## **RSC** Advances

### **Electronic Supplementary Information for**

# Role of pentahedrally coordinated titanium in titanium silicalite-1 in propene epoxidation

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Standard Ti *L*-edge X-ray absorption near edge structure (XANES) spectra of different coordinated Ti, and the characterization of samples by X-ray powder diffraction, Fourier-transform infrared spectroscopy, nitrogen physisorption and transmission electron microscopy were settled in the Electronic Supplementary Information, accompanied with the calculation process of different coordinated Ti contents and their TOFs.

#### 1. Ti *L*-edge XANES spectra

Ti *L*-edge XANES spectra of pure Ti species in Ti-silicate glasses were reported by Henderson et al.<sup>S.1</sup> The spectra of different coordinated Ti are shown in Figs. S.1 and S.2. The relative intensity of peak d to that of peak c (denoted as  $I_{H/L}$ ) in the figures is considered as the probe of content of different coordinated Ti. According to Fig. S.2, the  $I_{H/L}$  of pure framework tetrahedrally coordinated, pentahedrally coordinated Ti and anatase TiO<sub>2</sub> are 1.17, 3.70 and 0.74, respectively. In other words, the larger the  $I_{H/L}$  is, the more pentahedrally coordinated Ti exists, while the lower the  $I_{H/L}$  is, the more anatase TiO<sub>2</sub> generates.



Fig. S.1 Ti *L*-edge XANES spectra of  $Ti_2O_3$ , anatase and rutile  $TiO_2$ .



Fig. S.2 Ti *L*-edge XANES spectra of fresnoite,  $Ba_2TiO_4$  and rutile TiO<sub>2</sub>.

#### 2. Characterization of the samples

The as-synthesized TS-1 samples were characterized with X-ray powder diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, nitrogen physisorption and transmission electron microscopy (TEM). XRD patterns were measured on a Rigaku D/MAX-2400 using Cu K $\alpha$  radiation. FT-IR spectra were recorded from 4000 to 400 cm<sup>-1</sup> on a Bruker EQUINOX55 spectrometer, and the KBr pellet technique was adopted. Nitrogen physisorption was carried out on a Quantachrome AUTOSORB iQ2 physical sorption apparatus at 77 K. The appearances of the TS-1 samples were obtained on a Hitachi S-4800 scanning electron microscope (SEM) and a Tecnai G<sup>2</sup>20 S-Twin transmission electron microscope (TEM). The XRD patterns of the samples were shown in Figs. S.3~S.5. The characteristic peaks of MFI topology<sup>S.2</sup> ( $2\theta = 7.8^{\circ}$ , 8.8°, 23.0°, 23.9°, 24.0°) were observed in the patterns of all samples, indicating that the *n*(Si/Ti), treatment with organic bases and adding of ammonium carbonate did little influence on the structure of TS-1. Two Classic TS-1 samples were prepared according to Ref. S.4 (Example 2) for comparison, the *n*(Si/Ti) of which were 40 and 60. The two samples were denoted as CTS-1-40 and CTS-1-60, respectively. The TS-1 synthesized by the classic method, which contain different amounts of extra-framework Ti (proved by UV-vis spectra), show the TOFs of 209.9 and 351.5 mol H<sub>2</sub>O<sub>2</sub>/(h·mol Ti), respectively. This also confirms the higher catalytic activity of pentahedrally coordinated Ti.



**Fig. S.3** XRD patterns of small-crystal TS-1 with different n(Si/Ti).



**Fig. S.4** XRD patterns of small-crystal TS-1 treated with different organic bases.



Fig. S.5 XRD patterns of nano-sized TS-1.

The FT-IR spectra were shown in Figs. S.6~S.7. The band at 960 cm<sup>-1</sup> was considered as one of the evidences of Ti introducing into the TS-1 framework.<sup>S.3</sup>



Fig. S.6 FT-IR spectra of small-crystal TS-1 treated with different organic bases.



Fig. S.7 FT-IR spectra of nano-sized TS-1.

Figure S.8 shows the  $N_2$  physisorption isotherms of untreated and organic bases treated small-crystal TS-1. TS-1-50 had a type I isotherm, which demonstrated the microporous structure of TS-1. After treatments, H4 hysteresis loops appeared

in the isotherms, indicating the generation of hollows in the crystals.

Figure S.9 shows the SEM images of small-crystal and nano-size TS-1. The crystal size of small-crystal TS-1 is about  $600 \text{ nm} \times 400 \text{ nm} \times 250 \text{ nm}$ , and that of nano-sized TS-1 is about 200 nm.

Figure S.10 shows the TEM images of treated TS-1 samples. Hollows were formed in every sample. This was consistent with the results of  $N_2$  physisorption.



**Fig. S.8** Nitrogen physisorption isotherms of small-crystal TS-1 treated with different organic bases.



**Fig. S.9** SEM images of small-crystal and nano-sized TS-1. ((a) TS-1-20, (b) TS-1-50, (c) TS-1-80, (d) TS-1-NA and (e) TS-1-AC)



**Fig. S.10**TEM images of small-crystal TS-1 treated with different organic bases. ((a) TS-1-EA, (b) TS-1-DEA, (c) TS-1-TMAOH and (d) TS-1-TPAOH)

Figure S.11 shows the UV-vis spectra of the TS-1 synthesized with the classic method in Ref. S.4. More anatase  $TiO_2$  and extra-framework Ti appeared in CTS-1-40 than those in CTS-1-60.



Fig. S.11UV-vis spectra of CTS-1-40 and CTS-1-60.

#### 3. Contents and TOFs of different coordinated Ti

The calculations of contents and TOFs of different coordinated Ti in small-crystal TS-1 were based on the XANES and TOF data. The  $I_{H/L}$  provides the contents of different coordinated Ti. The  $I_{H/L}$  of pure tetrahedrally coordinated Ti, pentahedrally coordinated Ti and anatase TiO<sub>2</sub> calculated from Fig. S.2 are

1.17, 3.70 and 0.74, respectively. We suppose that there is no tetrahedrally coordinated Ti existed in TS-1-80, and no pentahedrally coordinated Ti in TS-1-20, according to the UV-vis spectra in Fig. 2. Moreover, the anatase TiO<sub>2</sub> shows no activity in the oxidation reaction. We know that the  $I_{H/L}$  of TS-1-80 is 2.43 (Fig. 3). Therefore, the equations are listed below:

 $(1.17x_3 + 3.70y_3) / (x_3 + y_3) = 2.43$  $x_3 + y_3 = 1$ 

where  $x_3$  and  $y_3$  are the mole content of tetrahedrally coordinated Ti and pentahedral one in TS-1-80, respectively. From the equations, the mole content of tetrahedrally coordinated Ti and pentahedral one were obtained for 0.50 and 0.50.

Using the same method, the content of tetrahedrally coordinated Ti and anatase  $TiO_2$  in TS-1-20 was also obtained:

 $(1.17x_1 + 0.74z_1) / (x_1 + z_1) = 0.92$ 

 $x_1 + z_1 = 1$ 

where  $x_1$  and  $z_1$  are the mole content of tetrahedrally coordinated Ti and anatase TiO<sub>2</sub> in TS-1-20, respectively. From the equations the mole content of tetrahedrally coordinated Ti and anatase TiO<sub>2</sub> were obtained for 0.42 and 0.58.

Anatase TiO<sub>2</sub> is inert for oxidation, thus, the TOF over TS-1-20 (156.8 mol H<sub>2</sub>O<sub>2</sub>/(h·mol Ti)) is only contributed to tetrahedral Ti. 0.42a = 156.8

where *a* stands for the TOF of pure tetrahedral Ti, and equals to 373.3 mol  $H_2O_2/(h \cdot mol Ti)$ .

The TOF over TS-1-80 (903.8 mol  $H_2O_2/(h \cdot mol Ti)$ ) is attributed to both tetrahedral Ti and pentahedral Ti.

0.50a + 0.50b = 903.8

*b* represents the TOF of pure pentahedral Ti, and equals to 1434.3 mol  $H_2O_2/(h \cdot mol Ti)$ .

According to *a*, *b* and TOF over TS-1-50 (498.8 mol  $H_2O_2/(h \cdot mol Ti)$ ), we know that

 $373.3x_2 + 1434.3y_2 = 498.8$ 

 $x_2$  and  $y_2$  are the mole contents of tetrahedral Ti and pentahedral one in TS-1-50, respectively.

According to the  $I_{H/L}$  of TS-1-50, equations are listed:

 $(1.17x_2 + 3.70y_2 + 0.74z_2) / (x_2 + y_2 + z_2) = 1.59$ 

 $x_2 + y_2 + z_2 = 1$ 

 $z_2$  is the mole content of anatase TiO<sub>2</sub> in TS-1-50. Evidently,  $x_2$ ,  $y_2$  and  $z_2$  are 0.76, 0.21 and 0.03, respectively.

#### Notes and references

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