Supporting Information

Large-surface-area TS-1 nanocatalysts: a combination of nanoscale particle sizes and hierarchically micro/mesoporous structures

1. Catalyst preparation

1.1 Synthesis of traditional TS-1 zeolite

In a typical synthesis procedure, 10.42 g of TEOS was mixed with 18 g of deionized water, followed by the addition of 10.98 g of TPAOH. The above mixture was stirred at room temperature for 2~3 h to obtain a clear solution. Then, 0.34 g of TBOT dissolved in 6 g of IPA was added slowly into the above solution below 4℃ and kept stirring for 4 h to prevent the formation of isolated TiO_x phase. After that, the mixture was transferred into Teflon-lined stainless-steel autoclave under autogenous pressure at 150℃ for 15 h. After centrifugation, rinsing with deionized water, drying at 70℃ overnight and calcination in air at 550℃ for 6 h, conventional micrometer-sized TS-1 zeolite (denoted as *micro*TS-1) was obtained.

1.2 Synthesis of mesoporous TS-1 zeolite

In a typical synthesis procedure reported by Zhu et al,[1] 15.62 g of TEOS was mixed with 36 g of deionized water, followed by the addition of 10.98 g of TPAOH. The above mixture was stirred at room temperature for 2~3 h to obtain a clear solution. Then, 0.51 g of TBOT dissolved in 10 g of IPA was added slowly into the above solution below 4℃ and kept stirring for 12 h to prevent the formation of isolated TiO_x phase. Afterwards, the mixture was aged at 90℃ for 6 h to form zeolite nanoparticles. Then it was added into the surfactant solutions consisting of 1.8 g of CTAB in 150 g of deionized water. The above mixture was kept stirring at room temperature for another 6 h. After adding 30 g of ethanol, the mixture was transferred into Teflon-lined stainless-steel autoclave under autogenous pressure at 150℃ for 15 h. After repeated centrifugation, rinsing with deionized water and drying at 70 ℃ overnight, the precursor was calcined in air at 600℃ for 7 h to get mesoporous TS-1 zeolite (denoted as *meso*TS-1).

2. Figure Captions

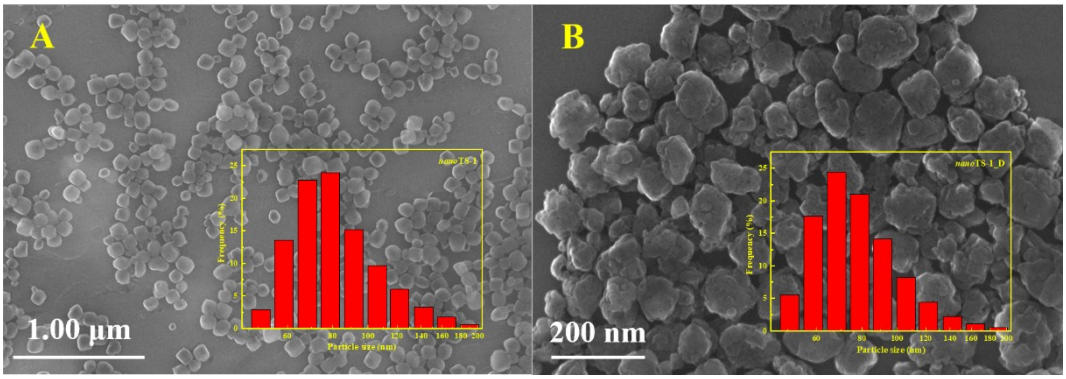

Fig. S1 SEM images of synthesized *nano*TS-1 (A) and *nano*TS-1_D (B). The insets in (A, B) are the Dynamic Light Scattering(DLS) particle size distributions.

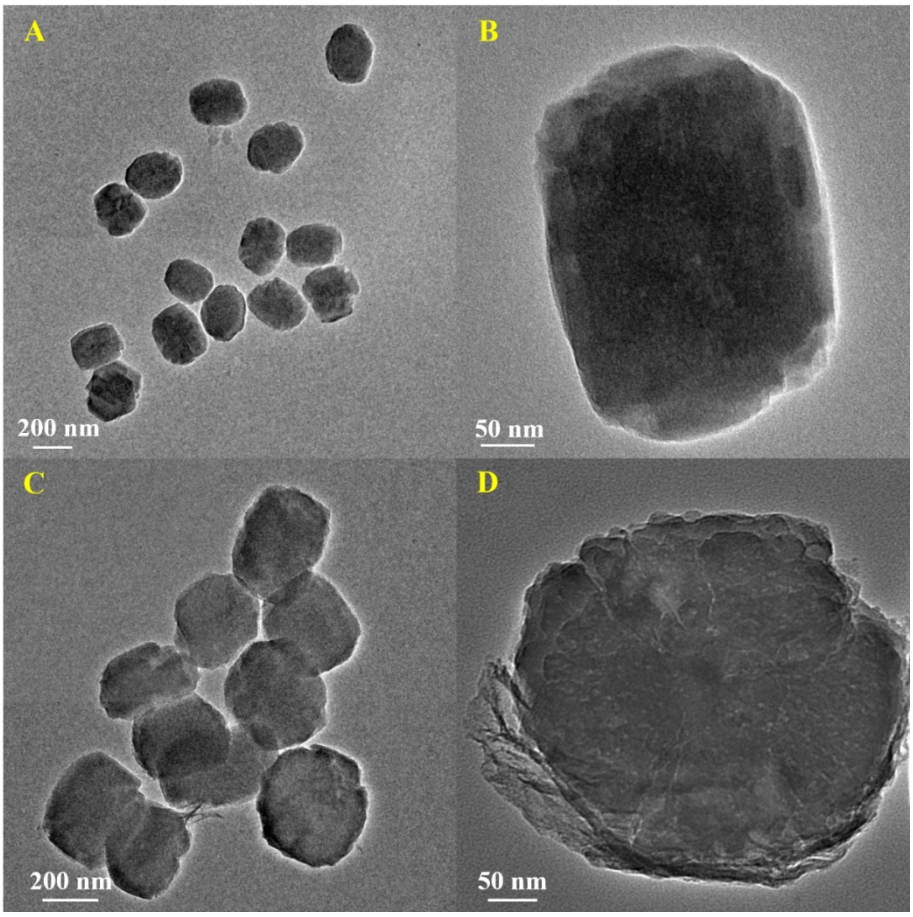

Fig.S2 TEM images of synthesized *micro*TS-1 (A, B) and *meso*TS-1 (C, D).

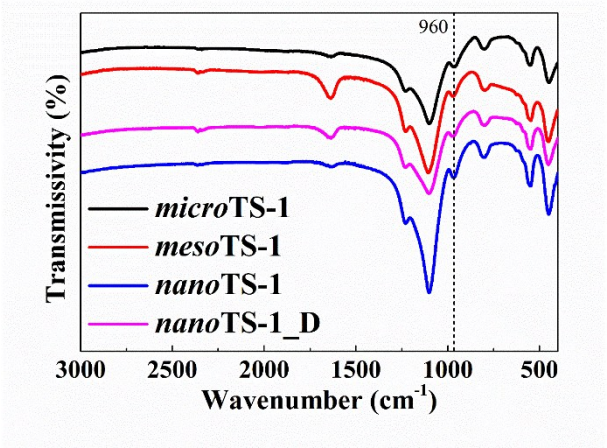

Fig. S3 FT-IR spectra of synthesized TS-1 zeolites.

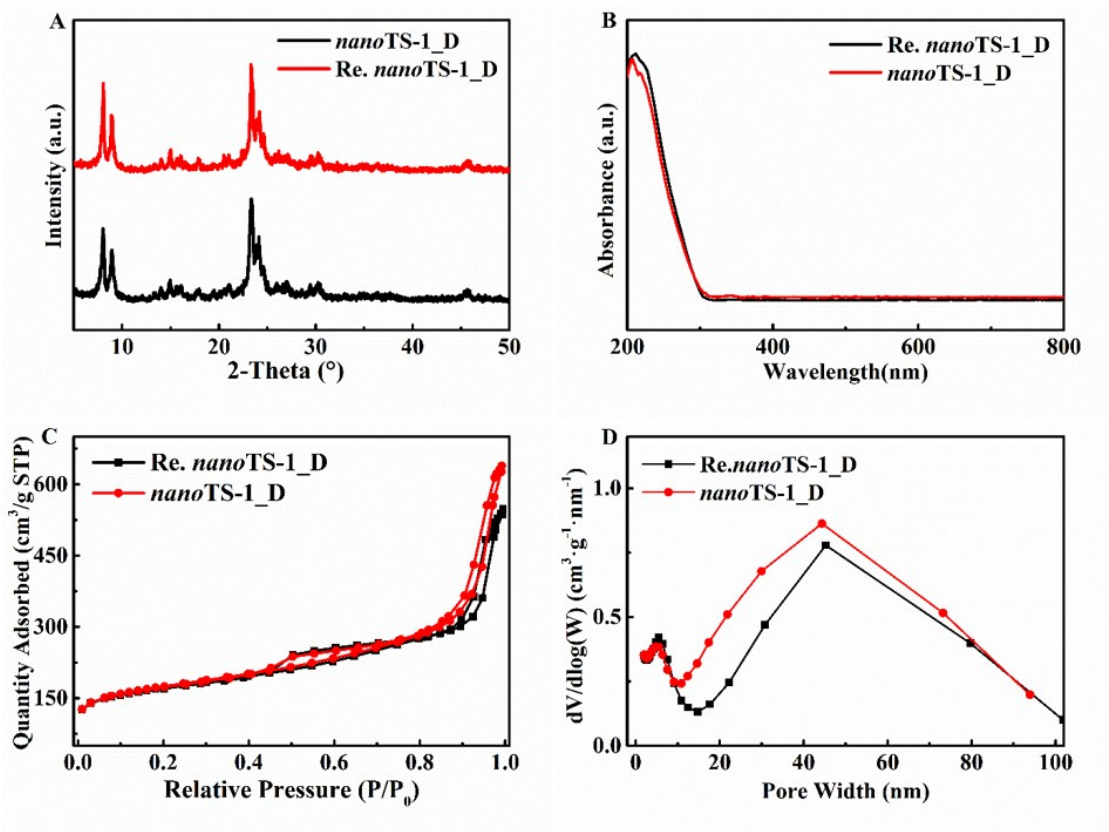

Fig. S4 (A) Powder XRD patterns, (B) UV-vis spectra, (C) N_2 sorption isotherms and (D) pore size distribution (PSD) of synthesized *nano*TS-1_D and Re. *nano*TS-1_D

Table S1 Chemical composition and structural characteristics of the synthesized TS-1 zeolites.

Sample	S_{BET} (m^2/g)	S_{exter} (m^2/g)	V_{total} (cm^3/g)	V_{meso} (cm^3/g)
*nano*TS-1_D	606	346	0.86	0.74
Re. *nano*TS-1_D	597	326	0.76	0.64

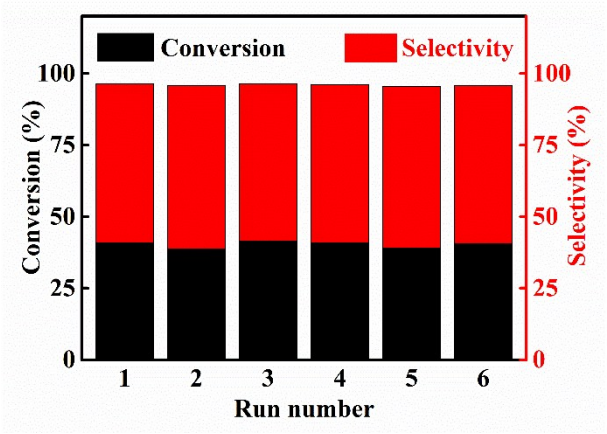

Fig. S5 Recyclable test of *nano*TS-1_D in the epoxidation of 1-hexene. (Even after 6 recycles, we can hardly see obvious loss in conversion or selectivity.)

Table S2 Catalytic performances of *nano*TS-1_D in the epoxidation of 1-hexene during the recyclable test.

Run number	1-hexene epoxidation	
	Conv.(%)	Sel.(%)
1	40.9	96.3

2	38.7	95.7
3	41.4	96.4
4	41.0	96.2
5	39.0	95.5
6	40.7	95.9

Supporting reference

1 Y. Zhu, Z. Hua, X. Zhou, Y. Song, Y. Gong, J. Zhou, J. Zhao and J. Shi, *RSC Adv.*, 2013, **3**, 4193.