Preparation and catalytic performance of a novel titanosilicate with FER topology

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Abstract
Ti-PLS-3, a kind of layered titanosilicates of FER topology was developed by hydrothermal synthesis with the help of using pure silica PLS-3 as seed. The Si/Ti ratio of this material can be adjusted in a wide range from 20 — ∞. The structure and active sites of Ti-PLS-3 were detected by various characterization. After mild acid treatment to eliminate the hexa-coordinated extra-framework Ti species, the resulting material turned out to be a more effective catalyst for epoxidation of 1-hexene with H2O2 than reported FER type Ti-containing material Ti-FER.

1. Introduction
Zeolites can be used as catalyst, adsorbent and ion exchanger because of its adjustable framework compositions and varied microporous crystalline structures [1]. H+ form FER-type zeolite composed of ferrierite sheets possesses a unique two-dimensional (2D) channel system (10 rings (10-R) intersected by 8-R channels) has already been proved to be an efficient Bronst acid heterogeneous catalyst for processing 1-butene isomerization, and the yield of the product isobutene can reach near to the thermodynamic equilibrium of this reaction [2—11].

The unique pore system plays a decisive role in its excellent catalytic performance for skeletal isomerization of 1-butene. Based on this special structure, if we can nd a way to introduce other heteroatom into the framework of FER, we may produce novel heterogeneous catalysts with excellent catalytic performance.

The synthesis of FER topology is usually conducted in inorganic system with alkali cation to assist crystallization [8]. But this classic method usually requires high temperatures for crystallization. There are also reports about preparing FER-type zeolite by using building units of calcined layered precursor RUB-36 which possesses CDO topology with the help of seeding technique [9]. It is a long-studied subject for hydrothermal synthesis of zeolites with FER topology using organic molecules as the structure-directing agents (SDA). There are over 30 kinds of organic SDA reported to be used for synthesizing FER zeolites, and most of them are ammoniums or amines with N atoms [10—12]. But for all these synthesis method, there are very few reports for introducing heteroatoms besides Al in the crystallization process, which greatly limits the application of this structure as a heterogeneous catalyst.

Except traditional 3D FER structures, the layered precursors of FER topology have also been studied. PREFER is the firstly reported FER-type 2D layered structure [13]. It is consisted of the interlaced arrangement of ferrierite sheets and organic SDA along [001] direction which is its layered direction. Calcination of PREFER will cause the decomposition of the template and the condensation of the interlayer silicon hydroxyls and to transform it into a 3D structure. The morphology of PREFER is plate-like and relatively large (ca. 20 × 100 μm). Later on, a dual templating strategy for synthesizing layered FER-type materials by using two organic molecules with different sizes has also been reported and structures similar to PREFER can be produced by this method [14—16]. However, these FER-type layered materials all possess a relatively large morphology which is adverse for catalyzing.
There is another layered precursor with the FER topology named as PLS-3 has been reported [17, 18]. Different from the materials previously reported, PLS-3 possesses crystal size of nanometer scale, only 50–150 nm, which will be beneficial to its catalytic performance. Indeed, Al-PLS-3, its Al-containing material, has been verified to be an efficient catalyst for isomerization of 1-butene [19]. But the hydrothermal synthesis and catalytic performance of PLS-3 containing other types of heteroatoms are not yet reported.

Zeolites with framework Ti as active sites are a kind of catalyst with industrial application value. They can be widely used in epoxidation of alkenes, ammoxidation of cyclohexanone, oxidation of saturated hydrocarbons and hydroxylation of aromatic hydrocarbons (benzene and phenol) process [20]. Among these, epoxidation of 1-hexene is a commonly used characterization of catalytic performance for Ti-containing zeolites, a variety of titanosilicate zeolites have been reported to be tested by this reaction, like TS-1 [21], Ti-MWW [22], ECNU-9 [23], and so on. The typical solvents for this reaction are CH3OH and CH3CN, which need to be selected according to the hydrophilicity of the catalyst [24]. For now, only three kinds of Ti-containing zeolite TS-1, Ti-MWW and Ti-MOR are applied in industry [25]. Developing of new titanosilicate zeolites with excellent catalytic performance and stability is of research significance. Our previous work has introduced Ti into the framework of interlayer expanded structure of FER generated from PLS-3. The resulting materials possess excellent catalytic performance for epoxidation of olefin [23, 26]. This result shows that the layer of FER zeolite is suitable for Ti active sites and the nanoscale morphology of PLS-3 is conductive to catalysis. However, the preparation of interlayer expanded structure is complicated and the cost is high. Meanwhile, the hydrothermal and thermal stability of the interlayer expanded structure are not as good as that of the conventional 3D structure. There are also reports about the preparing of titanosilicate of FER topology in non-aqueous alkali-free seeded system [27] or of CDO topology possessed ferrierite sheets [28]. But they only mentioned the synthesis of these materials, the catalytic properties are not involved. Thus, preparing of Ti-containing FER type zeolite with catalytic activity by directly hydrothermal synthesis is of research significance from the perspective of industrial application.

We have investigated the synthetic methods and catalytic properties for Ti-containing material of PLS-3, Ti-PLS-3, in this manuscript. Its physicochemical properties were tested by various means of characterization. Furthermore, its catalytic performance was characterized by epoxidation of 1-hexene and compared to the reported Ti-containing FER type material Ti-FER. With small crystal morphology and various Si/Ti ratios, Ti-PLS-3 has been verified to be a more effective catalyst than Ti-FER.

2. Materials and methods

2.1. Preparing of the materials

2.1.1. Preparing of pure silica PLS-3

Lamellar zeolite of FER topology, PLS-3, was hydrothermal synthesized according to the reference reported method [17]. H-kanemite, TEAOH (25 wt% water solution), NaOH and H2O were mixed uniformly with the molar ratio of 1.0 SiO2 : 0.04 NaOH : 0.2 TEA+ : 6.5 H2O. The starting mixture was reacted in the Teflon-lined autoclave at 443 K for 24 h. After filtration and washed with 500 ml deionized water, the product was used as seeds.

2.1.2. Preparing of Ti-PLS-3

The method for synthesis of titanosilicate Ti-PLS-3 was similar to pure silica PLS-3. Typically, H-kanemite, TBOT (tetrabutyl titanate), NaOH, TEAOH, H2O and pure silica PLS-3 as seed were mixed uniformly. The molar composition was 1.0 SiO2 : 0.2 TEA+ : 6.5 H2O : 1/a TBOT : b Seed : c NaOH (a ranged from 30 to 80, b ranged from 0 to 0.3, c ranged from 0 to 0.04). The starting mixture was reacted at 443 K for 1 d. After filtered, washed with distilled water, and dried at 353 K for 10 h, we got Ti-PLS-3-x (x means the original Si/Ti ratio of the reactant gel). The lamellar titanosilicate Ti-PLS-3 was calcined at 823 K for 10 h in air to give rise to its 3D FER structure.

2.1.3. Acid treatment of Ti-PLS-3

The layered zeolite Ti-PLS-3 was post-treated in 0.125 M HCl/H2O solution at 323 K for 5 h (S : L = 1 : 30). Then the resulting solid material was filtrated and washed with 500 ml deionized water. The resulting material named as Ti-PLS-3-x-acid. The Ti-PLS-3-n-acid materials were calcined at 823 K for 10 h in air to remove the organic substrates occluded between the layers and form their 3D structure.

2.2. Characterization methods

The type of x-ray diffractometer was X’ Pert PRO MPD (Cu-Kα radiation, λ = 1.5405 Å). The type of SEM instrument was Quanta200 microscope. N2 adsorption measurements were carried out on a BEL-MAX gas/vapor
adsorption instrument at 77 K (All the samples were evacuated at 573 K for 10 h before characterization). The $S_{\text{BET}}$ and $V_{\text{total}}$ were calculated by the Brunauer–Emmett–Teller method. UV–vis spectra were carried out on a PerkinElmer Lambda 35 spectrophotometer (190–500 nm, interval of 2 nm). The IR spectra were recorded on a Nicolet Nexus 670 FT-IR spectrometer in absorbance mode at a spectral resolution of 2 cm$^{-1}$ using KBr to dilute the samples (3 wt%). Ti content was tested by ICP on a VISTA–MPX atomic emission spectrometer. TG curves were tested on a METTLER TOLEDO TGA/SDTA 851® equipment (298 to 1073 K, 10 K min$^{-1}$).

2.3. Catalytic reactions
In a typical run, the reactants composed of 10 mmol 1-hexene, 10 mmol H$_2$O$_2$ (30 wt%), 50 mg catalyst (powder) and 7.8 g CH$_3$CN (solvent) were reacted in a 50 ml flask at 333 K for 2 h (water bath heating, magnetic stirring). The activity and selectivity of this reaction was analyzed by a Shimadzu GC-14B equipment. The activity was assigned to the conversion of reactant 1-hexene and selectivity was calculated for the main product 1,2- epoxy hexane.

3. Results and discussion
3.1. Hydrothermal synthesis of Ti-PLS-3
Figure S1 si available online at stacks.iop.org/MRX/7/045501/mmedia gives the XRD diffractions of the Ti-PLS-3 materials that were prepared using TBOT as Ti source with Si/Ti ratio of 50 and different Na/Si ratios. As shown in reference [17], the pure silica lamellar precursor PLS-3 is crystallized easily in this system. Obviously, the nucleation and crystallization process was disturbed by the heteroatom Ti in the reactant mixture. Crystallinity of Ti-PLS-3 was largely determined by the content of Na$^+$ according to figure S1. Decreasing the Na/Si ratio from 0.04 to 0, the crystallinity of the product reduced gradually (figures S1(a)–(c)). The addition of Na$^+$ was beneficial to the crystallization process. But the introduction of Na$^+$ usually adversely affects the activity of heteroatom Ti. In order to solve this problem, we introduced pure silica PLS-3 as seed to the synthesis system. Figures S2(b) and (c) exhibits the XRD diffractions of the materials that were synthesized in addition of uncalcined and calcined pure silica PLS-3 as seed, respectively. We can see that the sample synthesized with 30 wt% uncalcined pure silica PLS-3 as seed had similar crystallinity with the sample synthesized with Na/Si ratio equaled to 0.04. Thus, in order to ensure the activity of heteroatom Ti, we employed the synthesis system in addition of pure silica PLS-3 as seed without Na$^+$. Then we investigated the effect of seed addition on the crystallinity of the products. Figure S3 shows the XRD diffractions of the products that were prepared in addition of different amount of seed with Si/Ti ratio equaled to 50. The addition of seed was beneficial to the improvement of crystallization degree of the product. The more the seed was added, the higher the crystallinity of product can reach. When the addition amount of seed reached 30 wt% (figure S3(d)), the product was completely crystallized. Therefore, in later study in this paper, we took 30 wt% as the amount of seed.

Figure 1 exhibits the XRD diffractions of Ti-PLS-3 that were synthesized with different Si/Ti ratio from 20–80. The samples showed good crystallinity when Si/Ti ratio was more than 30. After calcined at 823 K for 10 h, the layered structure-related (200) diffraction of Ti-PLS-3 shifted from 7.6° to 9.4° because of the removal of occluded organic SDA and dehydration of interlayer hydroxyl groups (figure 2). The structure of layered zeolite Ti-PLS-3 was more modifiable and changeable than the conventional FER zeolite. After simply calcination, the layered structure can transform from precursor to its conventional 3D FER topology (figure 3).

Taking sample prepared from Si/Ti ratio equals to 50 as an example, figure 4(a) gives the representative SEM image of Ti-PLS-3-50. The morphology of Ti-PLS-3-50 was nanoscale like pure silica PLS-3 [17]. It was rod-like and with crystal size about 50–150 nm. There was no obvious amorphous phase in Ti-PLS-3–50 according to its SEM image, verifying that it was a highly crystallined pure phase material.

The textural properties of calcined Ti-PLS-3-40 and Ti-PLS-3-50 are shown in table S1 (No.1 and No.2) as examples. The $S_{\text{BET}}$ of these samples was given by the Brunauer–Emmett–Teller (BET) method. Since an obvious increase in the adsorbed volume occurred at $P/P_0 > 0.9$ (figure S4), the $V_{\text{total}}$ of Ti-PLS-3 materials was calculated from the isotherms at $P/P_0 < 0.9$. This was caused by the interparticle condensed macropores and adsorption of N$_2$ for small crystal material like Ti-PLS-3. This phenomenon was also reported in its pure silicon materials [17]. ICP data suggested that the bulk Si/Ti ratios of Ti-PLS-3 materials were close to the compositions of the reactants (table 1, No.2 and No.4), indicative of the condensation of Si source and Ti source were synchronized during crystallization.

IR spectra can be used to characterize Ti-containing zeolites, since they exhibit a characteristic absorbance in the structural vibration region around 960 cm$^{-1}$, which is confirmed to be the fingerprint of framework Ti [30]. Figure 5(A) exhibits the FT-IR spectra of Ti-PLS-3-n. As shown in figure 5(A), Ti-PLS-3 samples with various Si/Ti ratios all exhibited an expected symmetric band at 960 cm$^{-1}$. When the Ti contents of the sample
Figure 1. XRD diffractions of Ti-PLS-3-x prepared with Si/Ti ratio ranged from 20–80, 20 (a), 30 (b), 40 (c), 50 (d), 60 (e) and 80 (f). Other conditions: molar ratio, 1.0 SiO$_2$:0.2 TEA$^+$: 6.5 H$_2$O; 30% uncalcined seed; temp., 443 K; time, 1 d. (B) The corresponding calcined forms of figure 1(A).

Figure 2. The corresponding calcined forms of figure 1.

Figure 3. The schematic diagram of structural transformation from as made Ti-PLS-3 to its corresponding 3D FER structure.
increased, the peak intensity increased simultaneously. This indicated that we got titanosilicate zeolites having tetrahedrally coordinated framework Ti species.

UV–vis spectroscopy is widely used in detecting metallosilicates involved Ti, Sn or Zr atoms, since it can give the information about the coordination states of the transition metal atoms in zeolites [31]. Figure 5(B) shows the UV–vis spectra of Ti-PLS-3 materials prepared with different Ti contents. They all exhibited the characteristic peak of tetrahedrally coordinated framework Ti species at 210 nm. And when decreased the Si/Ti ratio in the starting gel, the intensity of 210 nm band increased simultaneously. This phenomenon indicated that there were framework Ti ions in Ti-PLS-3 and the Ti ions were incorporated mostly into the framework. There was also a weak absorption peak at 260 nm beside 210 nm existed whose peak intensity increased with the increasing of Ti contents. This was caused by the presence of minor hexa-coordinated extra-framework Ti species. It will adversely affect the catalytic performance of the Ti-containing zeolites [32].

3.2. Acid treatment of Ti-PLS-3

Harsh acid treatment conditions will lead to the formation of interlayer expanded structure [33] and result in TiO2 dense phase which cannot be removed by post-treatment [32]. Thus we used low concentrations and low temperature acid treatment to reduce the hexa-coordinated extra-framework Ti species. Figure 6(A) exhibits the

Table 1. Conversion and TON for the Epoxidation of 1-hexene over different Ti-containing zeolites.

| No. | Sample            | Si/Ti | Conv./% | TON |
|-----|-------------------|-------|---------|-----|
| 1   | Ti-PLS-3-20-cal   | 21    | —       | —   |
| 2   | Ti-PLS-3-30-cal   | 32    | —       | —   |
| 3   | Ti-PLS-3-40-cal   | 47    | 1.5     | 9   |
| 4   | Ti-PLS-3-50-cal   | 51    | 2.0     | 12  |
| 5   | Ti-PLS-3-60-cal   | 63    | 2.1     | 16  |
| 6   | Ti-PLS-3-80-cal   | 90    | 0.5     | 5   |
| 7   | Ti-PLS-3-20-acid-cal | 26   | 3.5     | 11  |
| 8   | Ti-PLS-3-30-acid-cal | 44   | 4.2     | 22  |
| 9   | Ti-PLS-3-40-acid-cal | 54   | 4.5     | 29  |
| 10  | Ti-PLS-3-50-acid-cal | 65   | 6.3     | 49  |
| 11  | Ti-PLS-3-60-acid-cal | 72   | 5.7     | 50  |
| 12  | Ti-PLS-3-80-acid-cal | 95   | 5.5     | 64  |
| 13  | Ti-FER e 1.3 wt% TiO2 | 1.3   | 3.2     | 6   |

* Reaction conditions: catalyst (0.05 g), CH3CN (7.8 g), 1-hexene (10 mmol), H2O2 (10 mmol; 31% aqueous solution), 333 K, 2 h.
* Given by ICP.
* Abbreviation of conversion, represented the proportion of reactant 1-hexene converted after reacted for 2 h.
* TON, Turnover number, represented molar amount of converted 1-hexene per Ti site in mol (mol-Ti)-1.
* Data in reference [29].
XRD patterns of Ti-PLS-3 sample with Si/Ti ratios of 20, 30, 50 and 80 after post-treated in 0.125 M HCl/H₂O solution at 323 K for 5 h and further calcination. These samples all showed the similar XRD patterns with 3D FER, indicated there was no interlayer expanded structure existed. The containing of organic SDA changes in lamellar precursor Ti-PLS-3 during the acid treatment and it was investigated by TG analysis. Figure S5 shows TG curves of as-synthesized Ti-PLS-3-50 and Ti-PLS-3-50-acid. The weight loss before 373 K of both these two materials was corresponding to the desorption of water, lost about 3.0 wt%. Then, a rapid weight loss of 9.5% for Ti-PLS-3-50-acid and 19.5% for Ti-PLS-3-50 was observed. This fact suggested that about 60% of the organic species were removed by the mild acid treatment of Ti-PLS-3. This was different from harsh acid treatment reported before [34]. The removing of intercalated SDA made room for Si species to form interlayer expanded structure. The less amount of template removal caused by mild acid treatment may be the reason why no interlayer expanded structure was formed. The morphology of the sample through acid treatment was the same as the parent material (figure 4(b)).

UV–vis spectra of Ti-PLS-3-acid materials with different Ti contents after calcination are given in figure 6(B). The weak band at 260 nm disappeared, implied the removal of hexa-coordinated extra-framework...
Ti species in these materials. The Si/Ti ratios of Ti-PLS-3-acid given by ICP were slightly higher than the original ones (table 1), indicating the small loss of Ti atom.

3.3. Catalytic performance

Epoxidation of 1-hexene using H$_2$O$_2$ as oxidant was used to evaluating the catalytic ability of Ti-containing catalysts prepared above. Illustration above table 1 is the schematic diagram of this reaction and the reaction process on the titanosilicate zeolites is as follows. Active sites in Ti-containing zeolites are dispersed Ti species which can be used as Lewis acid sites to activate hydrogen peroxide to form Ti–O$^–$–O$^–$–O$^–$–H intermediate. Oxygen near the Ti atom (O$^–$) is more electrophilic than the other oxygen (O$^–$), then the O$^–$ atom attacks the double bond group (C=C) with high electron cloud density in 1-hexene, achieving efficient oxygen transfer and finishing the epoxidation [24]. Figure S6 exhibits the catalytic performance of Ti-PLS-3-50-acid-cal for epoxidation of 1-hexene by time. Conversion of 1-hexene tended to balance after a growth stage. We chose two hours as the reaction time for other materials. The overall trend for catalytic performance of all Ti-PLS-3 materials we prepared is that, after the acid treatment, the catalytic activity of the samples increased compared to the samples without acid treatment. According to the UV–vis and ICP data discussed above, the result of acid treatment was to remove the hexa-coordinated non-framework Ti species and reduced the Ti content of the material. Thus the removal of hexa-coordinated extra-framework Ti species from the materials was beneficial to the improvement of their catalytic performance despite of the loss of Ti active sites during acid treatment. This result also indicated that the state of the active sites was more important than the content. Sample Ti-PLS-3-50-acid-cal exhibited the highest activity among all these materials because of its relatively high crystallinity and Ti content. Furthermore, the TON number of epoxidation of 1-hexene catalyzed by Ti-PLS-3-80-acid-cal can reach 64, which is much higher than the reported FER type Ti containing materials Ti-FER (table 1, Nos. 13) [29]. This should be due to its smaller crystal size.

4. Conclusions

A novel Ti-containing FER type zeolite Ti-PLS-3 has been synthesized by hydrothermal synthesis. We investigate the synthesis condition from Na/Si ratio, Si/Ti ratio, species and quantities of seeds. The results showed that: The addition of Na ions is necessary for crystallization without seeds, and the best ratio is Na/Si = 0.04. The addition of Ti ions as active site will bring negative impact on crystallization, when Si/Ti ratio is more than 30, we can prepare products with good crystallinity. The introduction of seeds can bring beneficial effects for crystallization, and using pure silica PLS-3 without calcination as seeds is better than calcined one. The resulting material possesses framework Ti and exhibits better catalytic properties than the reported FER type materials Ti-FER.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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