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Synthesis, characterization and catalytic properties of low cost titanium silicalite

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Abstract

The synthesis of titanium silicalite by two methods (gas–solid isomorphous substitution of Ti^{4+} for Si^{4+} and hydrothermal crystallization synthesis), aiming at decreasing its cost, and the characterization of the prepared catalyst are presented.

In the hydrothermal crystallization synthesis method of titanium silicalite-1 (TS-1), TPABr can be used to replace TPAOH and the amount of TPABr can be decreased to 0.05 (TPA^+/SiO_2). Organic amine cannot act as a template in the presence of TPA^+. It can only regulate the basicity of the gel. The order of the template effect of different templates is as follows: $TPA^+>TBA^+>TEA^+\gg$organic amine. In the preparation of titanium-containing zeolite by secondary synthesis, the nature of the precursor and the preparation conditions have great influence on the incorporation of titanium into the framework. The mechanism of gas–solid isomorphous substitution is proposed, and under its guidance, we have successfully prepared Ti-ZSM-5, Ti-ZSM-11, Ti-β, and Ti-mordenite.

The synthesized titanium-containing zeolites have been evaluated through catalytic hydroxylation of phenol, oxidation of styrene and epoxidation of propylene with aqueous H_2O_2. Results show that the Ti-containing zeolites possess high activity both in hydroxylation, styrene oxidation and in epoxidation. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Titanium silicalite; Gas–solid isomorphous substitution; Synthesis; Template effect; Selective oxidation; Reaction mechanism

1. Introduction

Titanium silicalite-1 (TS-1) was discovered in 1983 by research workers of Enichem [1]. Its distinctive catalytic properties have attracted attention of several other groups who also started research in this field [2–8]. TS-1 is usually synthesized by using tetrapropylammonium hydroxide (TPAOH) solution, which acts as the structure-directing agent and provides the alkalinity necessary for the crystallization of the zeolite. However, the synthesis requires stringent conditions, particularly the absence of alkali metal cations in the precursor gel. Therefore, TS-1 is a very expensive catalyst whose synthesis requires the preparation of alkali-free TPAOH solution. In order to decrease the cost of titanium silicalite, we have adopted two methods; one is gas–solid isomorphous substitution in which the use of the expensive TPAOH as the template is avoided, and the other is a hydrothermal method in which TPAOH is replaced by TPABr. Results of testing the prepared catalysts in selective oxidation reaction show that these two methods of preparing TS-1 are satisfactory.

In this paper we present the main results of preparing TS-1 with the above-mentioned methods and the characterization of the prepared catalysts. Effect of

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conditions in the gas–solid isomorphous substitution preparation and the nature of precursor on the incorporation of Ti into the product TS-1 are investigated. A mechanism for the gas–solid isomorphous substitution is put forward. The effects of the nature of the organic amine, the amount of TPABr and the effect of mixed template on the incorporation of titanium into the framework are discussed in detail.

2. Experimental

There are two methods of synthesizing titanium-containing zeolite: gas–solid isomorphous substitution of Ti^{4+} for Si^{4+} and hydrothermal crystallization synthesis, which have been described in the literature [9–12]. TS-1 samples used in this work were prepared as follows: according to the first method, the precursor was calcined at 540°C for 3–8 h to get rid of water and the organic templates, and then treated with aqueous HCl solution to remove Na^{+} and Al^{3+} (B^{3+}). In a vertical quarts reactor, the precursor was outgassed at 450°C for 4 h, then gaseous $TiCl_4$ and nitrogen were passed through the reactor. After reaction, the product was washed with ethanol. In the second method, the appropriate amount of tetrabutyl titanate in isopropyl alcohol was hydrolyzed in advance under ambient conditions. Then H_2O_2 and organic amines were added to the above solution. The resulting solution was added to the silica sol while stirring. The final gel was sealed in an autoclave and hydrothermal crystallization was carried out at 150–190°C for 3–8 days. After cooling, the resulting solids were separated, washed with deionized water and dried in air.

IR spectra of the prepared TS-1 samples were collected on a Perkin-Elmer FT-5DX spectrometer (KBr pellets), and UV–Vis measurements performed on Shimadzu UV-240 by using the diffuse reflectance technique in the range 190–490 nm. Freshly prepared silicalite was used as the reference. XRD spectra were recorded on an XD-3A powder diffractometer with Cu K_α radiation. MAS NMR spectra were recorded on a Bruker DRX 400 spectrometer at room temperature. For the measurement of ^{13}C CP/MAS NMR spectra, a relaxation delay of 2 s was used; contact time was 2 ms and the spinning frequency was 4–6 kHz. ^{13}C chemical shifts were referred to adamatane. For the measurement of ^{29}Si CP/MAS NMR spectra, a relaxation delay of 4 s was applied, the frequency of ^{29}Si was 79.5 MHz, and chemical shifts were referred to DSS.

The catalytic properties of titanium-containing zeolite samples were evaluated through three test reactions: hydroxylation of phenol, oxidation of styrene and epoxidation of propylene. The reaction conditions are similar to those described in the literature [9,10,13,14]. Typical reaction conditions are as follows: hydroxylation of phenol with H_2O_2, phenol/H_2O_2=1 (molar ratio), acetone as the solvent, wt. of catalyst=0.5 g, reaction temperature, 80°C, reaction time, 6 h. Oxidation of styrene with H_2O_2, styrene/H_2O_2=2.2 (molar ratio), acetone as the solvent, wt. of catalyst=0.6 g, reaction temperature, 70°C, reaction time, 6 h. Epoxidation of propylene with H_2O_2, vol. of methanol=31.6 ml, vol. of aqueous H_2O_2=2 ml, wt. of catalyst=0.4 g, propylene pressure, 0.8 MPa, reaction time, 90 min, reaction temperature, 60°C.

3. Results and discussion

3.1. Hydrothermal synthesis of TS-1 with cheap template

3.1.1. Hydrothermal synthesis of TS-1 with TPABr as the template

As is well known, TPAOH acts as the structure-directing agent and provides the alkalinity in the synthesis of TS-1. However, TPAOH is very expensive. There is no commercial product in the Chinese market, which makes the cost of the synthesized TS-1 very high. A possible way of decreasing the cost of TS-1 is to use TPABr (usually free from alkali metal cations) and some base to replace TPAOH, which has been reported by many authors [15–18]. Thus by using $Ti(OC_4H_9)_4$ as the titanium source, TPABr as the template, and different organic amines (1,6-hexanediamine, *n*-butylamine, ethylenediamine, diethylamine, triethanolamine, TBAOH and TEAOH) as the base we have successfully synthesized TS-1 (Si/Ti=33 in gel). Fig. 1 shows IR spectra of the titanium silicalites synthesized from different organic bases. From these spectra, we can see that they all have a characteristic peak at about 960 cm^{-1}, which indicates that titanium has been incorporated into the framework of zeolite. Using triethanolamine as the base, the

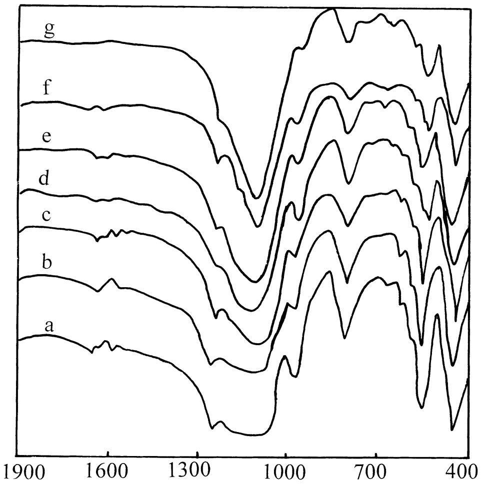

Fig. 1. IR spectra of TS-1 synthesized with TPABr and different amines as the base: (a) *n*-butylamine; (b) TEAOH; (c) TBAOH; (d) 1,6-hexanediamine; (e) ethylenediamine; (f) diethylamine; (g) triethanolamine.

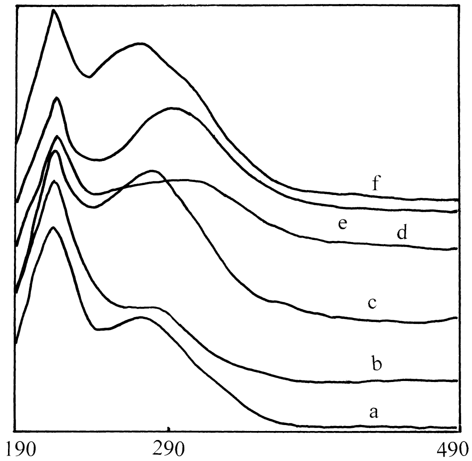

Fig. 2. UV–Vis spectra of TS-1 synthesized with different amines as the base: (a) *n*-butylamine; (b) TEAOH; (c) TBAOH; (d) 1,6-hexanediamine; (e) ethylenediamine; (f) diethylamine.

intensity of the 960 cm^{-1} peak is weaker than that in the spectra of samples obtained using other amines as the base and the XRD spectrum of the TS-1 shows low crystallinity. The reason is that triethanolamine coordinates with Ti^{4+} or Al^{3+} to form a stable complex, which prevents the incorporation of titanium into the framework and affects the crystallinity of TS-1 [19]. When *n*-butylamine was used as the base, increasing the amount of *n*-butylamine did not increase the intensity of the 960 cm^{-1} band. However, when using TEAOH as the base, decreasing the amount of TEAOH caused an increase in the intensity of 960 cm^{-1} peak. This phenomenon is being investigated. UV–Vis spectra of all prepared titanium silicalites (Fig. 2) show two absorption peaks: one at 220 nm, which is attributed to tetra-coordinated titanium, another at 270–280 nm, which is attributed to Ti^{4+} ions in an octahedral coordination with two water molecules in the coordination sphere or small hydrated oligomeric TiO_x species. This explanation is strongly supported by a decrease of the intensity in this region upon dehydration of the sample, and is in agreement with the work of Geobaldo et al. [20]. The peak at about 330 nm does not appear in all spectra, indicating that there is no anatase-TiO_2 present in the product. When TEAOH or *n*-butylamine was used as the base, the intensity of the absorption peak at 270–280 nm was low. Moreover, if MgO was used as the reference, the UV–Vis spectra of all the samples show one wide absorption peak at 230–250 nm. So, we suggest that the reference is mentioned if UV–Vis is used to characterize TS-1. In the system of TPABr and aqueous ammonia, the effect of Si/Ti in gel, of crystallization time and temperature and of the use of seeds on the synthesis of TS-1 was studied. Results show that the Si/Ti in the gel is similar to that in the product, and that the unit cell parameter increases with the increasing of Si/Ti ratio. This indicates that titanium has been incorporated into the framework. TS-1 can be synthesized with crystallization times of 2–5 days and crystallization temperature of 150–180°C. The addition of seeds decreases the crystal size [12,21].

^{13}C CP/MAS NMR is an important tool to study the mechanism of the reaction in the synthesis of TS-1. Fig. 3 gives ^{13}C CP/MAS NMR spectra of TS-1 synthesized with different organic amines as the base. It can be seen that the signals of the organic base do not appear in all the patterns, only the signal of TPA^+. So it can be concluded that only TPA^+ is trapped in the zeolite and acts as the structure-directing agent. The organic base serves to regulate the alkalinity of the gel. The above results provide a proof of the validity of substituting TPABr and a base for TPAOH.

The amount of TPABr used in the synthesis is a key factor in decreasing the cost of the synthesized TS-1. In the system of TPABr and $NH_3{\cdot}H_2O$, the effect of the

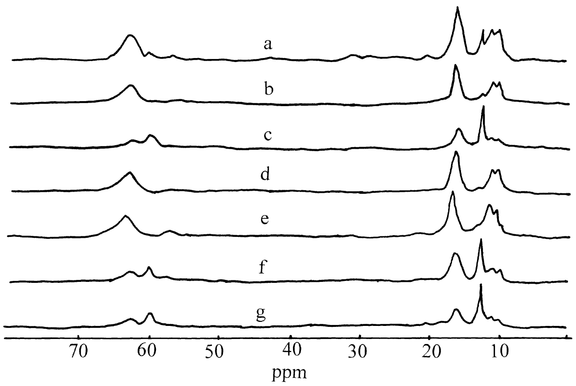

Fig. 3. ^{13}C CP/MAS NMR spectra of TS-1 synthesized with different amines as the base: (a) diethylamine; (b) *n*-butylamine; (c) 1,6-hexanediamine; (d) ethylenediamine; (e) aqueous ammonia; (f) triethanolamine; (g) no addition of base.

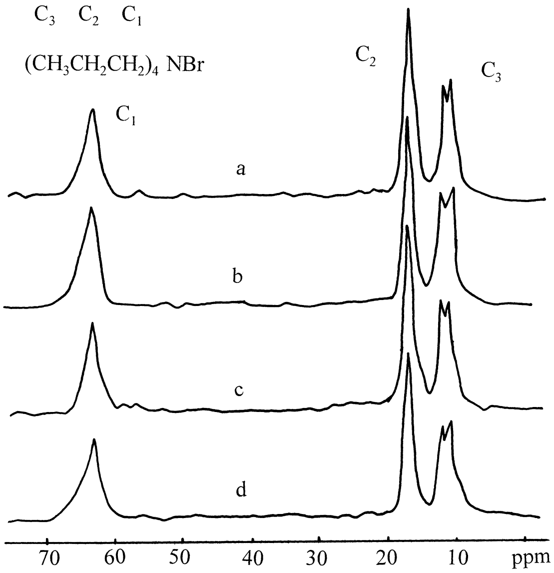

Fig. 4. ^{13}C CP/MAS NMR spectra of TS-1 synthesized in the presence of TPABr (TPABr/SiO$_2$=0.25) and *n*-butylamine (*n*BA): (a) *n*BA/SiO$_2$=0.2; (b) *n*BA/SiO$_2$=2.0; (c) *n*BA/SiO$_2$=0.2, and tripropylamine added; (d) *n*BA/SiO$_2$=0.2, and NaOH added.

amount of TPABr on the property of the synthesized product was studied in detail [22]. XRD spectra show that only when TPA$^+$/SiO$_2$$\geq$0.05, TS-1 with high crystallinity can be obtained. IR spectra show that when TPA$^+$/SiO$_2$<0.05, the amount of titanium incorporated into the framework decreases. ^{13}C CP/MAS NMR spectra show that all the patterns are similar. The above results indicate that the amount of TPABr used in the synthesis of TS-1 can be decreased to 0.05 (TPA$^+$/SiO$_2$).

In the system of TPABr and *n*-butylamine, when the amount of *n*-butylamine was increased to 10 times the original amount, still no *n*-butylamine was trapped in the zeolite (Fig. 4), which indicates that *n*-butylamine did not act as a template. Moreover, addition of tripropylamine and NaOH did not induce *n*-butylamine to act as a structure-directing agent. In the system of TPABr and TBAOH, both TPA$^+$ and TBA$^+$ played the role of a template, but the signal intensity of TPA$^+$ was higher than that of TBA$^+$ (Fig. 5). In the system of TPABr and TEAOH (Fig. 5), when TPA$^+$/SiO$_2$<0.05, both TPA$^+$ and TEA$^+$ acted as the template. Even if no TPABr was added, the signal intensity of TPA$^+$ originated from the seed added was higher than that of TEA$^+$. When TPA$^+$/SiO$_2$$\geq$0.05, only TPA$^+$ acted as the template. Hence, the order of templating effect can be arranged as follows: TPA$^+$>TBA$^+$>TEA$^+$$\gg$organic amine.

The catalytic properties of the TS-1 samples were studied in the catalytic epoxidation of propylene with

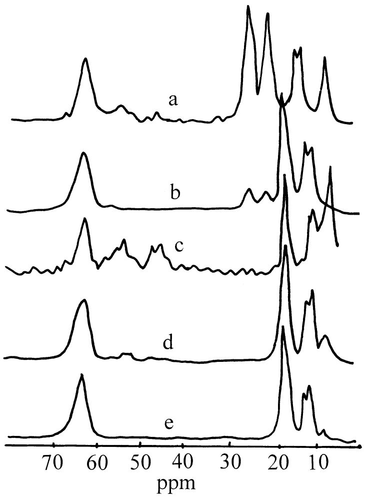

Fig. 5. ^{13}C CP/MAS NMR spectra of TS-1 synthesized in the presence of TPABr and TEAOH and of TBABr and TEOH. Molar ratios: (a) TBABr/SiO$_2$=0.25, TEAOH/SiO$_2$=0.4; (b) TPABr/SiO$_2$=0.25, TBAOH/SiO$_2$=0.1; (c) TPABr/SiO$_2$=0, TEAOH/SiO$_2$=0.4; (d) TPABr/SiO$_2$=0.02, TEAOH/SiO$_2$=0.4; (e) TPABr/SiO$_2$=0.04, TEAOH/SiO$_2$=0.4.

Table 1
Catalytic properties of TS-1 samples in propylene epoxidation[a]

Samples	Si/Ti in the gel	Base source	X (mol%)	U (mol%)	S (mol%)
1	33	$NH_3{\cdot}H_2O$	91.0	54.0	100
2	33	*n*-Butylamine	65.0	95.8	100
3	33	TEAOH	99.5	56.6	100
4	33	Diethylamine	98.1	74.9	100
5	39	TPAOH	95.5	66.5	100

X stands for the conversion of H_2O_2, U the utilization of H_2O_2, and S stands for the selectivity towards propylene oxide.

[a] Conditions: reaction temperature 60°C, reaction time 90 min, the pressure of propylene is kept at 0.8 MPa, 0.4 g of catalyst, 31.6 ml of methanol, 2 ml of 27% H_2O_2 aqueous solution.

H_2O_2. Results are listed in Table 1, which shows that TS-1 catalysts synthesized from different bases all have high selectivity. Samples 1, 3 and 4 have a high conversion of H_2O_2 and a low utilization of H_2O_2, By contrast sample 2 has a high utilization of H_2O_2 and a low conversion of H_2O_2. Compared with TS-1 synthesized according to the procedure given in literature [1], TS-1 samples synthesized from the TPABr system have similar catalytic properties. For industrial application of TS-1, both high conversion and high utilization of H_2O_2 are needed. So, the present method of the synthesis of TS-1 needs to be improved. It is interesting to note that, in the system of TEAOH and TPABr, when the amount of TEAOH was increased, the activity of TS-1 prepared decreased drastically. Only when $TEA^+/SiO_2<0.25$, the activity of TS-1 samples was improved which is in agreement with the IR results. In the system *n*-butylamine/TPABr, an increase in the amount of *n*-butylamine did not improve the activity of TS-1, but improved its utilization of H_2O_2 [19]. The above-mentioned TS-1 samples have larger crystal size (usually 2–3 μm from SEM) than TS-1 reported in literature [1]. Van der Pol et al. [23] have reported that when TS-1 particle size is larger than 0.3 μm, diffusion limitation governs the hydroxylation rate of phenol with H_2O_2. While in epoxidation of propylene with H_2O_2, TS-1 samples with 2–3 μm crystal size still have high activity. The reason is that the dynamic diameter of propylene (0.5 nm) is smaller than that of TS-1 (0.55–0.6 nm), so the diffusion limitation is not the controlling step during the epoxidation of propylene with hydrogen peroxide.

Fig. 6 shows IR spectra of TS-1 synthesized in the complex system with TPABr as the templating agent. Reaction results are listed in Table 2. It can be seen that TS-1 synthesized in the complex system has the characteristic absorption peak at 960 cm^{-1}, which is the finger proof that titanium has been incorporated into the framework. In catalyzing epoxidation of propylene TS-1 samples synthesized from *n*-butylamine and TPABr (sample 7), aqueous ammonia and TPABr (sample 12), TPABr and TBAOH (sample 13) showed high conversion of H_2O_2 and high utilization of H_2O_2. In the complex system of TPABr and *n*-butylamine (samples 6 and 7), we have found that the TS-1 synthesized with silica sol as the silicon source was superior to that synthesized with white carbon as the silicon source. Using silica sol as the silicon source

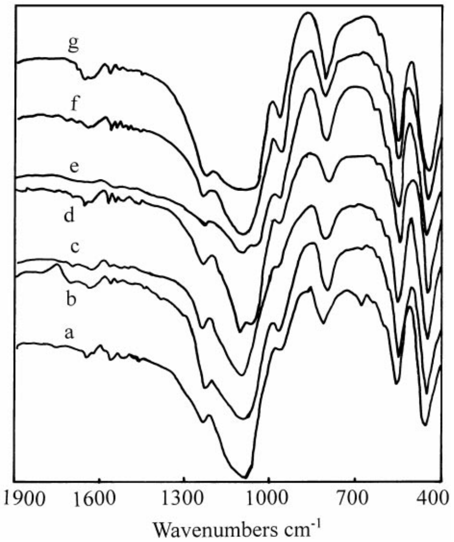

Fig. 6. IR spectra of TS-1 samples synthesized in the complex system: (a) sample 6 (b) sample 7 (c) sample 8 (d) sample 9 (e) sample 10 (f) sample 12 (g) sample 13 (synthesis components see Table 2).

Table 2
Catalytic epoxidation by TS-1 samples synthesized in the complex system[a]

Samples	Si/Ti in the gel	Silicon source	Base source	X (%)	U (%)	S (%)
6	33	White carbon	*n*-Butylamine	73.4	41.7	100
7	33	Silica sol	*n*-Butylamine	94.6	75.4	100
8	33	Silica sol	TEAOH	9.7	–	–
9	33	Silica sol	TEAOH[c]	74.2	81.3	100
10	33	TEOS	TEAOH	60.3	98.2	100
11	33	White carbon	TEAOH	66.0	67.7	100
12	33	Silica sol	$NH_3 \cdot H_2O$	93.7	87.6	100
13	33	Silica sol	TBAOH	98.3	71.1	100
14[b]	33	Silica sol	*n*-Butylamine	90.0	100	85

[a] The conditions are the same as in Table 1.
[b] TS-1 was synthesized in a 2 l stainless-steel autoclave.
[c] Stirred during the synthesis of TS-1.

and *n*-butylamine as the base, TS-1 (Si/Ti=33) with high crystallinity has been synthesized in a 2 l stainless-steel autoclave (stirring). The results (see Table 2) show that this TS-1 was superior to TS-1 synthesized in a 50 ml autoclave (stationary). Moreover, in the complex system of TPABr and TEAOH, we have found that stirring favors the crystallization of TS-1 and improves the catalytic properties of the prepared TS-1. TS-1 catalysts synthesized from TEOS as the silicon source gave high utilization of H_2O_2 in epoxidation of propylene.

3.1.2. Synthesis of TS-1 with TBABr as the template

TS-1 has been synthesized from TBABr and TEAOH, though TBA^+ is known to produce a favorable effect on the formation of the ZSM-11 (MEL) structure. IR spectra of the TS-1 show that Ti is incorporated into the framework. ^{13}C CP/MAS NMR spectra show that both TBA^+ and TEA^+ are trapped in the zeolite and act as the template (Fig. 5). In a 1:1 filling, TBA^+ and TEA^+ demand the same pore volume as TPA^+.

3.1.3. Synthesis of TS-1 with 1,6-hexanediamine as the template

In order to decrease the cost of TS-1 further, TS-1 has been synthesized by using 1,6-hexanediamine to replace TPAOH. The influence of various synthesis parameters (such as crystallization time and temperature, basicity of the reaction mixture, SiO_2/TiO_2 ratio) on the properties of the synthesized TS-1 has been investigated in detail ($TiOSO_4$ as the titanium source) [24]. Moreover, the combination of 1,6-hexanediamine and TEAOH were used in the synthesis of TS-1, ^{13}C CP/MAS NMR was used to study the effect of the organic base and showed that both 1,6-hexanediamine and TEAOH acted as the template (Fig. 7). However, TS-1 synthesized by this method has a low titanium content and increasing the amount of titanium leads to a decrease of crystallinity. Presumably 1 wt% is the upper limit of the amount of titanium incorporated into the framework.

3.2. Preparation of titanium silicalite by gas–solid isomorphous substitution

Besides using TPABr to replace TPAOH to decrease the cost of TS-1, secondary synthesis especially gas–solid isomorphous substitution was used in the synthesis of TS-1 to decrease their cost. This method consists of using ZSM-5 as the precursor to react with

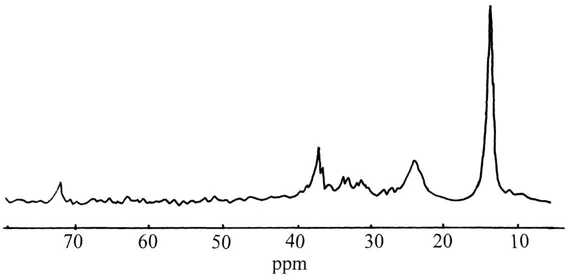

Fig. 7. ^{13}C CP/MAS NMR spectrum of TS-1 syntheized in the presence of TEAOH and 1,6-hexanediamine.

gaseous $TiCl_4$ at high temperatures. Since ZSM-5 can be easily synthesized from a cheaper template, in this way expensive template used in the synthesis of TS-1 can be avoided. Kraushaar and Van Hooff [25] adopted dealuminum ZSM-5 (Si/Al>2000) as the precursor to synthesize Ti-ZSM-5 and proved that titanium is incorporated into the framework. Their work also showed that higher temperature in the range 200–500°C favors the incorporation of titanium into the framework. However, Ferrini and Kouwenhoven [6] observed that, when dealuminated ZSM-5 (Si/Al=12.5) was used as the precursor, lower temperature in the range 200–500°C favors the incorporation of titanium into the framework.

3.2.1. *Effect of zeolite structure on the incorporation of Ti into the product TS-1*

Fig. 8 shows IR spectra of titanium-containing zeolite prepared by gas–solid isomorphous substitution, we can see that Ti-ZSM-5, Ti-ZSM-11, and Ti-β have been prepared by secondary synthesis. However, the IR spectra of Ti-Y and Ti-ZSM-48 do not show the characteristic peak at 960 cm^{-1} attributed to the incorporation of titanium into the framework. For Y zeolite, the absence of the peak at 960 cm^{-1} is due to the low SiO_2/Al_2O_3 and the collapse of the framework. For ZSM-48 zeolite, we first attributed the absence of this peak to the non-built-in of Ti to the unidimensional structure of ZSM-48. But, recently we have synthesized Ti-mordenite by using a dealuminated precursor. It seems that in ZSM-48, which is a high-silicon zeolite, it is more difficult to make hydroxyl nests than in mordenite. This might be more probable. Another reason is that upon dealumination of mordenite, mesopores are formed which help to facilitate the diffusion of $TiCl_4$ into the zeolite crystal, whereas no mesopores are formed in ZSM-48. In the preparation of Ti-ZSM-5, the effect of the conditions (nitrogen velocity, gas–solid isomorphous substitution temperature and time) and the nature of the precursor (including Na^+ content, SiO_2/Al_2O_3 and the template used in the synthesis of the precursor) were studied [26]. The product was investigated by using XRD, IR, and UV–Vis techniques. Results show that Ti is incorporated into the framework. Gas–solid isomorphous substitution temperature, time, crystal size, the ratio of silicon-to-aluminum, and the amount of Na^+ are the main factors that affect the incorporation of titanium into the framework. A study of the thermostability of Ti-ZSM-5 and Ti-ZSM-11 obtained showed that Na-containing Ti-zeolite collapsed upon calcination at 900°C for 2 h. However, when Na^+ was removed, the crystallinity of Ti-containing zeolite was very high. The crystallinity did not decrease even after calcining at 1000°C for 2 h. This indicates that, after Ti is incorporated into the framework, the zeolite still has high thermostability. IR spectra of the zeolites after being calcined at 1000°C for 2 h showed that the intensity of 960 cm^{-1} did not decrease. This indicates that once titanium is incorporated into the framework, it is difficult to remove it from the framework by calcination at a high temperature [27]. Ti-ZSM-5 and Ti-ZSM-11 were used to catalyze the oxidation of styrene with hydrogen peroxide [28]. The conversion of styrene reached 40 mol% (the molar ratio of styrene to H_2O_2 is 2.2, acetone being used as the solvent and the temperature was 80°C), the selectivity to form $PhCH_2CHO$ and PhCHO was 78.0 and 12.6 mol%, respectively, for Ti-ZSM-5. For Ti-ZSM-11 the selectivity to form $PhCH_2CHO$ and PhCHO was 48.5 and 41.3 mol%, respectively. In the hydroxylation of

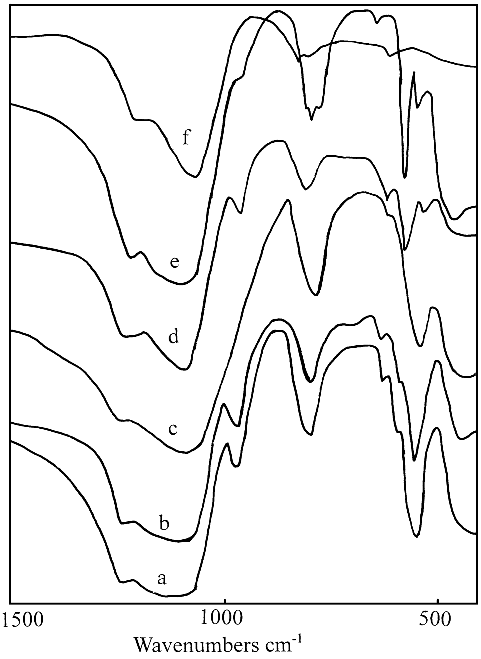

Fig. 8. IR spectra of titanium-containing zeolite prepared by gas–solid isomorphous substitution with $TiCl_4$ at 600°C: (a) Ti-ZSM-5, (b) Ti-ZSM-11, (c) Ti–ZSM-48, (d) Ti-β, (e) Ti-ZSM-12, and (f) Ti-USY.

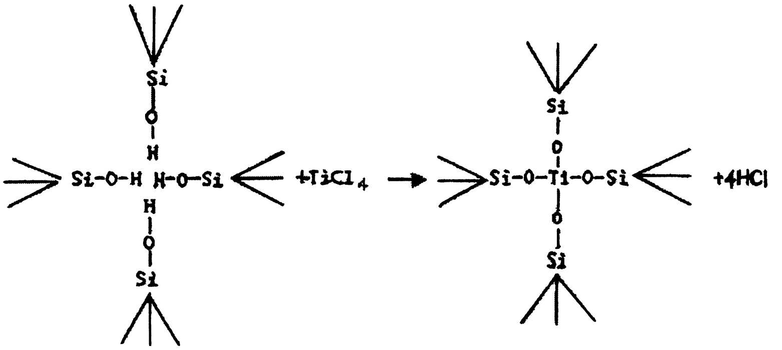

Fig. 9. Possible mechanism of gas–solid isomorphous substitution.

phenol, the conversion of phenol was 40% when the molar ratio of phenol to H_2O_2 was 1. However, the conversion of phenol decreased drastically when the ratio increased to 3, and the efficiency of H_2O_2 became less than 50 mol%.

As to the mechanism for the formation of TS-1 by gas–solid isomorphous substitution it seems that titanium is incorporated into the framework only after $TiCl_4$ has reacted with intra-crystalline defect structure (hydroxyl nests) (see Fig. 9). Although titanium is incorporated into the framework, the local environment of titanium in Ti-zeolite prepared by secondary synthesis seems to be different from that in TS-1 synthesized by the classical method. Ti-zeolite prepared by secondary synthesis has a lower activity in the hydroxylation of phenol with hydrogen peroxide than the standard TS-1, while in the oxidation of styrene, it shows high activity. This view has been proved by a ^{29}Si MAS NMR study [29].

3.2.2. Preparation of Ti-zeolite with boron-containing zeolites as the precursor

According to the above-mentioned mechanism, titanium can be incorporated into the framework when there are many hydroxyl nests in the zeolite, through reacting with them. However, it is difficult to make hydroxyl nests through the removal of aluminum. Because of the instability and weak acidity of framework boron, it is easy to remove boron from the framework to make nests. Rigutto et al. [30] described the preparation of Ti-beta zeolite using B-beta zeolite as the precursor. We also prepared Ti-beta [12], Ti-ZSM-5 [31] and Ti-ZSM-11 [32] zeolites with B-containing zeolites as the precursor. Fig. 10 shows the IR spectra of Ti-ZSM-5 synthesized with de-B-ZSM-5 as the precursor. The pattern of the as-synthesized B-ZSM-5 shows a band at 920 cm^{-1}, which is attributed to tetrahedral coordinated framework boron. The IR spectrum of the calcined B-ZSM-5 shows a new absorption peak at 1380 cm^{-1} of trigonal boron, BO_3, and the intensity of absorption at 920 cm^{-1} band becomes weak. Upon treatment of calcined B-ZSM-5 with 0.1 M aqueous HCl, 1380 and 920 cm^{-1} bands disappear, which proves the removal of extra-framework and framework boron. When the calcined sample is treated with $TiCl_4$, the IR spectrum of the product showed a weak absorption band at 960 cm^{-1}. By contrast, when the acid-treated sample was used as

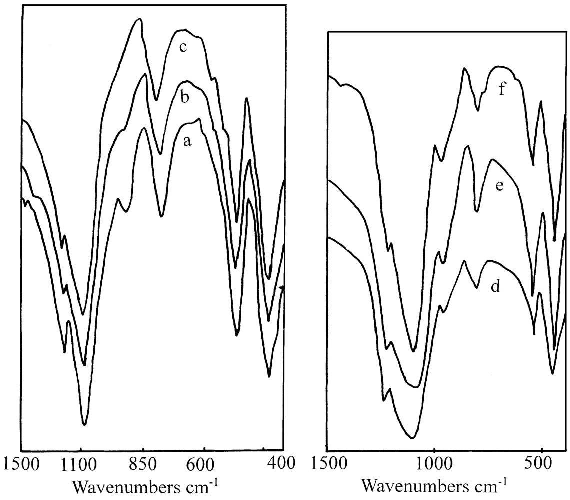

Fig. 10. IR spectra of BZSM-5 treated with different methods: (a) as synthesis; (b) calcined; (c) 0.1 M HCl and Ti-BZSM-5 prepared at different temperatures; (d) 200°C; (e) 400°C; (f) 600°C.

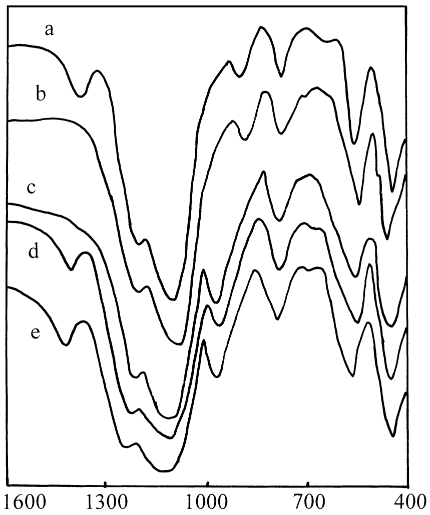

Fig. 11. IR spectra of B-ZSM-11 and Ti–B-ZSM-11: (a) B-ZSM-11 treated upon calcination; (b) B-ZSM-11, treated with 2 M HCl; (c) Ti–B-ZSM-11, using (a) as the precursor, reaction time 26 h; (d) Ti–B-ZSM-11, using (b) as the precursor, reaction time 6 h; (e) Ti–B-ZSM-11, using (b) as the precursor, reaction time 26 h.

the precursor, the IR spectrum of product shows a strong absorption band at 960 cm^{-1}, which indicates that titanium has been incorporated into the framework. The result shows that acidic deboronation favors the incorporation of titanium. Moreover, the intensity of 960 cm^{-1} band increases with the increase in the reaction temperature [31]. Similarly, Ti-ZSM-11 has been prepared by using B-ZSM-11 as the precursor (Fig. 11). Remarkably, treatment with acid only removes the extra-framework boron, and the removal of boron and incorporation of titanium by $TiCl_4$ takes place simultaneously [32]. Ammoxidation of cyclohexanone over Ti–B-ZSM-5 was studied; the conversion of cyclohexanone was 64.7 mol% and the selectivity to form oxime even reached 100 mol% [31]. Epoxidation of propylene over Ti-ZSM-11 was investigated. The conversion of H_2O_2 and the selectivity of propylene oxide were as high as 90 and 100 mol%, respectively. The utilization of H_2O_2 reached 70 mol% [32].

4. Conclusions

Titanium silicalite can be synthesized by hydrothermal crystallization method by using a cheap template or by secondary synthesis to decrease the cost. The catalytic activity of the as-synthesized titanium silicalite in the hydroxylation of phenol is lower than that of TS-1 synthesized according to the method given in the literature. The activity in the epoxidation of propylene over the as-synthesized titanium silicalite is similar to that of TS synthesized according to literature. The low cost TS-1 shows great promise in the future and should be further developed.

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References

[1] M. Taramasso, G. Perego, B. Notari, US Patent 4410501 (1983).
[2] M.G. Clerici, P. Ingallina, J. Catal. 140 (1993) 71.
[3] M.G. Clerici, G. Bellusi, U. Romano, J. Catal. 129 (1991) 159.
[4] C. Neri, F. Buonomo (Anic, s.P.A.), EP-A 102097 (1983).
[5] B. Notari, Stud. Surf. Sci. Catal. 60 (1991) 343.
[6] C. Ferrini, H.W. Kouwenhoven, Stud. Surf. Sci. Catal. 55 (1990) 53.
[7] J.S. Reddy, A. Sayari, Appl. Catal. A 128 (1995) 231.
[8] J.S. Reddy, P.A. Jacobs, Catal. Lett. 37 (1996) 213.
[9] X.W. Guo, G.R. Wang, X.S. Wang, Cuihua Xuebao 15(4) (1994) 309.
[10] X.S. Wang, X.W. Guo, Shiyou Jiagong (Petroleum Processing Section), Special issue for the 15th World Petroleum Congress, October 1997, p. 82.
[11] X.W. Guo, G.R. Wang, X.S. Wang, Shiyou Xuebao 11 (1995) 13.
[12] X.W. Guo, G. Li, X.F. Zhang, X.S. Wang, Stud. Surf. Sci. Catal. 112 (1997) 499.
[13] X.W. Guo, X.S. Wang, G.Y. Yu, Cuihua Xuebao 18 (1997) 24.
[14] X.W. Guo, X.S. Wang, M.F. Li, G.Y. Yu, Cuihua Xuebao 18 (1997) 428.
[15] U. Muller, W. Hoelderich, DE 4138155 (1991).
[16] A. Tuel, Stud. Surf. Sci. Catal. 105 (1997) 261.
[17] Q.H. Xia, Z. Gao, CN Pat. 9111650 (1995).
[18] W.Q. Pang et al., Gaodeng Xuexiao Huaxue Xuebao 9 (1989) 107.
[19] X.W. Guo, G. Li, X.S. Wang, Q. Zhao, X.H. Bao, X.W. Han, L.W. Lin, Cuihua Xuebao 19 (1998) 242.
[20] F. Geobaldo, S. Bordiga, A. Zecchina et al., Catal. Lett. 16 (1992) 109.
[21] G. Li, X.W. Guo, X.S. Wang, Shiyou Xueboa, Shiyou Jiagong 15 (1999) 90.

[22] X.W. Guo, G. Li, X.S. Wang, Q. Zhao, X.H. Bao, X.W. Han, L.W. Lin, Dalian Ligong Daxue Xuebao 38 (1998) 354.

[23] A.J.H.P. van der Pol, A.J. Verduy, J.H.C. van Hooff, Appl. Catal. A 92 (1992) 113.

[24] X.F. Zhang, G.R. Wang, X.S. Wang, Shiyou Xuebao, Shiyou Jiagong 10 (1994) 37.

[25] B. Kraushaar, J.H.C. Van Hooff, Catal. Lett. 1 (1988) 81.

[26] X.W. Guo, G.R. Wang, X.S. Wang, Cuihua Xuebao 16 (1995) 420.

[27] X.W. Guo, G.Y. Li, G.R. Wang, X.S. Wang, Cuihua Xuebao 16(4) (1995) 280.

[28] X.S. Wang, X.W. Guo, J. Liu, Dalian Ligong Daxue Xuebao 38 (1998) 348.

[29] Q. Zhao, X.W. Han, X.H. Bao, L.W. Lin, X.W. Guo, F.Z. Zhang, X.S. Wang, Wuli Huaxue Xuebao 14 (1998) 320.

[30] M.S. Rigutto, R. De Ruiter, J.M. Niederer, H. Van Bekkum, Stud. Surf. Sci. Catal. 84 (1994) 2245.

[31] M.F. Li, X.S. Wang, G.Y. Yu, Shiyou Jiagong 13(4) (1997) 35.

[32] F.Z. Zhang, X.W. Guo, X.S. Wang, Cuihua Xuebao 19 (1998) 5.