

## **Electronic Supplementary Information (ESI)**

### **Synthesis of anatase-free nano-sized hierarchical TS-1 zeolite and its excellent catalytic performance in alkenes epoxidation**

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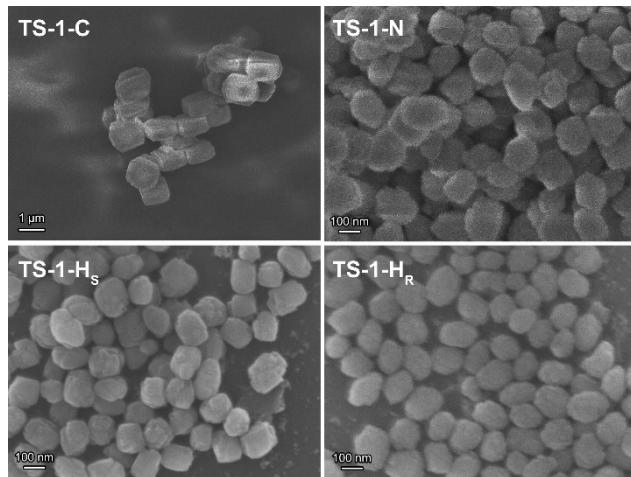


Fig. S1 SEM images of microporous TS-1 (TS-1-C and TS-1-N) and nano-sized hierarchical TS-1 (TS-1-H<sub>S</sub> and TS-1-H<sub>R</sub>).

Table S1 textural properties of TS-1-H<sub>R</sub> and TS-1-H<sub>S</sub> synthesized with different addition amount of Triton X-100.

samples	S <sub>BET</sub> (m <sup>2</sup> /g) <sup>a</sup>	S <sub>micro</sub> (m <sup>2</sup> /g) <sup>b</sup>	S <sub>ext</sub> (m <sup>2</sup> /g) <sup>b</sup>	V <sub>micro</sub> (cm <sup>3</sup> /g) <sup>b</sup>	V <sub>meso</sub> (cm <sup>3</sup> /g) <sup>c</sup>
TS-1-H <sub>S</sub> -A	406	296	110	0.15	0.29
TS-1-H <sub>S</sub> -B	414	292	122	0.14	0.30
TS-1-H <sub>S</sub> -C	430	260	170	0.12	0.38
TS-1-H <sub>R</sub> -A	414	300	114	0.15	0.30
TS-1-H <sub>R</sub> -B	429	295	134	0.14	0.32
TS-1-H <sub>R</sub> -C	455	289	166	0.14	0.38

A, B, C refer to Triton X-100 to SiO<sub>2</sub> molar ratio of 0.102, 0.204 and 0.408, respectively. a. S<sub>BET</sub> (total surface area) calculated using the BET method; b. S<sub>micro</sub> (micropore area), S<sub>ext</sub> (external surface area) and V<sub>micro</sub> (micropore volume) calculated using the t-plot method; c. V<sub>meso</sub> (mesopore volume) calculated using the BJH method (from adsorption).

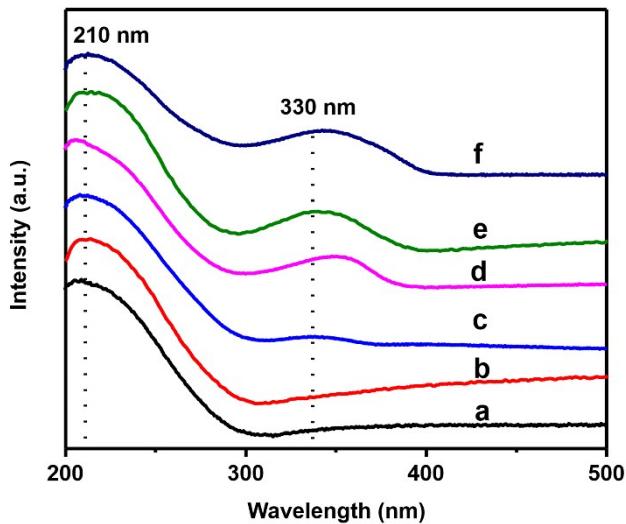


Fig. S2 UV/Vis spectra of TS-1-H<sub>R</sub> (a, b, c) and TS-1-H<sub>S</sub> (d, e, f) synthesized with Triton X-100 to SiO<sub>2</sub> molar ratio of 0.102, 0.204 and 0.408, respectively.

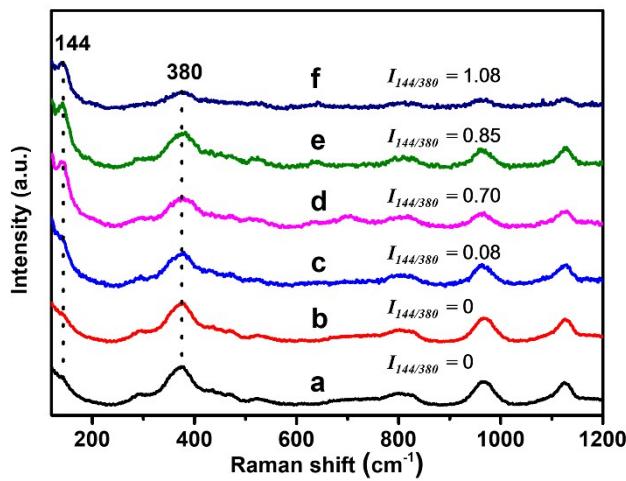


Fig. S3 UV-Raman spectra of TS-1-H<sub>R</sub> (a, b, c) and TS-1-H<sub>S</sub> (d, e, f) synthesized with Triton X-100 to SiO<sub>2</sub> molar ratio of 0.102, 0.204 and 0.408, respectively.  $I_{144/380}$  is used to estimate the content of anatase TiO<sub>2</sub>. The wavelength of the excitation light is 320 nm.

Table S2 Epoxidation of various alkenes over different TS-1 samples

	allyl chloride		1-heptene		cyclopentene	
	Conv. (%)	Sel. (%)	Conv. (%)	Sel. (%)	Conv. (%)	Sel. (%)
<b>TS-1-C</b>	27.7	100	12.2	99.5	23.8	100
<b>TS-1-N</b>	66.9	96.1	30.3	98.1	33.7	99.0
<b>TS-1-H<sub>S</sub></b>	63.7	94.3	36.1	98.4	40.2	97.7
<b>TS-1-H<sub>R</sub></b>	70.6	96.9	51.3	99.1	50.3	98.5

Reaction conditions: cat., 50 mg; alkenes, 10 mmol; H<sub>2</sub>O<sub>2</sub> (30 wt%), 10 mmol; CH<sub>3</sub>OH, 10 mL; temp., 333 K; time, 2 h.



Fig. S4 Recycling tests of TS-1-H<sub>R</sub> as catalyst for epoxidation of 1-hexene  
 Reaction conditions: cat., 50 mg; 1-hexene, 10 mmol; H<sub>2</sub>O<sub>2</sub> (30 wt%), 10 mmol; CH<sub>3</sub>OH, 10 mL; temp., 333 K; time, 2 h.

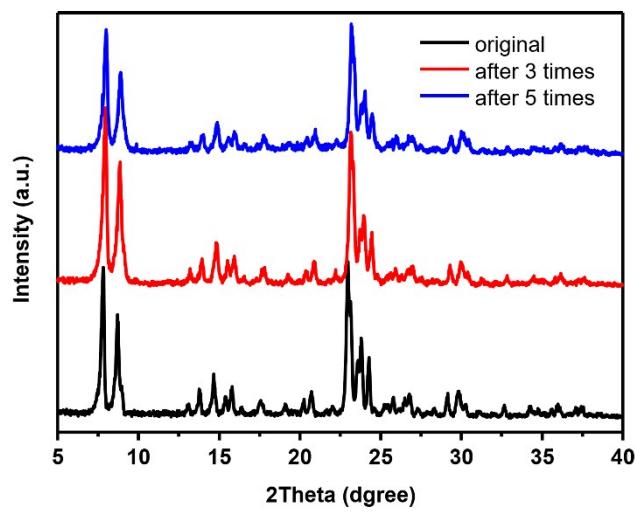


Fig. S5 XRD patterns of TS-1-H<sub>R</sub> in recycling test

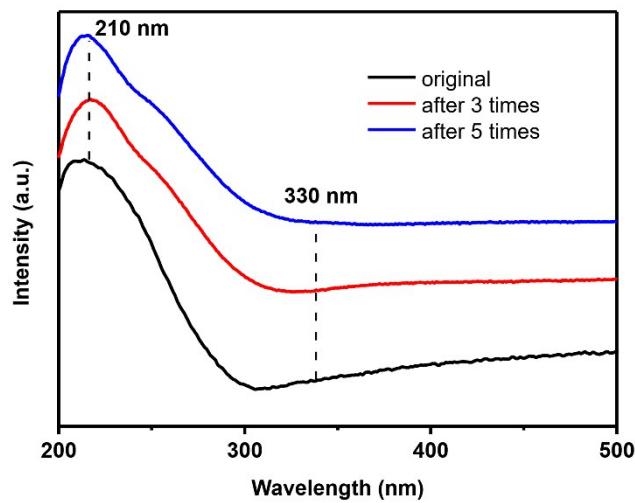


Fig. S6 UV/Vis spectra of TS-1-H<sub>R</sub> in recycling test