SBA-16 [132], and Ti-KIT-5 [133], have also been prepared. Generally, there are two strategies for synthesizing mesoporous titanosilicates: (i) direct HTS and (ii) the post-atom planting method [134]. In direct HTS, mesoporous titanosilicates are usually synthesized by adding Ti sources, such as TEOT, tetrapropyl orthotitanate, or TBOT, to the synthetic gels for the corresponding all-silica mesoporous materials and crystallization under similar conditions [129, 132]. However, some Ti atoms are trapped inside the amorphous pore walls and are inaccessible. Post-atom incorporation is a robust and universal method [134–136], which is more beneficial for introducing highly accessible Ti atoms than the direct HTS method. Benefiting from the high accessibility of the mesoporous structure, all of the above mesoporous titanosilicates are active in epoxidation reactions containing bulky substrates. The relationship between the synthesis conditions and formation of anatase TiO_2 is ambiguous although anatase TiO_2 has been observed in some mesoporous titanosilicates [132, 133]. Nevertheless, the anatase TiO_2 phase does not negatively affect epoxidation with organic hydroperoxides. In addition to the Ti coordination state, the hydrophilicity/hydrophobicity is another important property of mesoporous titanosilicates. The amorphous pore walls of mesoporous titanosilicates generate numerous silanol groups on the surface, which negatively

affect epoxidation reactions in terms of activity and epoxide selectivity [20]. Silylation with trimethylsilyl chloride [137] or hexamethyldisilazane [135] is simple but very effective for enhancing the hydrophobicity of mesoporous titanosilicates, although the thermal stability of such silylated samples is limited. In contrast, mesoporous titanosilicates silylated with fluorosilane species can be calcined at an elevated temperature of 500 °C in air [138]. After the silylation of Ti-SBA-15 with triethoxyfluorosilane, the adsorption capacity of water decreased by 85% compared to that of the parent material [138].

Mesoporosity was introduced into microporous zeolites for the fabrication of hierarchical zeolites to enhance the accessibility of active sites inside the micropores. The construction methods for hierarchical zeolites can be divided into top-down and bottom-up approaches. In the top-down route, a secondary pore structure is formed by the selective extraction of framework atoms from microporous zeolites via post-treatments, such as acid or alkaline leaching, steaming, or irradiation [139–145]. For titanosilicate zeolites, alkaline-derived desilication is more effective than acid-derived demetallation for introducing mesoporosity because of the Si-rich framework composition of titanosilicate zeolites. The concentration of NaOH aqueous solution should be below 0.2 mol L⁻¹ to avoid the collapse of zeolite structures when desilication of TS-1 is carried out in NaOH aqueous solution [146]. A hierarchical TS-1 zeolite with a hollow structure was synthesized using a mixture of TPAOH and NaOH. This TPAOH-assisted method is usually accompanied by a recrystallization process owing to the structure-directing nature of TPAOH, resulting in a well-preserved crystallinity and hierarchical structure. The removal of residual Na⁺ is necessary after desilication because the presence of Na⁺ is detrimental to the catalytic reactivity of the formed hierarchical titanosilicate zeolites [147]. In addition, hierarchical structures can be formed by treating microporous TS-1 zeolites with TBAOH and NaOH under appropriate treatment conditions [142]. Using bottom-up approaches, mesoporosity can be established during the synthesis of zeolites with or without the presence of a secondary template. Secondary templating methods can be further divided into hard- and soft-templating strategies. For hierarchical TS-1 zeolites obtained via hard-templating, the resultant shape and size of the mesopores are closely related to the template morphology. Nanocarbon particles, polymers, and biological materials can be used as hard templates for the synthesis of hierarchical titanosilicates [148–151]. This method can be used to successfully construct hierarchical zeolites with a controllable mesopore size distribution. The soft-templating route, using surfactants or organosilanes as secondary templates, is another option for constructing hierarchical titanosilicates. However, the relatively small SDAs for microporous structures and relatively large soft templates for mesoporous structures usually work in a competitive manner instead of cooperatively, leading to the formation of separated phases of microporous zeolites and mesoporous materials rather than hierarchical zeolite structures. Tuel et al. [152] reported the synthesis of a hierarchical TS-1 zeolite with organosilane as both a Si source and mesoporegenic agent that could be introduced into growing zeolite domains via the formation of covalent bonds with SiO₂ or TiO₂, thus avoiding the phase-separation phenomenon. Secondary soft templates,

which are used in the synthesis of hierarchical titanosilicate zeolites, can also direct the synthesis of mesoporous titanosilicates [153–155]. Secondary template-free strategies, including seed assistance, kinetic regulation of crystallization, and DGC, are efficient synthetic approaches for the construction of hierarchical zeolites [156]. The seed-assisted method is used not only to accelerate the crystallization process, enhance zeolite purity, adjust the morphology and crystalline size, and lower the synthetic cost but also to construct hierarchical titanosilicates [157]. However, significant challenges exist in constructing hierarchical titanosilicates with regular mesopore sizes and elucidating the formation mechanism of mesopores. In addition to the seed-assisted method, the kinetically regulated crystallization method has also been employed to construct hierarchical TS-1 zeolites by adjusting the zeolite nucleation and crystal growth, as well as manipulating the coordination and distribution of Ti species [158, 159].

1.6 Synthesis of ETSs

ETS is a class of zeolite-type titanosilicate materials that share SiO_4 tetrahedra and TiO_6^{2-} octahedra and possess strong Lewis basicity derived from the TiO_6^{2-} octahedra. The most representative ETS type titanosilicates are ETS-10 and ETS-4. The microporous titanosilicate ETS-10 was developed for the first time by Kuznicki [160]. It possesses a 12-MR pore channel approximately $4.9 \times 7.6 \text{ \AA}$ in diameter and is widely used in ion-exchange reactions, such as those involving rare-earth cations [161–164], dehydration [165], catalysis [166, 167], photocatalysis [168], and sensor materials [169]. ETS-10 can be hydrothermally synthesized in the presence of SDAs, including pyrrolidine, tetramethylammonium chloride, 1,2-diaminoethane, choline chloride, tetraethylammonium chloride, TPABr, tetrabutylammonium bromide, and hexaethyl diquat-5 bromide [170–177]. Several different Ti precursors, such as TiCl_3 [178], TiCl_4 [179], TiF_4 [178, 180], $(\text{NH}_4)_2\text{TiF}_6$ [178], and TiO_2 (anatase or rutile) [170, 178, 181], can be employed as Ti sources for the synthesis of ETS-10. The catalytic properties of ETS-10 are closely related to its morphology, which depends on the synthesis conditions and SDAs [182, 183]. ETS-10 can be synthesized as powders and pellets. In comparison with the powder form, ETS-10 in pellet form is easier to apply and recover. Moreover, self-bonded pellets avoid the negative effects of binders on the diffusion of reactants to the Ti species [184]. In addition, carbon nanotubes are also used for to prepare self-linked ETS-10 [185].

ETS-4, with two types of 8- and 12-MR pore channels, has a structure similar to that of mineral zorite [160, 186, 187]. Because the 12-MR pore channels are inaccessible owing to the pronounced stacking disorder along the *c*-direction, guest molecules can only enter the crystal interior via the 8-MR pore channels. The size of the 8-MR pore channels can be modulated by dehydration, i.e. the so-called molecular gate effect, which has been successfully applied in the commercial separation of nature gas [188]. The dehydration process is usually performed at 150–300 °C [188, 189]. The thermal stability of ETS-4 can be improved by using alkaline earth cations instead of Na^+ [188, 190]. The most representative example

is Sr-exchanged ETS-4, which has a thermal stability up to 350 °C [188]. In addition to the thermal adjustment of the pore size, replacing the anions in ETS-4 for the adjustment of openings can be used for the purification of multicomponent gases [191]. ETS-4 has been employed in the adsorption–separation of CH₄/N₂, O₂/Ar, O₂/N₂, and H₂/CH₄ [192–194]. In particular, Sr-exchanged ETS-4 shows high stability for the adsorption–separation of CH₄ and N₂ in pressure swing adsorption processes [195, 196]. ETS-4 can adsorb and enrich CH₄ from natural gases to alleviate energy shortages.

1.7 Conclusions

Titanosilicates, which can be divided into microporous, mesoporous, and hierarchical titanosilicates based on their textural properties and pore sizes, possess isolated tetrahedral Ti species as active sites and have expanded the application scope of zeolites as heterogeneous catalysts from the acid catalysis to redox fields. Although the HTS, DGC, fluoride-assisted media, and post-synthesis methods have achieved great success in the synthesis of titanosilicates, several challenges with regard to increasing the content and accessibility of Ti active sites still remain. Therefore, efforts should be directed toward developing hierarchical titanosilicates with high Ti contents and manipulating the coordination and distribution of Ti species.

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