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Synthesis of TS-1 zeolites from a polymer containing titanium and silicon†

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The synthesis of TS-1 zeolites is regarded as a milestone in zeolite history, and it has led to the revolution of the green oxidation system of using H₂O₂ as an oxidant, leaving only water as the byproduct. However, because of the highly hydrolyzable titanium source, the preparation of TS-1 requires complex synthesis conditions. Moreover, the difference in the hydrolysis rate between the silicon source and titanium source tends to increase the difficulty of titanium insertion into the framework, and it is easy to generate extra-framework Ti species during the synthesis. Here, a high-quality TS-1 zeolite with a large external surface area and free of extra-framework Ti species has been successfully synthesized by using a kind of novel polymer containing titanium and silicon. Due to the high hydrolysis resistance of the polymer reagent, a good matching of the hydrolysis rate between the silicon source and the titanium source is realized during crystallization, which facilitates the incorporation of titanium into the framework. Furthermore, the TS-1 zeolite exhibited excellent catalytic performance in *n*-hexane oxidation with hydrogen peroxide as the oxidant. This method of synthesizing zeolites from polymers is expected to be widely applied for the synthesis of other titanium-containing zeotype materials.

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Introduction

Titanium silicalite-1 (TS-1) is a very useful and special zeolite with an MFI-type framework composed of tetrahedral titanium and silicon atoms.^{1–3} In 1983, Taramasso *et al.* of Snamprogetti SPA filed the first patent for TS-1 zeolites.⁴ The discovery of TS-1 is regarded as a milestone in the history of zeolite and heterogeneous catalysis, and it has led to the revolution of the green oxidation system with H₂O₂ as an oxidant.^{5–11} TS-1 zeolites catalyse several oxidation reactions, most notably the epoxidation of propylene. Through this reaction, the oxygen atom in hydrogen peroxide (H₂O₂) is added to the propylene's carbon-carbon double bond. Propylene oxide, a widely used compound, is produced. Propylene oxide is always used as a raw material to manufacture the building blocks of polyurethane plastics.¹² Due to its great importance, the synthesis of TS-1 has been one of the most popular topics in zeolite synthesis research over the past few decades.¹³

The tetracoordinated titanium part of the TS-1 zeolite is also called framework titanium. The framework titanium in TS-1 zeolites has been thought to be the mononuclear active site.⁵

The tetrahedrally coordinated titanium can activate H₂O₂ and lead to the formation of an intermediate peroxo or hydroperoxo species.¹¹ More recently, Gordon *et al.* presented fresh evidence to suggest that the active sites in TS-1 are dinuclear.¹⁴ These findings might further the optimization of these titanium containing industrial catalysts. However, the synthesis of high-performance TS-1 zeolites with tetrahedrally coordinated titanium in the framework is still a challenging task. Previous studies showed that the easy hydrolysis of a titanium source such as tetraethyl titanate (TEOT) used in the zeolite synthesis made it difficult for titanium to be incorporated into the TS-1 framework.^{15–17} Thus, extra-framework Ti will be formed, including octahedrally coordinated Ti and anatase TiO₂. The anatase TiO₂ may cover the active sites in TS-1 and lead to the inefficient decomposition of H₂O₂.¹⁸ Therefore, the early TS-1 synthesis method using TEOT as a titanium source was complicated and needed to be performed in an ice water bath under a CO₂ atmosphere.⁵ Later, for an easier operation, tetrabutyl titanate (TBOT) was selected instead of TEOT as the titanium source in TS-1 synthesis because TBOT is more stable than TEOT.^{19,20} However, the subsequent steps of alcohol evaporation and aging processes would readily lead to the formation of extra-framework Ti species, which are unfavorable for the catalytic activity of TS-1.^{21–24} Therefore, numerous kinds of crystallization-mediating agents, such as hydrogen peroxide, ammonium carbonate, isopropyl alcohol or starch, were added into the system to inhibit the formation of extra-framework Ti species.^{15,19,25–27} Fan *et al.* reported the synthesis of titanium-rich

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TS-1 zeolites free of extra-framework titanium species based on the addition of $(\text{NH}_4)_2\text{CO}_3$.²¹ Zhang *et al.* proposed a strategy to synthesize anatase-free TS-1 zeolites by using Triton X-100 and rotational crystallization conditions.²⁸ However, most of the as-synthesized TS-1 samples still need to be treated with an acid to eliminate the extra-framework octahedral Ti species and anatase TiO_2 .^{21,29}

In this work, a polymer containing titanium and silicon was used to synthesize the TS-1 zeolite, which overcame the problems faced in the conventional synthesis of the zeolite and made the synthesis conditions less difficult and easier to perform, as well as avoiding the formation of extra-framework Ti species. This method of synthesizing zeolites from polymers is expected to have widespread applications.

Results and discussion

Ti-diol-Si polymer preparation and characterization

The polymer containing titanium and silicon was synthesized by using alkyl titanates, alkyl silicates and alkyl diols as the reactants through transesterification reactions. In these reactions, the alkoxy groups of the alkyl titanate and alkyl silicate were transesterified with alkyl diols to form a network-like polymer compound (Fig. 1a). The product was named Ti-diol-

Si polymer. During the transesterification reactions, the alkyl titanate served as both the reactant and the transesterification catalyst. The Ti-diol-Si polymer is similar to polyethylene terephthalate (PET), a widely used polymer, with the exception that the terephthalate in the PET polymer structure is substituted by a silicate or titanate.³⁰ The polymer sample (Ti-PEG-Si polymer) shown in Fig. 1b was synthesized with TEOT, tetraethyl orthosilicate (TEOS), and polyethylene glycol (PEG200). The photos show that the liquid raw materials are successfully transformed into a transparent solid product through transesterification polymerization, as shown in Fig. 1d. In this study, a series of polymers were prepared by varying the diols in the studies (Fig. 1c). The resulting polymers generally have polymerization degrees of 10–13 with a maximum of 15 (Table S1†). The degree of polymerization is determined by several parameters: the type of diol, reaction time, temperature, *etc.* The type of diol also affects the water solubility of the synthesized polymers. The polymers (Fig. 1e) synthesized with ethylene glycol (EG), 1,3-propanediol (PDO), 1,4-butanediol (BDO), 1,6-hexanediol (HDO) and polyethylene glycol 200 (PEG) have good water solubility, whereas those synthesized with 1,4-cyclohexanediol (CHD), 1,4-cyclohexanedimethanol (CHDM), and *p*-phenylenedimethanol (PXG) are insoluble in water. Regardless of which diol is used, the common feature of the

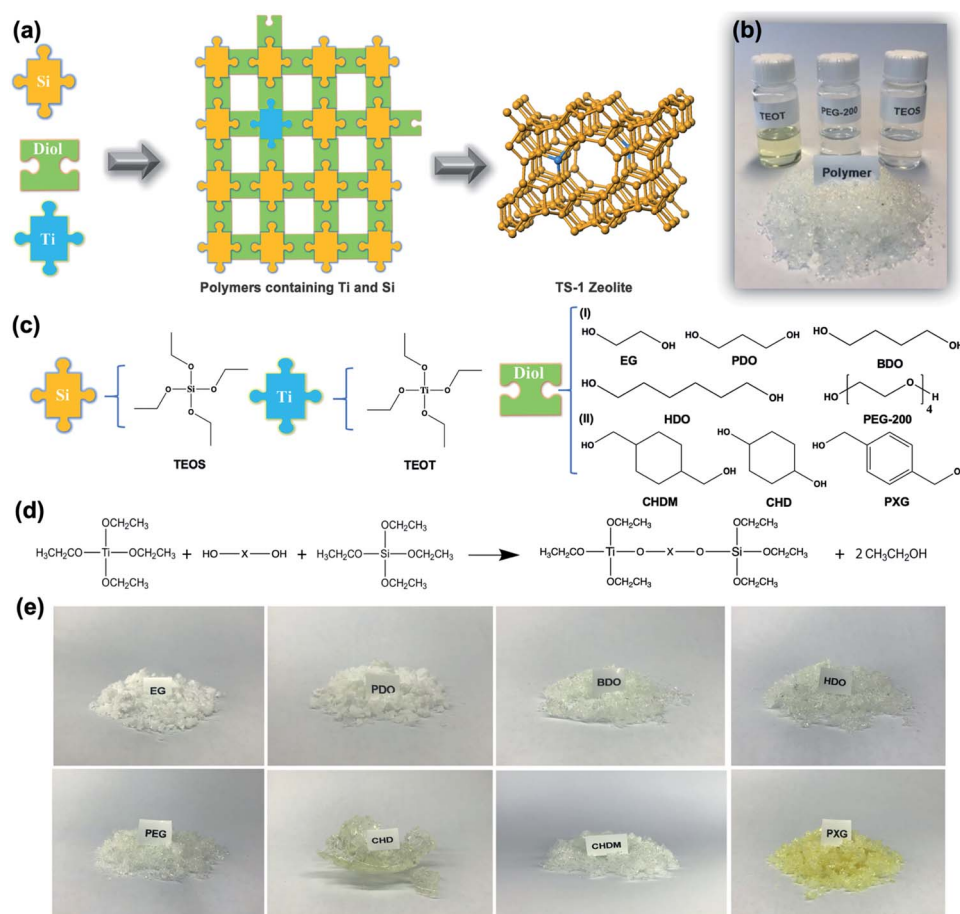


Fig. 1 (a) Synthesis of the TS-1 zeolite from Ti-diol-Si polymers. (b) Photos of the liquid raw materials and solid polymer products. (c) Types of alkyl titanates, alkyl silicates and alkyl diols used. (d) Transesterification reaction. (e) Photos of the Ti-diol-Si polymers.

polymer is that it is stable in water and difficult to hydrolyze. For example, TEOT, a quite easily hydrolyzed ester, was used as a raw material to synthesize the Ti-PEG-Si polymer with PEG as the diol reactant. The obtained polymer was observed to be stable and to dissolve in water and did not hydrolyze after more than 12 months at room temperature, as shown in Fig. S1.† It is known that the synthesis of the TS-1 zeolite requires strict avoidance of the rapid hydrolysis of the titanium source, so the synthesis conditions are complicated and harsh.¹³ From this point of view, the hydrolysis-resistant Ti-diol-Si polymers should be an ideal raw material for the synthesis of TS-1 zeolites. In the following experiments, the TS-1 zeolite was successfully synthesized from the polymers, and the synthesis process was a very simple, mild and easy operation.

As a representative sample among the synthesized polymers, the Ti-CHDM-Si polymer (polymer synthesized by using TEOT, TEOS and CHDM) is thoroughly investigated and presented here. Fig. 1e shows that the Ti-CHDM-Si polymer is a transparent solid with a certain toughness. Fig. 2f shows the thermogravimetric

analysis (TGA) result for the Ti-CHDM-Si polymer. It can be seen that the sample decomposes significantly at approximately 500 °C, which means that the polymer has quite high thermal stability and provides clear evidence of the successful polymerization of titanium and silicon esters with the diol species. The ¹³C MAS NMR analysis shows that the peaks of the methylene and methyl groups on the silicon ester and the titanium ester at 58.2 and 18.2 ppm, respectively, are significantly weakened and lowered, which proves that the ethyl groups of the original TEOS and TEOT are removed in the transesterification reactions (Fig. 2f II). From the ¹³C MAS NMR spectra of the other polymers, it can also be seen that the peaks at 58.2 and 18.2 ppm are significantly weakened. Other Ti-diol-Si polymers have similar properties, such as a transparent solid appearance, high decomposition temperature, and hydrolysis resistance.

TS-1 zeolite preparation and characterization

The synthesis procedures of TS-1 zeolites from the Ti-diol-Si polymers are illustrated as follows: the water-soluble polymers

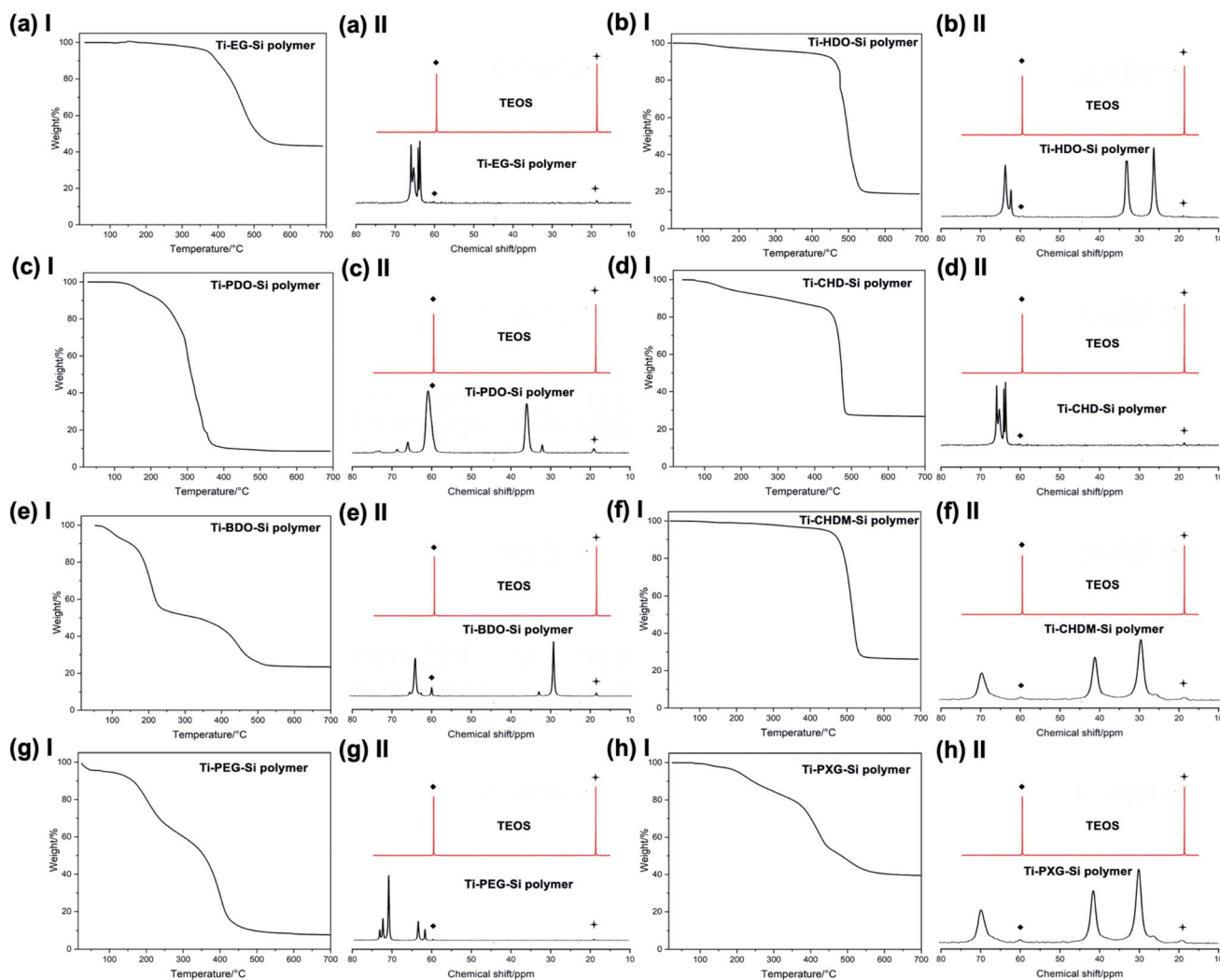


Fig. 2 (I) Thermogravimetric analysis (TGA) and (II) ¹³C MAS NMR spectrum of the Ti-diol-Si polymer. Different diols in Ti-diol-Si polymers (a) EG (b) HDO (c) PDO (d) CHD (e) BDO (f) CHDM (g) PEG (h) PXG.

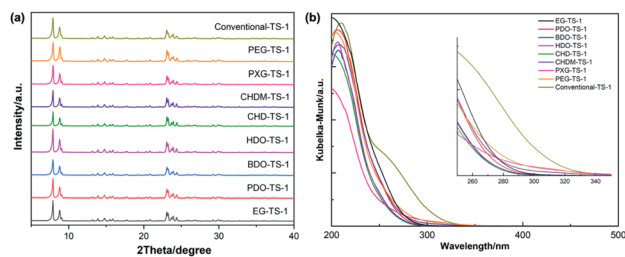


Fig. 3 (a) XRD patterns and (b) UV-Vis spectra of conventional TS-1 and TS-1 synthesized from different polymers. Inset: enlarged UV-Vis spectra in the region between 250 nm and 350 nm.

are dissolved in an aqueous solution of tetrapropylammonium hydroxide (TPAOH) with a certain ratio at room temperature and then are crystallized with or without rotation at a certain temperature. For the insoluble polymers, they are put into an aqueous solution of TPAOH and then directly crystallized under similar conditions to the water-soluble polymers. TPAOH with different ratios is provided in the ESI.† The molar ratio of titanium to silicon in the polymers is controlled at 1 : 24. The above methods did not require conventional alcohol evaporation and aging steps. Fig. 3a shows the X-ray diffraction (XRD) patterns of zeolites synthesized with eight different polymers, named EG-TS-1, PDO-TS-1, BDO-TS-1, HDO-TS-1, CHD-TS-1, CHDM-TS-1, PXG-TS-1, and PEG-TS-1. These patterns are in good agreement with the XRD patterns typical of the MFI topology. All the samples have five characteristic diffraction peaks of the MFI framework, which proves that the synthesized TS-1 zeolites have a pure phase and high crystallinity.³¹

UV-Vis spectroscopy was used to detect the coordination state of titanium in TS-1 (Fig. 3b). All the TS-1 zeolites synthesized from different polymers have a strong absorption band at a wavelength of 210 nm. The absorption peak here represents the tetrahedrally coordinated titanium in the framework. This tetracoordinated titanium part of the zeolite, which is also called framework Ti, is widely recognized as the active center of a catalytic oxidation reaction.^{32,33} Peaks in the wide band between 240 and 280 nm as well as at 330 nm are generally considered to indicate extra-framework titanium species.^{18,34} All the TS-1 samples synthesized using different polymers have no absorption band here, which proves that the extra-framework titanium species is not significantly formed in TS-1 during crystallization.

UV-Raman spectroscopy with excitation lines at 244 nm was employed to characterize the Ti species in TS-1 zeolites synthesized from different polymers, as shown in Fig. S19.† The Raman spectra of the TS-1 zeolites synthesized from different polymers showed strong Raman bands at 490, 530, and 1125 cm^{-1} , which had been assigned to the symmetric stretching and asymmetric stretching vibrations of framework Ti–O–Si species due to the resonance Raman effect.²² Besides, the Raman bands at 960 cm^{-1} also came from the asymmetric stretching of the framework TiO_4 units. It can be seen from the UV-Raman spectrum that titanium was incorporated in the framework of the TS-1 zeolites synthesized from different polymers.

In order to study the coordination environment of Ti species more clearly, the samples were also characterized by X-ray photoelectron spectroscopy (XPS), as shown in Fig. S20.† In the Ti 2p region, signals at binding energies of 458.4 and 464.1 eV appeared for all samples, while signals at binding energies of 459.8 and 465.2 eV appeared mainly in the samples synthesized by conventional methods. Generally, the binding energy values of 458.4 and 464.1 eV are assigned to the $2\text{P}_{3/2}$ and $2\text{P}_{1/2}$ photoelectrons of tetrahedrally coordinated framework Ti(IV) species. On the other hand, the binding energy values of 459.8 and 465.2 eV were mainly attributed to the $2\text{P}_{3/2}$ and $2\text{P}_{1/2}$ photoelectrons of octahedrally coordinated Ti(VI) species in extra-framework positions.^{35,36} The tetrahedrally coordinated framework Ti species are the dominating species in the TS-1 zeolites synthesized from different polymers. However, a significant increase of the octahedrally coordinated Ti(VI) species (extra-framework Ti) were observed in TS-1 synthesized by conventional methods. This also proved that TS-1 zeolites synthesized from the Ti–diol–Si polymer could effectively match the hydrolysis rate of the silicon source and titanium source and avoid the formation of extra-framework titanium species.

FTIR was used to evaluate the titanium species in the TS-1 zeolite samples. As shown in Fig. S22,† all the samples showed a band at 960 cm^{-1} , which was ascribed to the stretching vibration of the Si–O–Ti bond or the Si–O bond perturbed by the presence of Ti atoms in the framework.³⁷ Besides, the band at 800 cm^{-1} is characteristic of the MFI topology.³⁸ Therefore, the presence of titanium in the framework could be inferred from the FTIR analysis as shown in Fig. S22.†

Previous studies have found that the different hydrolysis rates of Si and Ti alkoxides lead to the formation of extra-framework titanium species during TS-1 crystallization.²¹ Therefore, many strategies, such as careful operation of the alcohol evaporation and aging steps and the addition of crystallization-mediating agents, have been used to control the hydrolysis rate, mainly that of the titanium source, to suppress extra-framework titanium formation.^{17,21,27} However, in the method described herein, an extra-framework titanium-free TS-1 zeolite could be synthesized easily and conveniently without complicated steps or additional crystallization-mediating agents. The mechanism might be interpreted as follows. When the Ti–diol–Si polymers were used for the synthesis of TS-

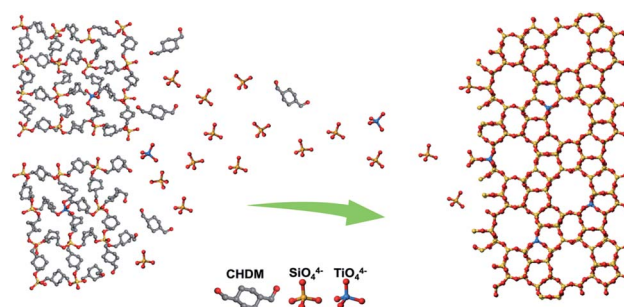


Fig. 4 Titanium sources and silicon sources were detached uniformly from the Ti–diol–Si polymers during crystallization.

Table 1 Brunauer–Emmett–Teller (BET) surface area and pore volume of TS-1 synthesized from different polymers

Samples	S_{BET}^a m ² g ⁻¹	S_{micro}^b m ² g ⁻¹	S_{ext}^b m ² g ⁻¹	V_{micro}^b cm ³ g ⁻¹	V_{meso}^c cm ³ g ⁻¹
EG-TS-1	406	304	102	0.15	0.04
PDO-TS-1	409	303	106	0.15	0.05
BDO-TS-1	407	303	104	0.14	0.06
HDO-TS-1	406	300	106	0.15	0.05
PEG-TS-1	410	286	124	0.13	0.06
HDO-TS-1-R	408	308	100	0.15	0.04
CHD-TS-1	405	311	94	0.15	0.05
CHDM-TS-1	398	317	81	0.14	0.05
PXG-TS-1	402	334	68	0.14	0.10
TS-1-C ^d	395	351	44	0.15	0.02

^a S_{BET} (total surface area) calculated using the BET method. ^b S_{micro} (micropore area), S_{ext} (external surface area) and V_{micro} (micropore volume) calculated using the *t*-plot method. ^c V_{meso} (mesopore volume) calculated using the BJH method (from adsorption). ^d TS-1 synthesized by conventional processes.

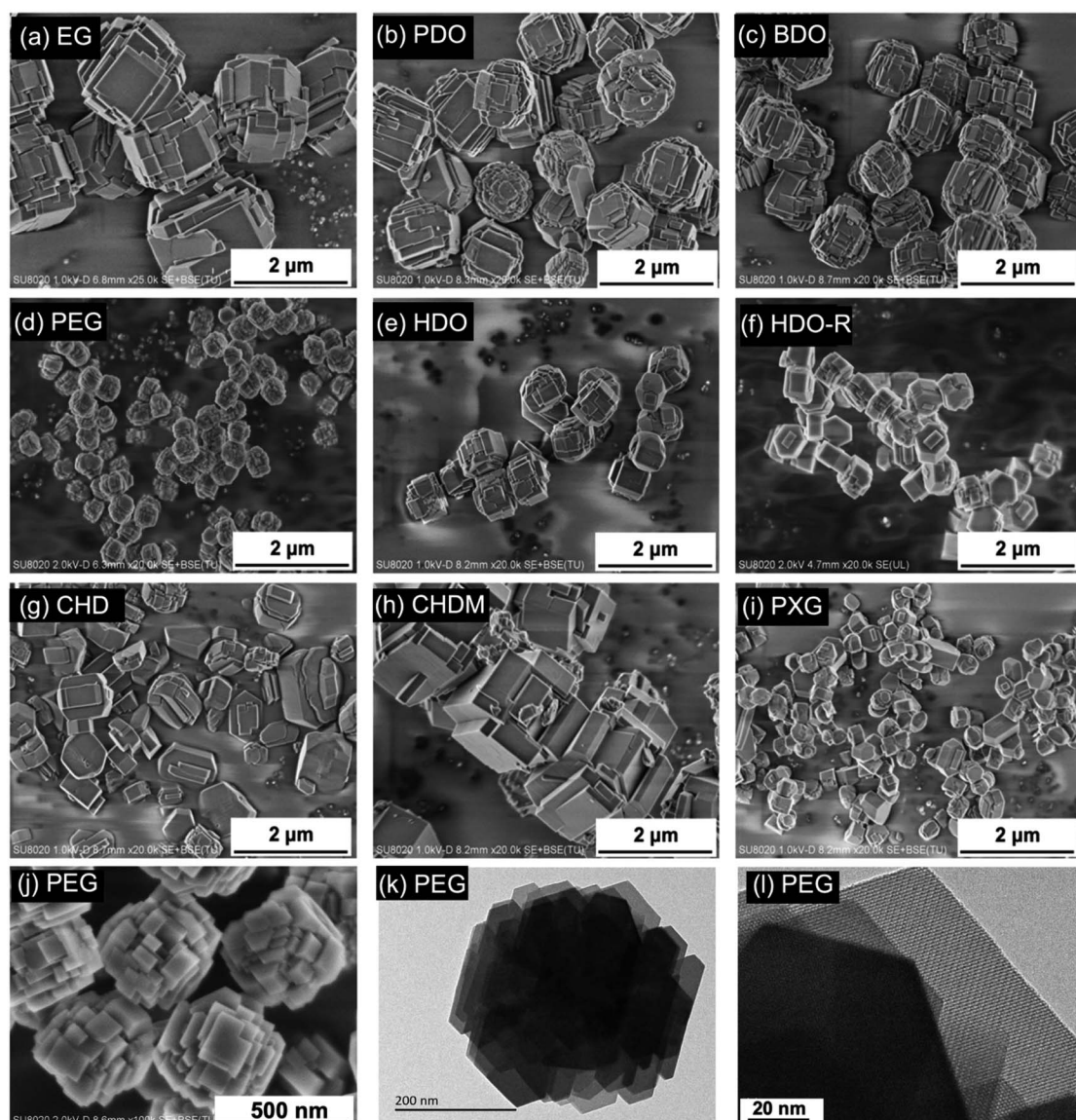
**Fig. 5** (a)–(j) SEM and (k) and (l) TEM images of TS-1 synthesized from Ti-diol-Si polymers.

Table 2 Catalytic results of the prepared TS-1 for the oxidation of *n*-hexane^a

Sample	Si/Ti ratio ^b in the catalyst	Conv. [%] based on <i>n</i> -hexane	Sel. [%]		H ₂ O ₂	
			2- and 3-ol	2- and 3-one	Conv. [%]	Sel. [%]
EG-TS-1	48.6	78.0	41.3	58.7	59.9	76.0
PDO-TS-1	52.8	78.5	45.4	54.6	53.1	87.5
BDO-TS-1	55.0	74.9	52.1	47.9	45.89	86.4
HDO-TS-1	48.8	77.5	41.3	58.7	61.4	80.7
CHD-TS-1	52.1	69.0	49.8	50.2	46.7	77.8
CHDM-TS-1	55.0	56.4	52.2	47.8	37.1	73.0
PXG-TS-1	52.0	52.2	39.3	60.7	26.4	47.14
PEG-TS-1	35.8	74.4	51.1	48.9	56.1	74.9
HDO-TS-1-R	53.3	78.8	46.3	53.7	48.9	97.6
TS-1-C ^c	43.3	34.4	39.3	60.7	26.4	47.1

^a Reaction conditions: 0.1 g of catalyst, 60 °C, 4 h, 10 ml of CH₃OH as solvent, 10 mmol of *n*-hexane, and 20 mmol of H₂O₂ (30% in aqueous solution). ^b The elemental compositions of TS-1 are determined by ICP. ^c TS-1 synthesized by conventional processes.

1, the titanium source and the silicon source in the polymers are uniformly connected by diols, so the opportunities for the titanium source and the silicon source to be detached from the polymers are equal. Therefore, a good matching of the hydrolysis rate between the silicon source and titanium source is realized during crystallization. As a result, the method of zeolite synthesis from Ti-diol-Si polymers can effectively promote the incorporation of titanium into the lattice and avoid the generation of extra-framework Ti species (Fig. 4).

In addition, it is noteworthy that the conventional alcohol evaporation process is transferred to the synthesis process of the polymers. Therefore, the alcohol evaporation and aging processes are omitted in zeolite synthesis, which will reduce the probability of extra-framework Ti species formation. Furthermore, in contrast to the conventional alcohol evaporation process, the polymer synthesis process produces anhydrous alcohol, which will facilitate recycling of the subsequent alcohol byproducts and reduce the cost of synthesis. The characterization of the low-temperature N₂ physical adsorption (Fig. S10,† Table 1) revealed that TS-1 synthesized from Ti-diol-Si polymers has a higher external surface area (124 m² g⁻¹) than the samples synthesized by conventional methods (44 m² g⁻¹).²⁸ These results suggest that the diols in the polymers may play an important role in the formation of the external surface area.³⁹

SEM and TEM images of the TS-1 zeolites synthesized from the polymers are displayed in Fig. 5. All samples have a typical MFI hexagonal morphology with a size distribution ranging from 0.3 μm to 1.8 μm. Besides, the TS-1 zeolites exhibit a knobbed surface spherical morphology with the assembly of nano-size particles, and this imparts a high external surface area character. The TEM images (Fig. 5k and l) of the TS-1 zeolites synthesized from Ti-PEG-Si polymers also demonstrated that the TS-1 zeolites had a vertical arrangement of all these nanoparticles. It was also found that the solubility of the Ti-diol-Si polymers has important effects on the morphology and crystal sizes of the TS-1 products. For soluble polymers such as Ti-EG-Si, Ti-HDO-Si, and Ti-PEG-Si, the crystals of the TS-1 products are uniform, as shown in Fig. 5a to e. For insoluble polymers (Ti-CHD-Si and Ti-CHDM-Si), the resultant TS-1

products had a large particle size, and the size distribution of the zeolite crystal was broad, as shown in Fig. 5g to i. Crystallization under rotating conditions was also investigated, and the sample was named HDO-R. The results show that the particle size of the samples obtained using rotating crystallization is uniform and small and that the crystal size is approximately 500 nm (Fig. 5f).

On the basis of the above characterization results, TS-1 zeolites synthesized from polymers has high crystallinity, a large external surface area, small particle size, and no extra-framework titanium species. All these properties indicate that the TS-1 samples should have good catalytic activities. The catalytic performances of the synthesized TS-1 samples were tested in the oxidation of *n*-hexane with hydrogen peroxide as the oxidant (Table 2). The results show that the TS-1 zeolite synthesized from polymers has excellent oxidation performance. Among the zeolites tested, the zeolite sample synthesized from HDO-based polymers under rotating conditions (HDO-TS-R) has the highest conversion rate of *n*-hexane (78.8%), and the utilization rate of hydrogen peroxide can reach 97.6%. Besides, there are no obvious changes of the *n*-hexane conversion with several reaction-regeneration cycles on TS-1 zeolites synthesized from polymers, as shown in Fig. S23.† The TS-1 zeolites synthesized from polymers also show higher activities in the oxidation of 1-hexene (Table S2†) and large molecules such as cyclohexene (Table S4†).

Conclusions

In summary, the method of synthesizing TS-1 from a polymer containing titanium and silicon (Ti-diol-Si polymers) is proven to be effective, simple, mild and easy to operate. Due to the hydrolysis resistance of the Ti-diol-Si polymers, a good matching of the hydrolysis rate between the silicon source and the titanium source is realized during crystallization, which facilitates the production of high-quality TS-1 zeolites free of extra-framework titanium species. Different crystallization procedures are selected according to the water solubilities of the polymers. The diol species in the polymers can also increase the

external surface area of TS-1. Most importantly, TS-1 synthesized from polymers showed excellent catalytic performance in *n*-hexane oxidation with hydrogen peroxide as the oxidant. It is worth mentioning that the synthesis method of zeolites from the Ti-diol-Si polymers could be successfully applied to the preparation of other titanium-containing materials, such as mesoporous titanium materials (Ti-MCM-41, Ti-MCM-48, *etc.*) and Ti-MOF materials (Ti-MIL125); the related work will be presented in subsequent reports. In addition, the titanium in the Ti-diol-Si polymers can be replaced by other heteroatoms, such as zirconium, tin, aluminum, phosphorus, and boron, and the resulting polymers can be used for the synthesis of heteroatom-doped materials, thereby reducing the difficulty in synthesizing or obtaining relevant materials with enhanced properties.

Experimental

Synthesis of polymers containing titanium and silicon

Polymers were synthesized basically according to the following molar composition: $0.96 \text{ SiO}_2 : 0.04 \text{ TiO}_2 : 2 \text{ diol}$. Polymers with a titanium content of 2% and 3% were also synthesized by the same method, and if not particularly emphasized, polymers with a titanium content of 4% were used as raw materials. A certain amount of diols was added to a round bottom flask. The diols used here were chosen among ethylene glycol (EG, 98.0 wt%, Aladdin), 1,3-propanediol (PDO, 98.5 wt%, Aladdin), 1,4-butanediol (BDO, 99.0 wt%, Aladdin), 1,6-hexanediol (HDO, 99.0 wt%, Aladdin), 1,4-cyclohexanediol (CHD, 98.0 wt%, Aladdin), 1,4-cyclohexanedimethanol (CHDM, 99.0 wt%, Aladdin), *p*-phenylenedimethanol (PXG, 99.0 wt%, Aladdin), and polyethylene glycol 200 (PEG, $M_n = 200$, Macklin). Then, tetraethyl orthosilicate (TEOS, 99.0 wt%, Aladdin) was added to the round bottom flask and stirred at 110 °C in an oil bath, followed by addition of tetraethyl titanate (TEOT, 35 wt% TiO_2 , Aladdin). In the process of product polymerization, the by-produced ethanol was collected by using a condensation tube, and the temperature of the oil bath was controlled according to the rate of ethanol distillation and gradually increased to 170 °C and maintained at 170 °C for 1 h. In order to promote the polymerization of the product and accelerate the reaction, the system was vacuumed at 170 °C, and vacuum treated for 1 h. After the reaction is completed, the polymerized solid product can be collected. Through the amount of ethanol collected in the reaction process, the number of ethoxy groups in TEOS and TEOT participating in the reaction can be calculated, and the degree of polymerization can be estimated.

Synthesis of TS-1 zeolites from polymers

TS-1 zeolites were synthesized from the above polymers. The synthesized eight different polymers had different water solubility. The water soluble polymers were Ti-EG-Si, Ti-PDO-Si, Ti-BDO-Si, Ti-HDO-Si, and Ti-PEG-Si polymers. The method for synthesizing TS-1 is as follows: a certain amount of polymers was directly dissolved in an aqueous solution of tetrapropylammonium hydroxide (TPAOH, 25.0 wt% aqueous solution,

SACHEM Americas) at room temperature to obtain a clear solution, without heating to evaporate alcohol as well as aging to hydrolyze titanium and silicon sources under a water bath. The clear solution was directly transferred to a stainless steel autoclave with a Teflon liner and crystallization at 170 °C for 24 h under static conditions by using a conventional oven. The water insoluble polymers were Ti-CHD-Si, Ti-CHDM-Si, and Ti-PXG-Si; a certain amount of polymers was added to an aqueous solution of tetrapropylammonium hydroxide (TPAOH) at room temperature, transferred to a stainless steel autoclave with a Teflon liner directly, and crystallized at 170 °C for 24 h under static conditions by using a conventional oven. The optimized molar composition of the synthetic TS-1 is as follows: $0.96 \text{ SiO}_2 : 0.04 \text{ TiO}_2 : 0.5 \text{ TPAOH} : 40 \text{ H}_2\text{O}$. The solid product was centrifuged, washed several times with deionized water, dried overnight in an oven at 100 °C, and then calcined at 550 °C for 6 h. The samples were named according to the polymer used: EG-TS-1, PDO-TS-1, BDO-TS-1, HDO-TS-1, PEG-TS-1, CHD-TS-1, CHDM-TS-1, and PXG-TS-1. If not specially specified, the polymers with a titanium content of 4% were used for the synthesis of TS-1 zeolites.

TPAOH with different ratios is also investigated and the Ti-PEG-Si polymer is used as the precursor; the molar composition is $0.96 \text{ SiO}_2 : 0.04 \text{ TiO}_2 : 0.2 \text{ TPAOH} : 40 \text{ H}_2\text{O}$. When the concentration of TPAOH in the system decreases, TS-1 zeolites can also be synthesized. The size of the TS-1 zeolites is increased, up to 1.5 μm (Fig. S16 and S21†).

For the TS-1-HDO-Rotation sample, the same synthetic procedure as described above was used, except for using a rotary oven and crystallization at 170 °C for 1 day with a rotation rate of 35 rpm.

Synthesis of conventional TS-1 zeolites

Titanium tetra-butoxide (TBOT, 99.0 wt%, Aladdin) and tetrapropylammonium hydroxide (TPAOH, 25.0 wt% aqueous solution, SACHEM Americas) were mixed under stirring. After 30 minutes, tetraethyl orthosilicate (TEOS, 99.0 wt%, Aladdin) as the silicon source was added to the solution. Then, the solution was heated to 353 K to remove alcohol produced by hydrolysis. After cooling down, the clear solution was directly transferred to a stainless steel autoclave with a Teflon liner and crystallized at 170 °C for 3 days under static conditions by using a conventional oven. The optimized molar composition of the synthetic conventional TS-1 is as follows: $0.96 \text{ SiO}_2 : 0.04 \text{ TiO}_2 : 0.5 \text{ TPAOH} : 40 \text{ H}_2\text{O}$. The solid product was centrifuged, washed several times with deionized water, dried overnight in an oven at 100 °C, and then calcined at 550 °C for 6 h.

Catalyst reaction

The oxidation of *n*-hexane was carried out by using hydrogen peroxide as an oxidizing agent (30 wt% aqueous solution, Aladdin) in a closed stainless steel reactor with a Teflon liner under vigorous stirring. The reaction temperature was controlled at 60 °C with a water bath, and the reaction time was 4 h. In a typical run, 0.1 g of catalyst, 10 ml of methanol, 10 mmol of *n*-hexane, and 20 mmol of hydrogen peroxide

(30 wt%) were mixed in the reactor. After the completion of the reaction, the product was analyzed with a gas chromatograph (Agilent 7890A), equipped with a 50 m capillary column (HP-PONA), and an FID detector was used. All products were confirmed by GC-MS (Agilent 7890B-5977A). The amount of the unconverted H_2O_2 was determined with a 0.1 M aqueous solution of $\text{Ce}(\text{SO}_4)_2$ by using a titration method. The changes of the *n*-hexane conversion with several reaction-regeneration cycles on TS-1 zeolites synthesized from polymers (TS-1-HDO-R) were carried out as follows: after the first catalytic reaction, the catalyst was recovered by filtration and washed with ethanol and acetone several times. The catalyst was dried at 120 °C and further calcined at 550 °C for 3 h under air before checking the catalytic recyclability.

The oxidation of 1-hexene was carried out by using hydrogen peroxide as an oxidizing agent (30 wt% aqueous solution, Aladdin) in a closed stainless steel reactor with a Teflon liner under vigorous stirring. The reaction temperature was controlled at 60 °C with a water bath, and the reaction time was 2 h. In a typical run, 0.05 g of catalyst, 10 ml of methanol, 10 mmol of *n*-hexane, and 10 mmol of hydrogen peroxide (30 wt%) were mixed in the reactor. After the completion of the reaction, the product was analyzed with a gas chromatograph (Agilent 7890A), equipped with a 50 m capillary column (HP-PONA), and an FID detector was used. All products were confirmed by GC-MS (Agilent 7890B-5977A). The amount of the unconverted H_2O_2 was determined with a 0.1 M aqueous solution of $\text{Ce}(\text{SO}_4)_2$ by using a titration method. The oxidation of cyclohexene was carried out by the same process with the following reaction conditions: 0.1 g of catalyst, 60 °C, 4 h, 5 ml of acetonitrile as the solvent, 4.5 mmol of cyclohexene, and 4.5 mmol of H_2O_2 (30% in aqueous solution). The results of the oxidation of the substrates were calculated as follows:

$$\text{Substrate conversion (mol\%)} = \frac{(\text{initial moles} - \text{final moles})}{\text{initial moles}} \times 100\%$$

$$\text{Product selectivity (\%)} = \frac{\text{moles of a defined product}}{\text{moles of products produced}} \times 100\%$$

$$\text{H}_2\text{O}_2 \text{ conversion (mol\%)} = \frac{\text{moles of H}_2\text{O}_2 \text{ consumed}}{\text{moles of H}_2\text{O}_2 \text{ in the feed}} \times 100\%$$

$$\text{H}_2\text{O}_2 \text{ selectivity (\%)} = \frac{\text{moles of products produced}}{\text{moles of H}_2\text{O}_2 \text{ consumed}} \times 100\%$$

Material characterization

The X-ray diffraction (XRD) patterns were acquired using a PANalytical X'Pert PRO X-ray diffractometer using Cu-K α radiation with $\lambda = 1.54059 \text{ \AA}$, operating at 40 kV and 40 mA. The samples were scanned at $12^\circ \text{ min}^{-1}$ between 2θ angles of $5\text{--}65^\circ$. Scanning Electron Microscopy (SEM) images were collected

with a Hitachi SU8020 scanning electron microscope. Transmission Electron Microscope (TEM) images were collected with a JEOL2100 transmission electron microscope. N_2 adsorption-desorption isotherms of the samples were obtained at 77 K on a Micromeritics Gemini VII system after the zeolites were degassed at 623 K for 4 h. The specific surface areas (S_{BET}) and total pore volume (V_t) were obtained using the Brunauer-Emmett-Teller (BET) equation. Micropore surface areas (S_{micro}) were calculated based on the *t*-plot method. The solid state ^{29}Si -NMR and ^{13}C -NMR experiments were conducted on a Bruker Avance III spectrometer equipped with a 14.1 T wide-bore magnet. The UV-Vis DRS (diffuse reflectance spectroscopy) spectra of the catalyst were recorded over the range of 200 nm to 600 nm against the support as the reference, on a VARIAN CARY 5000. Thermogravimetric analysis (TGA) measurement was conducted on a TA Q-600 analyzer with a heating rate of $10^\circ \text{C min}^{-1}$ from ambient temperature to 700 °C in a 100 ml min^{-1} N_2 flow. Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis was performed with a PerkinElmer 7300DV. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher ESCALAB 250Xi spectrometer (monochromated AlK α , $h\nu = 1486.6 \text{ eV}$, 15 kV, and 10.8 mA) with a resolution of pass energy of 50 eV. The XPS peaks were calibrated with the binding energy of C 1s peaks at 284.8 eV. UV-Raman spectra were recorded using a home-made single stage UV-Raman spectrograph with a spectral resolution of 2 cm^{-1} . The single-frequency UV laser line at 244 nm was from an efficient external cavity frequency doubler (WaveTrain, Spectra-Physics) of a 488 nm single-frequency laser (Genesis, CX 488, Coherent). The exciting source had an output of 10 mW and the power of the laser at the sample was about 2.0 mW. Fourier transform infrared spectroscopy (FTIR) was performed on a Bruker Vextex70 spectroscopy equipped with an MCT detector.

Author contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript. Yunpeng Xu and Zhongmin Liu conceived and guided the research project. Jiacheng Xing and Danhua Yuan designed and carried out the experiments and characterization. The manuscript was drafted by Jiacheng Xing and Danhua Yuan. Hanbang Liu and Yansi Tong took part in the discussion of experimental data and gave some suggestions.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 D. R. C. Huybrechts, L. Debruycker and P. A. Jacobs, *Nature*, 1990, **345**, 240–242.
- 2 T. Tatsumi, M. Nakamura, S. Negishi and H. Tominaga, *J. Chem. Soc., Chem. Commun.*, 1990, 476–477.
- 3 C. Li, G. Xiong, Q. Xin, J. K. Liu, P. L. Ying, Z. C. Feng, J. Li, W. B. Yang, Y. Z. Wang, G. R. Wang, X. Y. Liu, M. Lin, X. Q. Wang and E. Z. Min, *Angew. Chem., Int. Ed.*, 1999, **38**, 2220–2222.
- 4 M. Taramasso, G. Perego and B. Notari, *US Pat.*, 4410501, 1983.
- 5 X. B. Wang, X. F. Zhang, Y. Wang, H. O. Liu, J. S. Qiu, J. Q. Wang, W. Han and K. L. Yeung, *ACS Catal.*, 2011, **1**, 437–445.
- 6 Y. Kuwahara, K. Nishizawa, T. Nakajima, T. Kamegawa, K. Mori and H. Yamashita, *J. Am. Chem. Soc.*, 2011, **133**, 12462–12465.
- 7 G. J. Hutchings, D. F. Lee and A. R. Miniham, *Catal. Lett.*, 1995, **33**, 369–385.
- 8 J. E. Gallot, M. P. Kapoor and S. Kaliaguine, *AIChE J.*, 1998, **44**, 1438–1454.
- 9 C. Shen, Y. J. Wang, J. H. Xu and G. S. Luo, *Chem. Eng. J.*, 2015, **259**, 552–561.
- 10 Z. C. Shan, Z. D. Lu, L. Wang, C. Zhou, L. M. Ren, L. Zhang, X. J. Meng, S. J. Ma and F. S. Xiao, *ChemCatChem*, 2010, **2**, 407–412.
- 11 O. J. Kerton, P. McMorn, D. Bethell, F. King, F. Hancock, A. Burrows, C. J. Kiely, S. Ellwood and G. Hutchings, *Phys. Chem. Chem. Phys.*, 2005, **7**, 2671–2678.
- 12 V. Russo, R. Tesser, E. Santacesaria and M. Di Serio, *Ind. Eng. Chem. Res.*, 2014, **53**, 6274–6287.
- 13 L. Nemeth and S. R. Bare, in *Advances in Catalysis*, Vol. 57, ed. F. C. Jentoft, Elsevier Academic Press Inc, San Diego, 2014, vol. 57, pp. 1–97.
- 14 C. P. Gordon, H. Engler, A. S. Tragl, M. Plodinec, T. Lunkenbein, A. Berkessel, J. H. Teles, A.-N. Parvulescu and C. Coperet, *Nature*, 2020, **586**, 708–713.
- 15 A. Keshavaraja, V. Ramaswamy, H. S. Soni, A. V. Ramaswamy and P. Ratnasamy, *J. Catal.*, 1995, **157**, 501–511.
- 16 A. Thangaraj, M. J. Eapen, S. Sivasanker and P. Ratnasamy, *Zeolites*, 1992, **12**, 943–950.
- 17 A. Thangaraj and S. Sivasanker, *J. Chem. Soc., Chem. Commun.*, 1992, 123–124.
- 18 Z. F. Liu and R. J. Davis, *J. Phys. Chem.*, 1994, **98**, 1253–1261.
- 19 A. Thangaraj, R. Kumar and P. Ratnasamy, *J. Catal.*, 1991, **131**, 294–297.
- 20 A. Tuel and Y. Bentaarit, *Appl. Catal., A*, 1994, **110**, 137–151.
- 21 W. B. Fan, R. G. Duan, T. Yokoi, P. Wu, Y. Kubota and T. Tatsumi, *J. Am. Chem. Soc.*, 2008, **130**, 10150–10164.
- 22 Q. Guo, K. J. Sun, Z. C. Feng, G. N. Li, M. L. Guo, F. T. Fan and C. Li, *Chem.–Eur. J.*, 2012, **18**, 13854–13860.
- 23 J. Su, G. Xiong, J. C. Zhou, W. H. Liu, D. H. Zhou, G. R. Wang, X. S. Wang and H. C. Guo, *J. Catal.*, 2012, **288**, 1–7.
- 24 J. Q. Zhuang, G. Yang, D. Ma, X. J. Lan, X. M. Liu, X. W. Han, X. H. Bao and U. Mueller, *Angew. Chem., Int. Ed.*, 2004, **43**, 6377–6381.
- 25 E. Jorda, A. Tuel, R. Teissier and J. Kervennal, *Zeolites*, 1997, **19**, 238–245.
- 26 J. G. Wang, Y. B. Wang, T. Tatsumi and Y. L. Zhao, *J. Catal.*, 2016, **338**, 321–328.
- 27 T. Zhang, Y. Zuo, M. Liu, C. Song and X. Guo, *ACS Omega*, 2016, **1**, 1034–1040.
- 28 T. Zhang, X. Chen, G. Chen, M. Chen, R. Bai, M. Jia and J. Yu, *J. Mater. Chem. A*, 2018, **6**, 9473–9479.
- 29 T. Tatsumi, K. A. Koyano and Y. Shimizu, *Appl. Catal., A*, 2000, **200**, 125–134.
- 30 R. D. Daubeney and C. W. Bunn, *Proc. R. Soc. London, Ser. A*, 1954, **226**, 531–542.
- 31 M. M. J. Treacy, J. B. Higgins and R. vonBallmoos, *Zeolites*, 1996, **16**, 327–328.
- 32 F. Geobaldo, S. Bordiga, A. Zecchina, E. Giamello, G. Leofanti and G. Petrini, *Catal. Lett.*, 1992, **16**, 109–115.
- 33 G. N. Vayssilov, *Catal. Rev.: Sci. Eng.*, 1997, **39**, 209–251.
- 34 G. Xiong, Y. Y. Cao, Z. D. Guo, Q. Y. Jia, F. P. Tian and L. P. Liu, *Phys. Chem. Chem. Phys.*, 2016, **18**, 190–196.
- 35 J.-P. Nogier, Y. Millot, P. P. Man, C. Methivier, M. Che and S. Dzwigaj, *Catal. Lett.*, 2009, **130**, 588–592.
- 36 B. Tang, W. Dai, X. Sun, N. Guan, L. Li and M. Hunger, *Green Chem.*, 2014, **16**, 2281–2291.
- 37 Z. F. Liu and R. J. Davis, *J. Phys. Chem.*, 1994, **98**, 1253–1261.
- 38 S. L. Burkett and M. E. Davis, *Chem. Mater.*, 1995, **7**, 920–928.
- 39 S. T. Du, F. Li, Q. M. Sun, N. Wang, M. J. Jia and J. H. Yu, *Chem. Commun.*, 2016, **52**, 3368–3371.