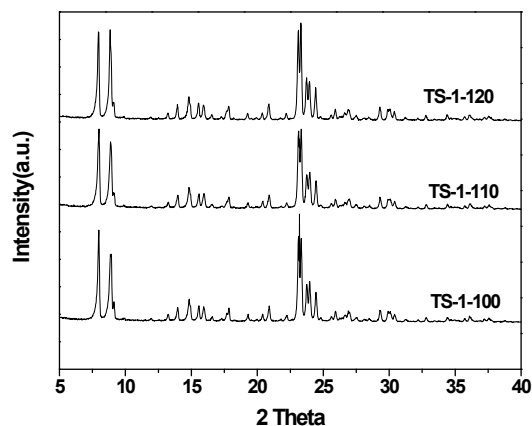


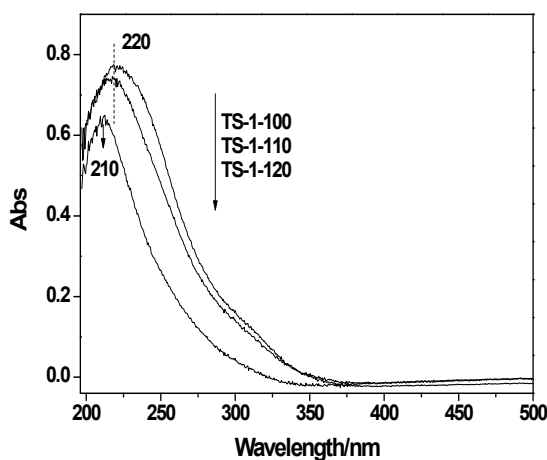
## Supporting Materials

### Part A.



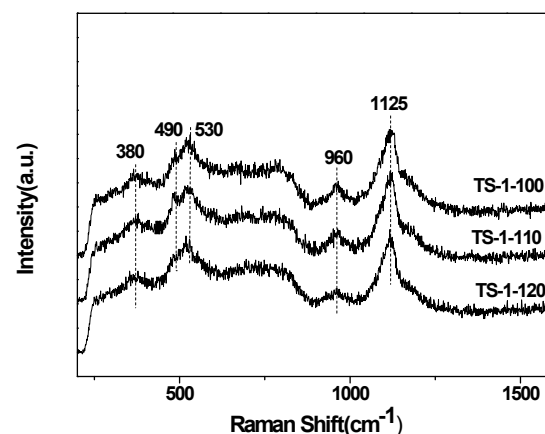
**Fig. S1** XRD patterns of the TS-1 samples with different  $\text{SiO}_2/\text{TiO}_2$  ratios.

The XRD patterns of TS-1 samples with different  $\text{SiO}_2/\text{TiO}_2$  ratios are shown in Figure S1. All the samples exhibit the characteristic peaks of MFI topology at  $2\theta=7.8^\circ$ ,  $8.8^\circ$ ,  $23.2^\circ$ ,  $23.8^\circ$  and  $24.3^\circ$ , indicating that all the samples keep the MFI topology.

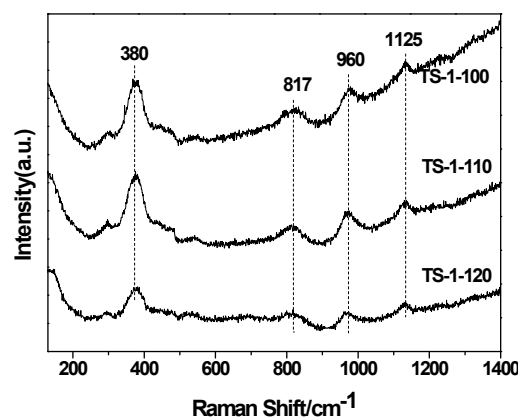


**Fig. S2** UV-Vis spectra of the TS-1 samples with different  $\text{SiO}_2/\text{TiO}_2$  ratios.

The TS-1 samples with the  $\text{SiO}_2/\text{TiO}_2$  ratios of 100, 110, 120 exhibit the peak at 210-220 nm. This indicates that only the framework Ti species exists in the TS-1 with high  $\text{SiO}_2/\text{TiO}_2$  ratio. What's more, the contents of the framework Ti species increase as the  $\text{SiO}_2/\text{TiO}_2$  ratio decreases from 120 to 100. At the same time, the band assigned to framework Ti species is shifted from 210nm to 220nm. The shift of the framework titanium absorption maximum to longer wavelength may be due to the tightly coordinated surrounding Si-O bands, which implies that the local coordination environment of the framework titanium species in TS-1-120 is slightly different from that in TS-1-100.

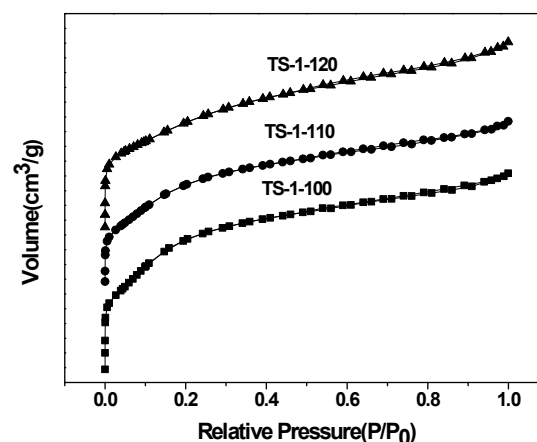


**Fig. S3** UV-Raman spectra of the TS-1 samples with different  $\text{SiO}_2/\text{TiO}_2$  ratios.



**Fig. S4** Raman spectra of the TS-1 samples with different  $\text{SiO}_2/\text{TiO}_2$  ratios (325nm)

In comparison, the TS-1-100, TS-1-110 and TS-1-120 samples show the Raman peaks at 380, 817, 960 and 1125  $\text{cm}^{-1}$ , which are assigned to MFI structure. The bands of anatase  $\text{TiO}_2$  are absent in these samples. The results of the Raman are in consistent with that of UV-Vis(See Fig.S2).



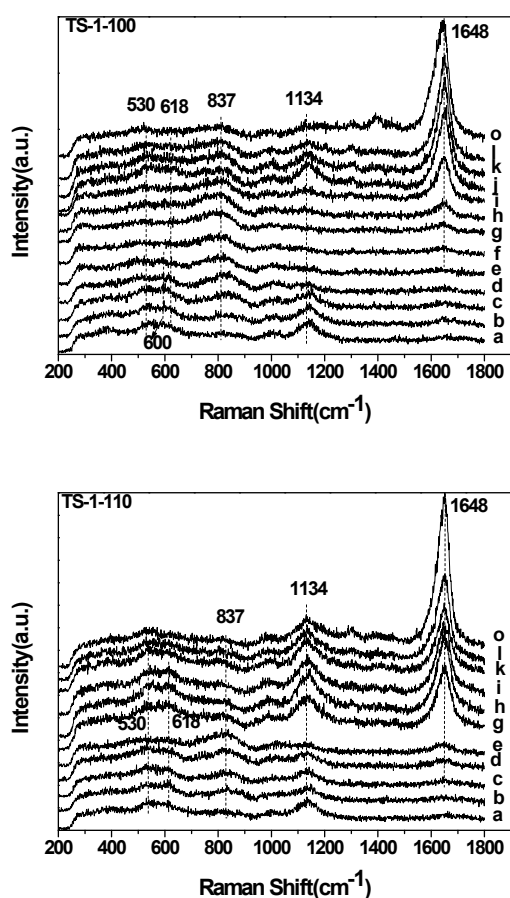
**Fig.S5** N<sub>2</sub> adsorption isotherms of the TS-1 samples with different SiO<sub>2</sub>/TiO<sub>2</sub> ratios

It can be seen that the samples with high SiO<sub>2</sub>/TiO<sub>2</sub> ratios (100,110,120) do not show abrupt jump at high pressure zone, indicating the absence of intercrystalline pore.

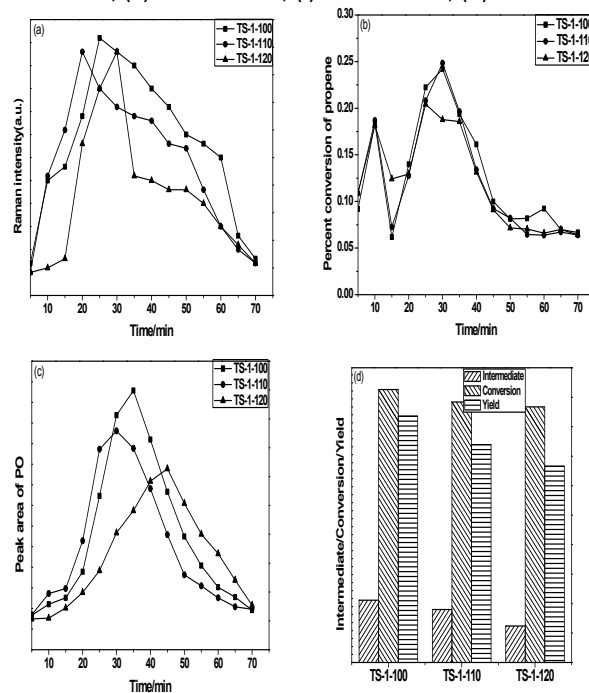
**Tab. S1** Textural properties of TS-1 samples with different SiO<sub>2</sub>/TiO<sub>2</sub> ratios

samples	S <sub>BET</sub> (m <sup>2</sup> /g)	S <sub>micro</sub> (m <sup>2</sup> /g)	S <sub>ext</sub> (m <sup>2</sup> /g)	V <sub>Total</sub> (cm <sup>3</sup> /g)	V <sub>micro</sub> (cm <sup>3</sup> /g)	V <sub>meso</sub> (cm <sup>3</sup> /g)
TS-1-100	433.2	394.8	38.4	0.2437	0.1985	0.0452
TS-1-110	430.6	393.7	36.9	0.2362	0.1927	0.0435
TS-1-120	440.8	392.5	48.3	0.2379	0.1821	0.0558

The role of framework Ti species of the low-cost TS-1



**Fig.S6** In situ Raman spectra of the TS-1/H<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>O/CH<sub>3</sub>OH system obtained at different times during the methanol included epoxidation reaction, collected with a 244nm laser line: Raman spectra obtained at the (a) 5th minute; (b) 10th minute; (c) 15th minute; (d) 20th minute; (e) 25th minute; (f) 30th minute; (g) 35th minute; (h) 40th minute; (i) 45th minute; (j) 50th minute; (k) 55th minute; (l) 60th minute; (o) 70th minute

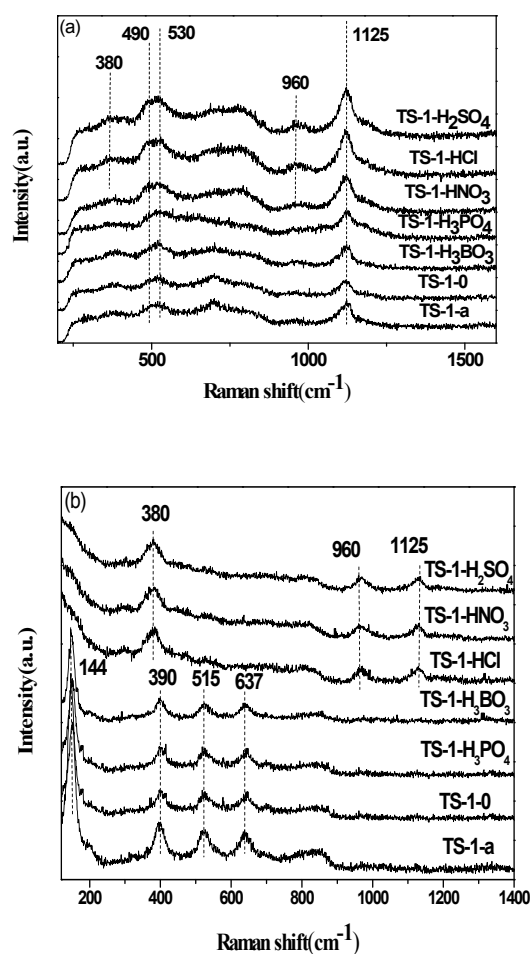


**Fig.S7** (a) The UV-Raman intensity of the 837 cm<sup>-1</sup> band at different times during the epoxidation reaction. (b) The conversion of propene in the TS-1/H<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>O/CH<sub>3</sub>OH system at different times. (c) The peak area of PO in the GC spectra at different times. (d) The total column of the intermediate, conversion and yield with different SiO<sub>2</sub>/TiO<sub>2</sub> ratios.

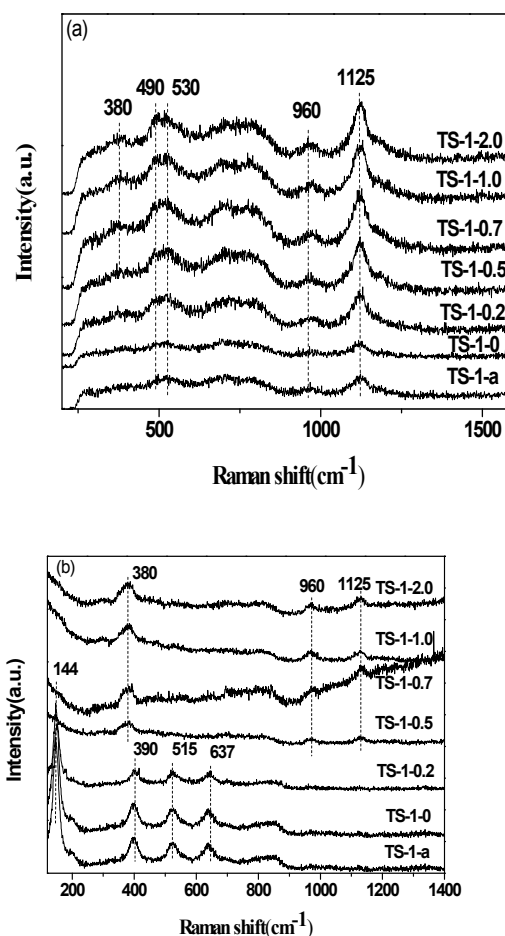
The intensity of the band at 837cm<sup>-1</sup>, the conversion of propylene and the yield of PO at different times are shown in Fig.S7a, S7b and S7c, respectively. The integrated peak areas are shown in Fig.S7d. The integrated intensity of the band at 837cm<sup>-1</sup> decreases as the SiO<sub>2</sub>/TiO<sub>2</sub> ratio increases. The UV-Vis spectra in Fig.S2 show that the intensity of the 210-220nm band decreases as the SiO<sub>2</sub>/TiO<sub>2</sub> ratio increases. A good correlation

between the intensity of the 210nm peak and the 837cm<sup>-1</sup> band means the more the framework Ti species in the TS-1 the higher the concentration of the reaction intermediate Ti-OOH( $\eta^2$ ). The propylene conversion and the yield of the PO show the same trend as the reaction time increases. This result indicates that the isolated Ti species in the framework of the low-cost TS-1 zeolite is the active center for the propylene epoxidation.

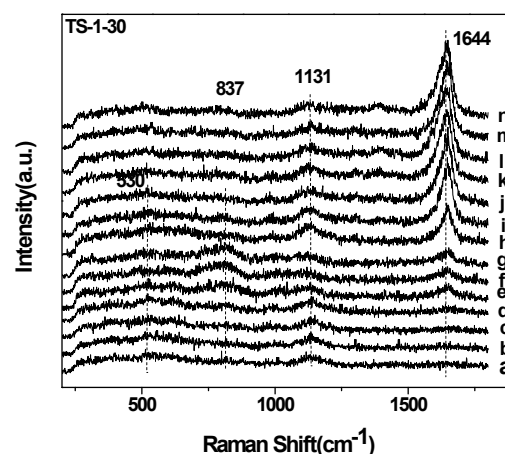
## Part B.

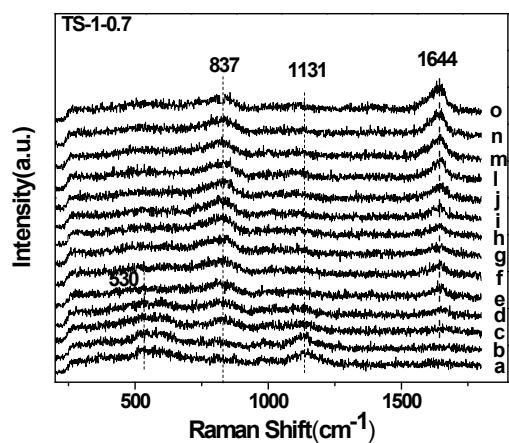


**Fig S1.** (a) Raman (244nm) spectra of the TS-1 samples modified with different acids  
(b) Raman (325nm) spectra of the TS-1 samples modified with different acids



**Fig. S2** (a) Raman(244nm) spectra of the TS-1 samples modified in HCl solution with different concentrations  
(b) Raman (325nm) spectra of the TS-1 samples modified in HCl solution with different concentrations





**Fig.S3** In situ Raman spectra of the TS-1 ( $\text{SiO}_2/\text{TiO}_2=30/\text{H}_2\text{O}_2/\text{H}_2\text{O}/\text{CH}_3\text{OH}$  system obtained at different times during the methanol-included epoxidation reaction, collected with a 244nm laser: (a) Raman spectrum obtained at the 5th minute, (b) 10th minute, (c) 15th minute, (d) 20th minute, (e) 25th minute, (f) 30th minute, (g) 35th minute, (h) 40th minute, (i) 45th minute, (j) 50th minute, (k) 55th minute, (l) 60th minute, (m) 65th minute, (n) 70th minute, (o) 75th minute.