The active sites in different TS-1 zeolites for propylene epoxidation studied by ultraviolet resonance Raman and ultraviolet visible absorption spectroscopies

Fa-Zhi Zhang [a,*], Xin-Wen Guo [a], Xiang-Sheng Wang [a], Gang Li [a], Ji-Cheng Zhou [a], Jian-Qiang Yu [b] and Can Li [b]

[a] *Laboratory of Comprehensive Utilization for Carbonaceous Resources, Dalian University of Technology, Dalian 116012, PR China*
E-mail: F.Z.Zhang@263.net
[b] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China*

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The titanium species in four kinds of titanium-containing MFI zeolites have been studied by ultraviolet (UV)-Raman and ultraviolet visible (UV-Vis) absorption spectroscopies and by the epoxidation of propylene with diluted H_2O_2 solution (30%). UV-Raman spectroscopy is proved to be a suitable means to estimate qualitatively the framework titanium in TS-1 zeolites. Based on the comparison of the relative intensity ratio I_{1125}/I_{380} of UV-Raman spectra, the TS-1(conv.) sample synthesized hydrothermally by the conventional procedure shows the highest amount of framework titanium. UV-Vis spectroscopy reveals that besides minor anatase, titanium species are mainly tetrahydrally coordinated into the framework for TS-1(conv.) or the Ti-ZSM-5 sample prepared by gas–solid reaction between deboronated B-ZSM-5 and $TiCl_4$ vapor at elevated temperatures. For the TS-1(org.) and TS-1(inorg.) samples synthesized hydrothermally using tetrapropylammonium bromide (TPABr) as template and tetrabutylorthotitanite (TBOT) and $TiCl_3$ as titanium source, respectively, the presence of mononuclear and isolated TiO_x species which are proposed to bond to the zeolite extraframework is observed. In addition to the framework titanium species, these isolated TiO_x species are assumed to be also active for propylene epoxidation.

KEY WORDS: titanium silicalite; UV-Raman spectroscopy; UV-Vis absorption spectroscopy; mononuclear and isolated TiO_x; propylene epoxidation

1. Introduction

Because of its remarkable catalytic activity in selective oxidation of organic compounds under mild conditions, especially the use of diluted H_2O_2 as oxidant, titanium silicalite TS-1 has received much attention during the last decade [1–3]. Studies on the coordinated state of titanium ions and the reaction mechanism are the hot points since the synthesis of TS-1. Ti^{4+} ions in the framework isolated from each other by the silicalite matrix are commonly supported to be the active centers in the catalyzed oxidation, while crystalline anatase TiO_2 can only catalyze the H_2O_2 decomposition. For TS-1 the structure of active sites and the oxidation mechanism are mainly studied with tetrahedral Ti^{4+} ions in zeolite framework only [2,3]. However, in many but not all cases, another titanium species which is identified by a 250–290 nm band in the UV-Vis spectra of Ti-containing zeolites unexpectedly appears during the crystallization of Ti-containing zeolites [4–7]. The exact function, particularly in catalyzed oxidation, of this part of titanium species characterized by 250–290 nm UV-Vis absorption has not been investigated systematically.

Recently, UV-Raman spectroscopy was first used by us [8] to identify framework titanium in TS-1 zeolite. This technique can successfully avoid the fluorescence interference from zeolite samples, so the Raman spectrum in the UV region gives better signal-to-noise ratio than in the visible region [9–11]. Most importantly, the Raman bands directly associated with the framework titanium species Ti–O–Si in zeolite can be selectively enhanced owing to the resonance Raman effect. UV-Vis spectroscopy, depending on its clear assignment of the absorption bands and relatively simple experimental technique, is a routine method for characterization of almost all types of Ti-containing zeolites. In this paper, using UV-Raman and UV-Vis spectroscopies, we characterize four kinds of Ti-containing MFI zeolites synthesized by different procedures and raw materials. The different titanium species in each Ti-containing MFI are distinguished and the catalytic properties of the Ti-containing samples for propylene epoxidation are discussed.

2. Experimental

2.1. Zeolite synthesis

The TS-1(conv.) sample was synthesized hydrothermally by a conventional procedure described in [1], while the other two TS-1 samples (TS-1(org.) and TS-1(inorg.)) were synthesized hydrothermally following the modified procedures created in our laboratory at Dalian University of Technology [12,13]. The employed raw materials for the synthesis of the three TS-1 samples and the samples designation are listed in table 1.

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[*] To whom correspondence should be addressed. New address: Department of Chemistry, Tsinghua University, Beijing 100084, PR China.

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Table 1
The employed raw materials for the synthesis of TS-1 and the sample notations.

Sample	Employed raw materials			Ref.
	Silicon source	Titanium source	Template	
TS-1(conv.)	Tetraethylortho silicate (TEOS)	Tetraethylortho titanate (TEOT)	Tetrapropylammonium hydroxide (TPAOH)	[1]
TS-1(org.)	Silica sol.	Tetrabutylortho titanate (TBOT)	Tetrapropylammonium bromide (TPABr)	[12]
TS-1(inorg.)	Silica sol.	$TiCl_3$	TPABr	[13]

The SiO_2/TiO_2 molar ratio 33 in gel was obtained for all three kinds of TS-1 samples.

The Ti-ZSM-5 sample was prepared by gas–solid reaction between deboronated B-ZSM-5 and $TiCl_4$ vapor at elevated temperature. The detailed preparation procedure was described elsewhere [14,15]. The B-ZSM-5 sample was first synthesized according to the literature [16], with SiO_2/B_2O_3 molar ratio 10 in mixed gel. After pretreatment with 2 M HCl solution at 80 °C, the deboronated B-ZSM-5 sample was adopted as precursor for the gas–solid reaction.

2.2. Characterization

UV-Raman spectra were recorded on a home-made UV-Raman spectrometer built at State Key Laboratory of Catalysis (Dalian Institute of Chemical Physics, PR China). The spectral resolution was estimated to be 1.0 cm^{-1} and the acquisition time is 10 min. UV-Vis spectra were recorded on a Shimadzu UV240 spectrometer, and a pure powdered MgO sample was used as a reference. FT-IR spectra were obtained on a Nicolet 20 DXB spectrometer, and KBr pellet technique was adopted. XRD was performed on a Shimadzu XD-3A diffractometer (Cu K_α).

2.3. Catalytic activity

The propylene epoxidation was carried out in a 200 ml stainless-steel autoclave equipped with a magnetic stirrer, a constant temperature water bath, an inlet for gas reagent and an outlet for exhausting gas. For a typical run, 0.4 g catalyst, 31.6 ml methanol and 3.0 ml H_2O_2 (30%) were charged into the autoclave. The reaction was started when the slurry was heated at 333 K under pressure of propylene (0.4 MPa) by vigorously stirring. Products were analyzed by a gas chromatograph (ShangFen 1102), using a flame ionization detector and a capillary column (30 m × 0.25 mm) containing polyethylene glycol as the stationary phase. The amount of unreacted H_2O_2 was determined by iodometric titration. The efficiency of H_2O_2 was calculated as the amount of H_2O_2 consumed in the formation of the oxidized products. The selectivity to propylene oxide (PO) referred to the content of PO in the oxidized products.

3. Results and discussion

3.1. Synthesis of different Ti-containing MFI zeolites

Four kinds of titanium-containing MFI zeolites were prepared by different procedures. The XRD patterns show that samples synthesized by the hydrothermal method possess perfect MFI structure and high crystallinity. For the Ti-ZSM-5 sample, the XRD pattern matches well with that of the deboronated B-ZSM-5 precursor, despite a decrease of about 10% crystallinity after gas–solid reaction. FT-IR spectra (figure 1) show the band at 960 cm^{-1} for each Ti-containing zeolite. This band has been widely used to characterize the incorporation of titanium in the framework lattice. Although the exact assignment of the 960 cm^{-1} band is controversial, it seems likely that this band corresponds to the stretching Si–O vibration mode perturbed by the neighboring Ti^{4+} ions [3].

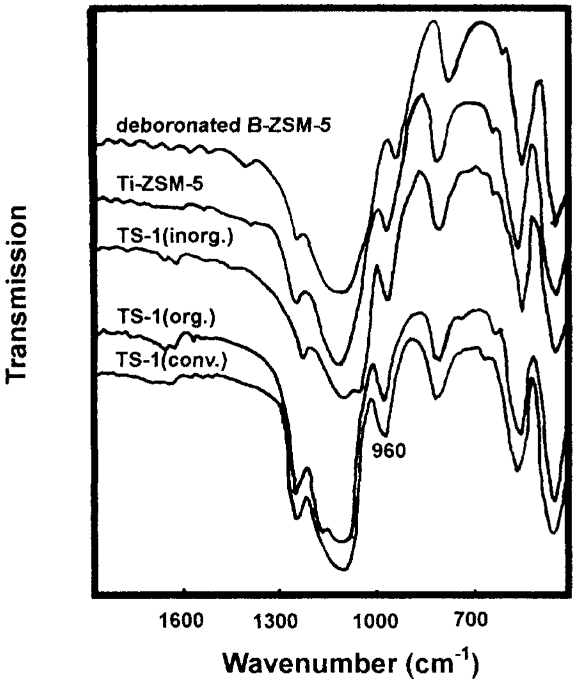

Figure 1. FT-IR spectra of Ti-containing MFI zeolites and deboronated B-ZSM-5 precursor.

For the deboronated B-ZSM-5 sample, a band at 920 cm^{-1} appears. This band is assigned to Si–OH groups in the silanol nests, which are created by the emigration of boron from the zeolite framework [14,17]. After the gas–solid reaction between the deboronated B-ZSM-5 precursor and $TiCl_4$ vapor, the 920 cm^{-1} band is shifted to 960 cm^{-1}. The IR results directly indicate the insertion of titanium in the zeolite framework [14].

Different from the TS-1(conv.) sample prepared by the conventional method in which TPAOH is used as the template, the TS-1(org.) and TS-1(inorg.) samples are synthe-

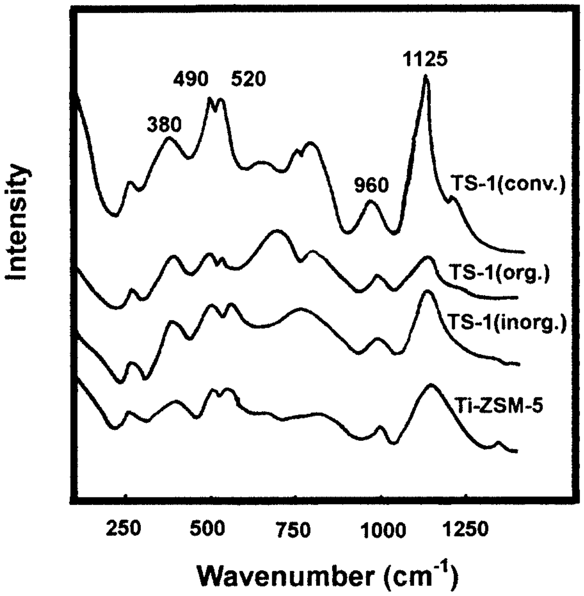

Figure 2. UV-Raman spectra of Ti-containing MFI zeolites.

Table 2
Comparative characterization of Ti-containing MFI zeolites by UV-Raman and UV-Vis spectroscopies.

Sample	I_{1125}/I_{380} ratio of UV-Raman spectra	Predominant bands in UV-Vis 210 or 225 nm	280 nm	330 nm
TS-1(conv.)	5.2	Strong	–	Strong
TS-1(org.)	1.2	Strong	Strong	Very weak
TS-1(inorg.)	3.2	Strong	Weak	Very weak
Ti-ZSM-5	3.5	Strong	–	Weak

sized by modified procedures using TPABr as template. Recently, instead of the use of the relative expensive template TPAOH, TPABr with one kind of organic or inorganic ammonium (e.g., 1,6-hexamethylene diamine, *n*-butylamine, $NH_3{\cdot}H_2O$) has been adopted as a cheaper template system in the TS-1 synthesis in order to decrease the synthesis cost [12,13,18,19]. The studies show that, when the TPABr/SiO_2 ratio in the mixed gel is above 0.05, the additional organic or inorganic ammonium can only act as a base to regulate the pH value in the gel.

3.2. UV-Raman spectroscopy

Figure 2 shows the UV-Raman spectra of the four kinds of Ti-containing MFI samples. Three resonance enhanced Raman bands at 490, 520 and 1125 cm^{-1} are observed exclusively for these samples, and the relative intensities of these bands, especially the one at 1125 cm^{-1}, are quite different from each other. The 490, 520 and 1125 cm^{-1} bands are the characteristics of the framework titanium species in the TS-1 sample and these bands increase in intensity with the crystallization time of TS-1 [8]. A band at 380 cm^{-1} also appears for each sample. This band is supposed to be the identification of the MFI stucture [8]. Table 2 shows that, TS-1(conv.) synthesized by the conventional method using TPAOH as template can obtain the highest intensity ratio I_{1125}/I_{380} of 5.2, which indicates that TS-1(conv.) possesses the largest amounts of titanium in its framework in comparison with TS-1(org.) and TS-1(inorg.). The results of UV-Raman spectra suggest that very effective insertion of titanium into the framework can be obtained by using TPAOH as template during the synthesis of TS-1.

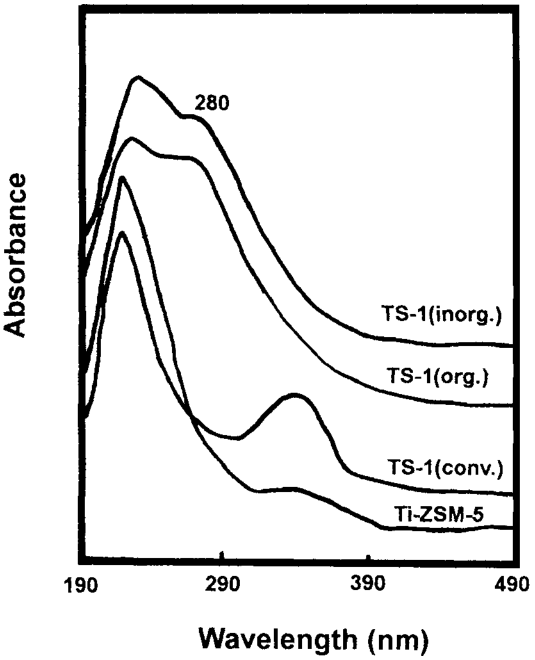

Figure 3. UV-Vis spectra of Ti-containing MFI zeolites.

Compared to TS-1(org.) synthesized using TBOT as titanium source, the TS-1(inorg.) sample using $TiCl_3$ as titanium source possesses a higher I_{1125}/I_{380} ratio of 3.2 than that of 1.2. It can be proposed that inorganic titanium source $TiCl_3$ can match well with the inorganic silicon source silica sol. during the crystallization of TS-1. The relative intensity of the 1125 cm^{-1} band is almost identical for Ti-ZSM-5 and TS-1(inorg.), and both are lower than that for the TS-1 (conv.) sample.

3.3. UV-Vis spectroscopy

UV-Vis spectra of the Ti-containing MFI are shown in figure 3. Two main charge-transfer absorption bands around 210 and 330 nm are observed for the TS-1(conv.) and Ti-ZSM-5 samples. The former with absorption onset at about 270 nm is attributed to tetrahedrally coordinated framework titanium; the latter with absorption onset at about 390 nm is typical for anatase TiO_2. It can be seen that the relative intensity of the 330 nm band is much lower in Ti-ZSM-5 than in TS-1(conv.). The UV-Vis spectra of TS-1(org.) and TS-1(inorg.) show the similar absorption: Besides a band centered around 225 nm which is assigned to framework titanium, the absorption with a maximum at about 280 nm and an onset at 390 nm is observed. It can be seen that the band assigned to framework titanium species is shifted from 210 nm in TS-1(conv.) to 225 nm in TS-1(org.) and TS-1(inorg.). Compared to that of TS-1(conv.), the isolated framework titanium in TS-1(org.) and TS-1(inorg.) may be loosely coordinated to the surrounding Si–O band, resulting in a shift of the framework titanium absorption maximum to higher wavelength. This implies that the local coordinated environment of part of the framework titanium in TS-1(org.) and TS-1(inorg.) is slightly different from that in TS-1(conv.) [4].

A broad band, with a maximum around 280 nm and an absorption onset at 390 nm is present in the UV-Vis spectra of TS-1(org.) and TS-1(inorg.). Although the exact assignment of the band around 280 nm is still under discussion, it can be accepted that these titanium species are quite different from tetrahedrally coordinated framework titanium characterized by the band about 210 nm. Three main types of structure of these non-framework titanium species, in the spectrum of TS-1 [4], Ti-β [5,6], Ti-ZSM-12 [7] or zeolite-hosted mononuclear titanium oxide species [20], have been proposed: (1) the formation of hexacoordinated species with two water molecules in the coordination sphere [4]; (2) the formation of partly aggregated hexacoordinated species, Ti–O–Ti [5–7]; and (3) the formation of isolated single-bonded TiO_x species attached to the zeolite lattice [20]. It can be seen that the relative intensity of the band around 280 nm in TS-1(org.) is stronger than that in TS-1(inorg.), which indicates that the former occupies more isolated or partly polymerized non-framework titanium species.

In comparison with TS-1(conv.), no obvious charge-transfer absorption at 330 nm in TS-1(org.) and TS-1(inorg.) is observed. However, the absorption onset of anatase at about 390 nm is also present. It seems that the signal of anatase in TS-1(org.) and TS-1(inorg.) spectra should be covered by the broad band around 280 nm.

For the sake of brevity, the observed UV-Vis bands of four kinds of Ti-containing zeolites are compared in table 2. Based on the above mentioned UV-Raman and UV-Vis results, it can be concluded that for TS-1(org.) and TS-1 (inorg.), the coexistence of framework titanium, isolated or partly polymerized non-framework titanium, and anatase is observed, while only two kinds of titanium species, tetrahedral Ti^{4+} ions and anatase, are present in TS-1(conv.) and Ti-ZSM-5.

3.4. Epoxidation of propylene with diluted H_2O_2

A summary of the performance of the Ti-containing MFI in the epoxidation of propylene with diluted H_2O_2 is given in table 3. Both TS-1(conv.) and TS-1(org.) samples show higher H_2O_2 conversion and efficiency. The Ti-ZSM-5 sample gives the lowest H_2O_2 conversion and efficiency under the same reaction conditions. With framework Ti^{4+} only, many studies on TS-1 have discovered that the active centers in catalysis must be the Ti^{4+} in framework position isolated from each other by the silicalite matrix. The more Ti^{4+} species exist in the framework, the higher activity can be obtained for TS-1. In accordance with the above speculation, TS-1(conv.) having larger amounts of framework titanium (see figure 2 and table 2) can obtain higher H_2O_2 conversion and efficiency.

Table 3
The results of propylene epoxidation over Ti-containing MFI zeolites.[a]

Sample	Conv. of H_2O_2 (%)	Eff. of H_2O_2 (%)	Sel. for PO[b] (%)
TS-1(conv.)	94.0	86.6	97.9
TS-1(org.)	97.4	94.6	92.1
TS-1(inorg.)	84.1	90.2	94.5
Ti-ZSM-5	58.0	83.2	99.3

[a] Reaction conditions: catalyst 0.4 g, methanol 31.6 ml, H_2O_2 (30%) 3 ml, propylene pressure 0.4 MPa, 333 K, 1.5 h.

[b] PO: propylene oxide. The by-products are glycol and monomethyl ethers.

Surprisingly, the TS-1(org.) sample with the lowest intensity ratio I_{1125}/I_{380} in the UV-Raman spectrum can obtain 97.4% of H_2O_2 conversion and 94.6% of H_2O_2 efficiency. For the propylene epoxidation, a TiO_2/SiO_2 heterogeneous catalyst has been developed by Shell. The formation of the titanyl group $\rangle Ti{=}O$ which is attached to vicinal silanol groups is suggested to explain the catalysis of this kind of catalyst in epoxidation [21]. According to Klaas et al. [20], the 290 nm band in the UV-Vis spectrum of zeolite-hosted mononuclear titanium oxide species is assigned to single-bonded TiO_x species, which are in a mononuclear and isolated way attached to the zeolite lattice. The structure of these TiO_x species can be described as follows:

$$(\equiv Si–O)–Ti(OH)_3$$

It is assumed that for TS-1(org.) the 280 nm band in the UV-Vis spectrum may correspond to such mononuclear and isolated TiO_x species. These TiO_x species are suggested to be transformed into the active titanyl group $\rangle Ti{=}O$ structure after calcination. When reacted with H_2O_2, the titanyl group would produce surface titaniumhydroperoxo compounds, which would then react with propylene to produce the epoxide. It is proposed that the coexistence of two kinds of active sites: framework Ti^{4+} and highly isolated TiO_x species in TS-1(org.) cause the higher activity for propylene epoxidation.

Compared to TS-1(org.), TS-1(inorg.) with smaller content of TiO_x species obtains lower H_2O_2 conversion. Based on UV-Raman and UV-Vis spectroscopy, Ti-ZSM-5 occupies a low amount of framework Ti^{4+} and almost no isolated TiO_x species can be obtained. So, the conversion of H_2O_2 is lower for Ti-ZSM-5 in comparison with the other three TS-1 samples.

4. Conclusion

Four kinds of Ti-containing MFI zeolites have been synthesized by different procedures and raw materials. Using UV-Raman spectroscopy, framework titanium in these Ti-containing MFI is estimated qualitatively. The TS-1 (conv.) sample synthesized hydrothermally by the conventional method obtains the highest amount of framework titanium. The relative content of framework titanium in Ti-ZSM-5 prepared by gas–solid reaction is lower compared to TS-1(conv.). UV-Vis spectra show that mononuclear and isolated TiO_x species which are absent in the above two Ti-containing MFI, are observed in the TS-1(org.) and TS-1 (inorg.) samples synthesized hydrothermally by the modified procedure. Framework titanium, in combination with isolated TiO_x species if existing in TS-1 are supposed to be the active sites for propylene epoxidation according to the characterization and reaction results.

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