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Supplementary Materials

for

Hierarchically core/shell-structured TS-1 with multiple mesopores for highly efficient epoxidation of olefins

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Experimental Section

1. Materials synthesis

1.1 Synthesis of various TS-1 materials

Microsized TS-1

The TS-1 bulk crystal with a microsize was synthesized in a cheap way using colloidal silica as silicon source and TPA^+ as SDA. The representative gel composition is 1 SiO_2 : 0.025 TiO_2 : 0.03TPAOH : 0.03 TPABr : 12 H_2O, in which the combination of TPAOH and TPABr allows to reduce greatly the amount of organic SDA. In a typical synthesis, tetrapropylammonium hydroxide (TPAOH, 20 wt%) was added into deionized water. Tetrabutyl titanate (TBOT) as titanium source was then added dropwise into the solution under vigorous stirring. The mixture was further stirred for 6 hours to completely hydrolyze TBOT. When the solution become transparent, tetrapropylammonium bromide (TPABr) and colloidal silica (30 wt%) was added into the solution. The resultant gel was stirred at room temperature for another 24 hours. The synthesis gel was transferred into a Teflon-lined stainless steel autoclave, in which the crystallization was continued at 443 K for 72 hours. The solid product was collected by filtration, washed with deionized water and dried at 353 K in air overnight. After calcined at 823 K to eliminate the organic species, the resultant product was designated as TS-1.

Nanosized TS-1 and layered TS-1

For control, nanosized TS-1 and layered TS-1 were also hydrothermally synthesized.

Nanosized TS-1 (TS-1-nano) was synthesized according to classic method developed by ENI Chem,[1] from a gel with a composition of 1 SiO_2: 0.025 TiO_2: 0.25 TPAOH: 10 H_2O. Tetraethyl orthosilicate (TEOS) and TBOT were added into a flask under vigorous stirring for another 1 hour, giving rise to solution A. Solution B was prepared by TPAOH with deionized water. Solution A was then added dropwise into solution B under stirring to allow a simultaneous hydrolysis of TEOS and TBOT. The resultant mixture was heated to 333 K and stirred for 1 hour till a gel was formed. A further removal of ethanol was carried out by heating the gel to 348 K and stirred for 3 hours. Finally, the synthesis gel was transferred into a Teflon-lined stainless autoclave and heated to 443 K for 2 days. NH_4Cl was added into the resultant suspension to flocculate zeolite crystals. The final product was filtered, washed with deionized water and calcined at 823 K in air for 6 hours to eliminate TPA^+ , resulting in TS-1-nano sample.

Synthesis of lamellar TS-1 (LTS-1) composed of MFI nanosheets was synthesized following previously reported procedures.[2] Firstly, the SDA was synthesized in two steps according to previous report.[3] Firstly, 0.01 mol of *N,N*-dimethyloctadecylamine and 0.1 mol of 1,6-dibromohexane were dissolved into 300 mL mixture of acetonitrile and toluene (1:1 volume ratio). The mixture was then heated and stirred at 343 K for 16 hours. After evaporating the solvents, the first-step product $[C_{18}H_{37}Me_2N^+(CH_2)_6]Br^-$, designated as $C_{18\text{-}6\text{-}0}$, was gained. Secondly, 0.01 mol of $C_{18\text{-}6\text{-}0}$ was mixed with 0.02 mol of tripropylamine in chloroform, stirred under refluxing conditions for 16 hours. The final product of $[C_{18}H_{37}Me_2N^+(CH_2)_6N^+Pr_3]Br^{2-}$ (designated as $C_{18\text{-}6\text{-}3}$) was acquired via filtration and vacuum drying. $C_{18\text{-}6\text{-}3}$ was then ion-exchanged into hydroxide form in a column filled with anion-exchange resin.

The synthesis of layered TS-1 was according to previously reported literature.[1] In a typical synthesis, TEOS and TBOT was hydrolyzed in an aqueous solution of $C_{18\text{-}6\text{-}3}(OH)_2$, forming a synthetic gel with a molar composition of 1.0 SiO_2 : 0.0167 TiO_2 : 0.08 $C_{18\text{-}6\text{-}3}(OH)_2$: 100 H_2O : 4.0 EtOH. The resultant gel was transferred to a Teflon-lined stainless steel autoclave, which was heated at 423 K for 20 days under rotation (60 rpm). After crystallization, the solid product was filtered, washed with distilled water, and dried at 393 K. The product was further calcined to eliminate the OSDA. The resultant solid catalyst was designated as LTS-1.

1.2 Synthesis of hierarchical TS-1 by desilication-recrystallization

The abovementioned microsized TS-1 was treated with NaOH in presence of Gemini surfactant $C_{18\text{-}6\text{-}3}$. In a typical treatment, TS-1 powder, NaOH solid and $C_{18\text{-}6\text{-}3}$ were added directly into deionized water, forming a mixture with a molar composition of 1 SiO_2: 0.13 $C_{18\text{-}6\text{-}3}$: 0.07 NaOH : 45 H_2O. After the mixture was homogenized, the mixture was transferred to a Teflon-lined stainless autoclave, which was heated to 423 K under rotation (60rpm) for 120 hours. After treatment, the solid product was filtered and washed with deionized water. The product was further calcined to eliminate the residue of organic species. After the calcination, the solid was washed with 1 M HCl water/EtOH solution at 353 K for 3 hours to recover the Ti sites poisoned by Na^+ during alkaline treatment. The resultant solid product was designated as HTS-1

Microsized TS-1 was also subject to desilication-recrystallization using TPA. The control experiment was conducted under the same conditions mentioned above but using TPABr of TPAOH instead of C_{18-6-3} as SDA. The final product was designated as TS-1-TPA and TS-1-TPAOH correspondingly.

2. Characterization methods

The powder X-ray diffraction patterns were recorded on a Rigaku Ultima IV X-ray diffractometer using Cu-Kα radiation (λ=1.5405 Å) at 35 kV and 30 mA. The SEM images were taken on a Hitachi S-4800 Scanning electron microscope. The TEM images were collected on a TECNAI GsF30 Transmission Electron microscope. The nitrogen adsorption isotherms were recorded at 77 K on a BELSORP-MAX instrument after activating the samples at 393 K overnight. The UV-visible diffuse reflectance spectra were recorded on a SHIMADZU UV-2700 spectrometer using $BaSO_4$ as a reference. The FTIR spectra were collected on a NEXUS 670 FT-IR spectrometer in absorbance mode at a spectral solution of 2 cm^{-1}. The spectra in the region of zeolite framework vibration were measured using the KBr technique. The spectra of hydroxyl stretching were measured on self-supported wafers (2 cm in diameter and 4.8 mg cm^{-2} in thickness). The samples were evacuated for 2 h at 723 K in a quartz IR cell sealed with CaF_2 windows, which were connected to a vacuum system. All spectra were collected at room temperature. ^{29}Si solid-state MAS NMR and ^{1}H-NMR were recorded on a VARIAN VNMRS-400WB spectrometer. Si and Ti content were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer after the sample was dissolved in aqueous HF solution. The surface Ti state and quantity was measured by X-ray photoelectron spectra on PHI 5000 Versa probe using monochromatic Al Kα X-ray source.

3. Catalytic reactions

The epoxidation of alkenes with H_2O_2 (30 wt% aqueous solution) was carried out in a reaction tube equipped with reflux condenser. In a typical run, 50 mg of catalyst, 10 mL of methanol, 10 mmol of alkene and 10 mmol of H_2O_2 were mixed in the tube and stirred vigorously at 333 K for 2 h. The epoxidation of propylene was carried out in a 50 mL Teflon-lined autoclave reactor. First, 50 mg of catalyst, 10 mL of methanol, and 10 mmol of H_2O_2 were added into the reactor. Then the reactor was then charged with excess propylene at 0.6 MPa. The reaction was carried out under vigorous stirring at 333 K for 2 h. All products were analyzed on a Shimadzu GC-2014 gas chromatograph equipped with a DM-WAX-30m column (Dikma Technologies Inc.) and an FID detector.

The epoxidation of alkenes in the presence of poisoning agents were carried out following literature method.[4] It is possible to investigate the contribution of the Ti sites located in different spatial positions by employing amines with changeable molecular dimensions. The reactions were carried out the abovementioned conditions but only adding 2 mmol of amine (trimethylamine, TMA or triphenylamine, TPhA) into the reaction system.

1. M. P. G. Taramasso and B. Notari, US Pat, 4410501, 1983.
2. K. Na, C. Jo, J. Kim, W.-S. Ahn and R. Ryoo, *ACS Catal.*, 2011, **1**, 901.
3. L. Xu, C.-G. Li, K. Zhang and P. Wu, *ACS Catal.*, 2014, **4**, 2959.
4. P. Wu and T. Tatsumi, *J. Phys. Chem. B*, 2002, **106**, 748.

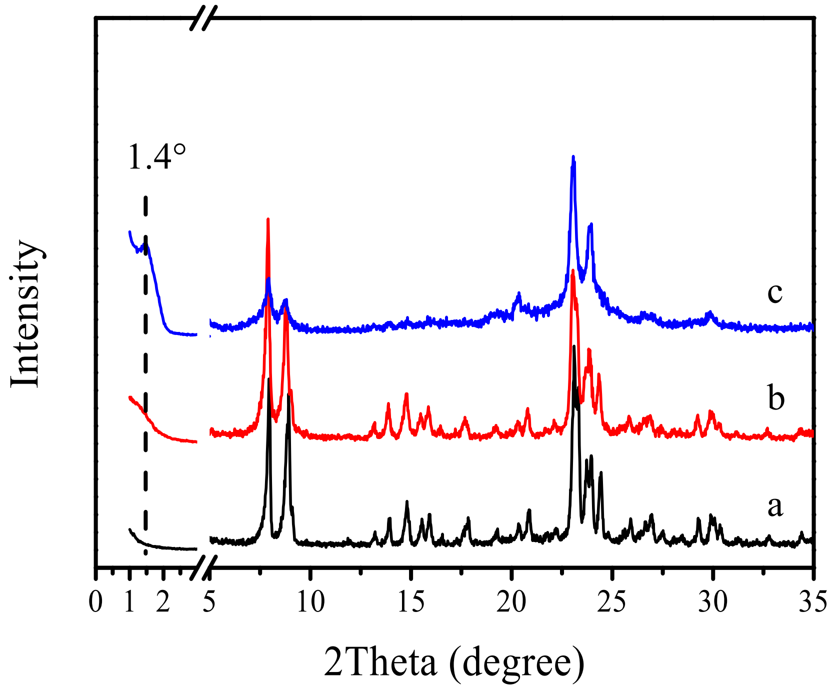


Fig. S1 X-ray diffraction patterns of pristine microsized TS-1 (a), HTS-1 as-synthesized by desilication-recrystallization method, (b) and as-synthesized conventional LTS-1 (c).

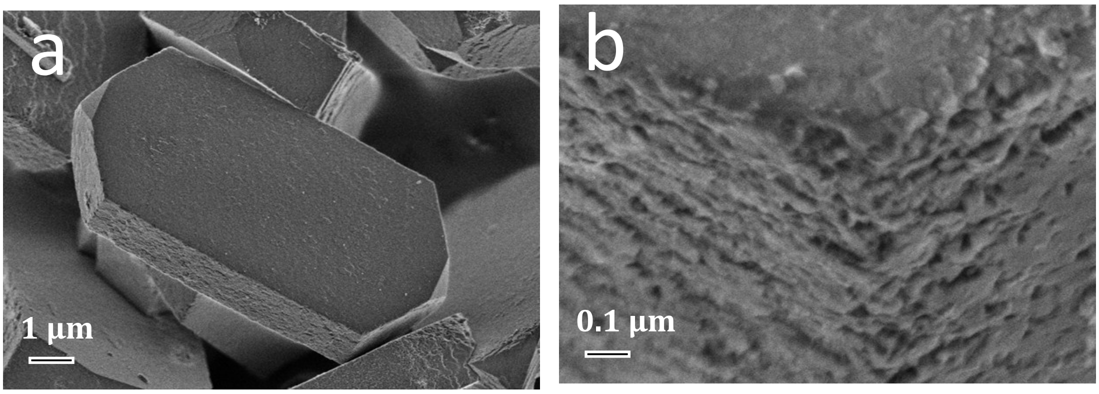


Fig. S2 SEM images of pristine microsized TS-1 (a, b).

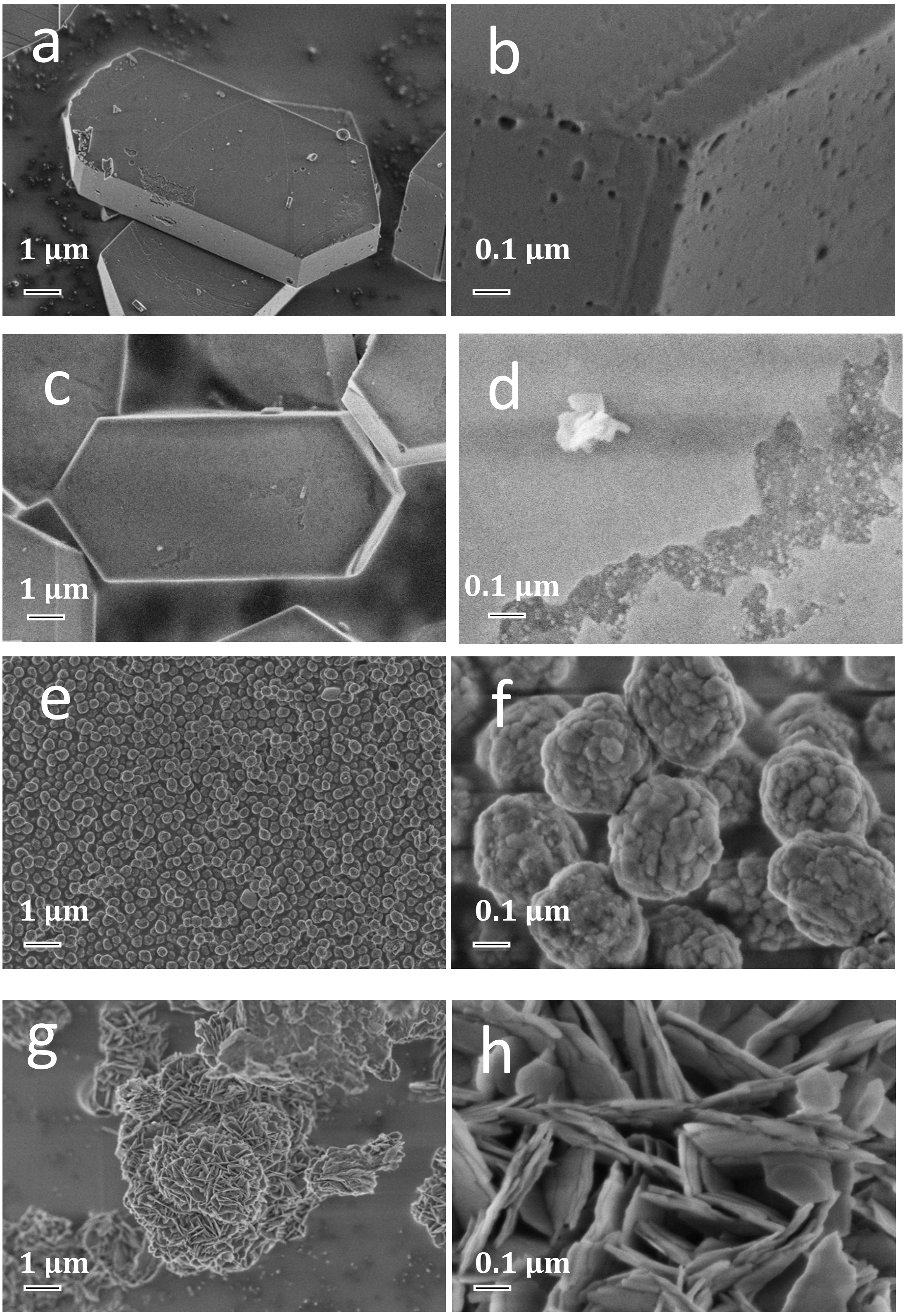


Fig. S3 SEM images taken with different magnifications for TS-1-TPA (a, b), TS-1-TPAOH (c, d), TS-1-nano (e, f) and LTS-1 (g, h).

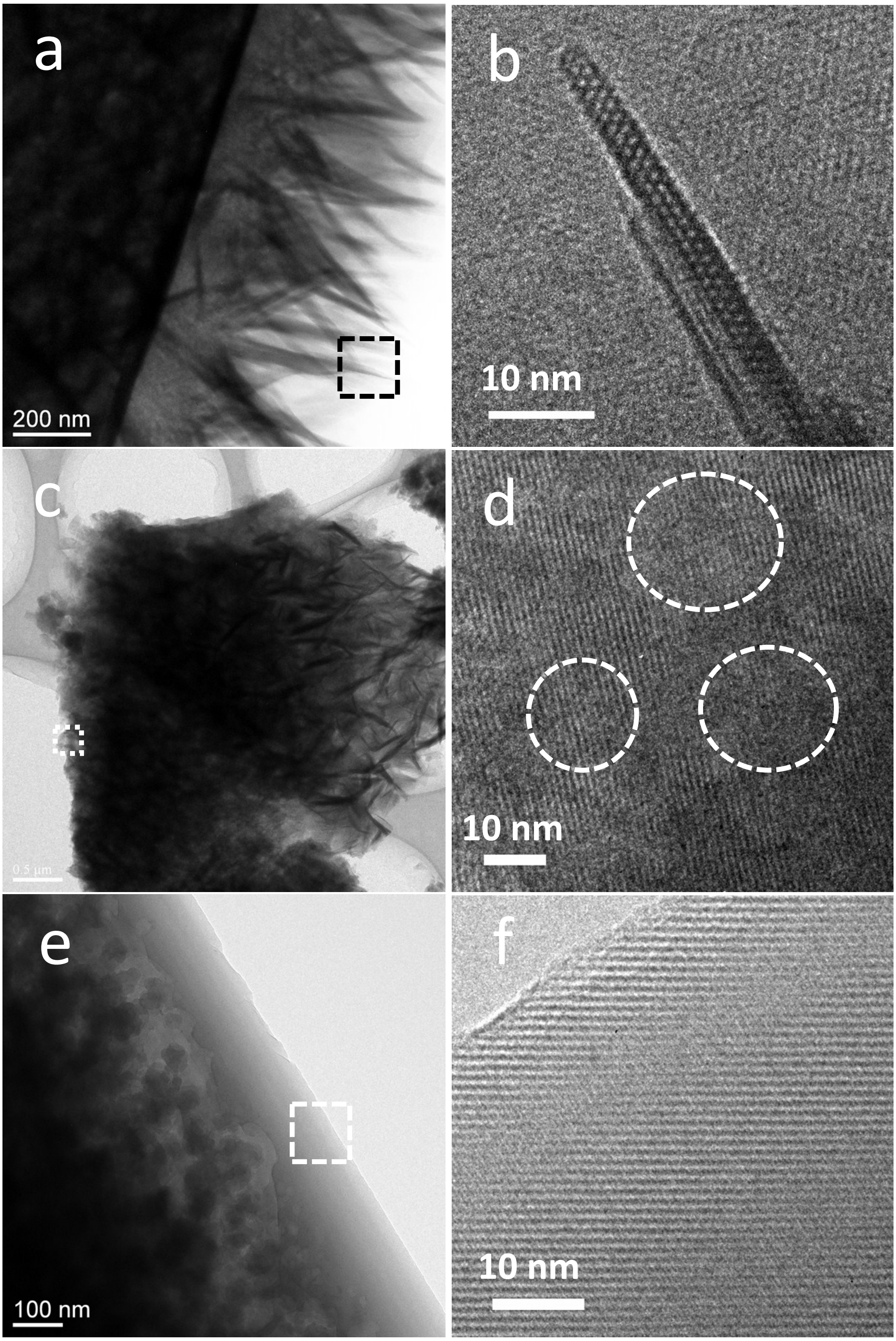


Fig. S4 TEM images of HTS-1 (a, b), smashed HTS-1 crystal (c, d) and TS-1-TPA (e, f). The b, d and f images represent the enlarged ones of selected region.

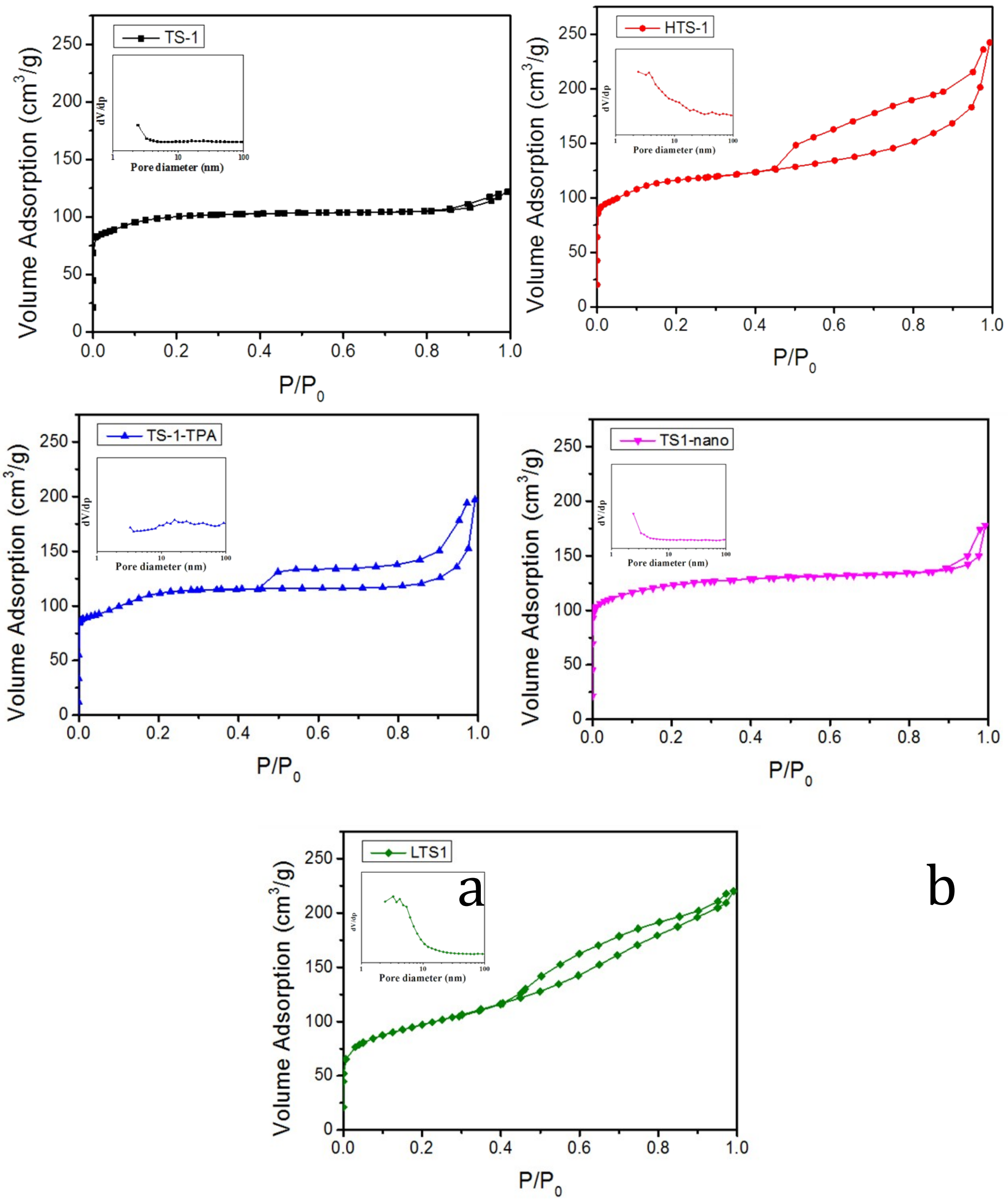
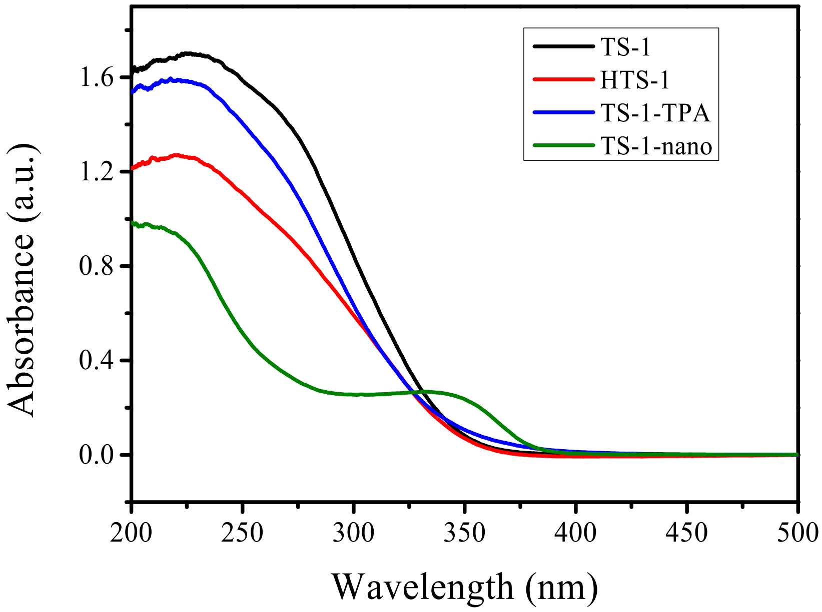


Fig. S5 N_2 adsorption/desorption isotherms and pore-size distribution calculated by BJH method of microsized TS-1 (a), HTS-1(b), TS-1-TPA (c), TS-1-nano (d) and LTS-1 (e).



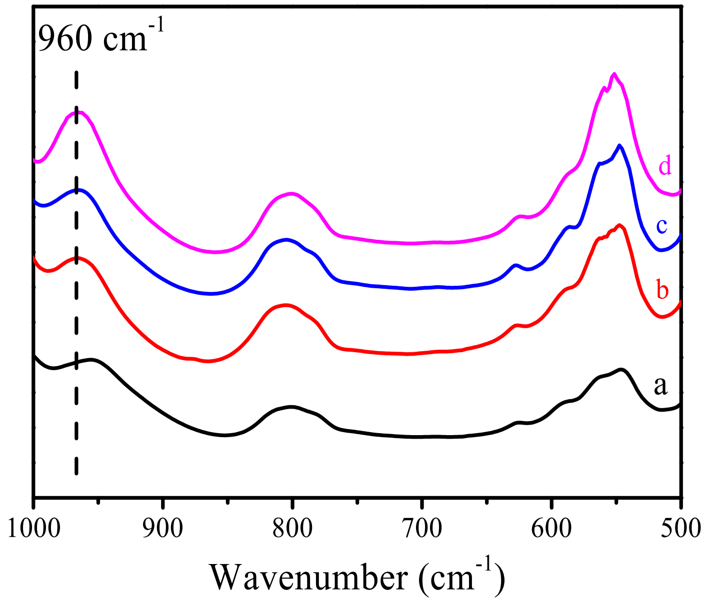


Fig. S6 DR UV-Vis spectra (uper) and FTIR spectra in the framework vibration region (down) of TS-1 (a), HTS-1 (b), TS-1-TPA (c) and TS-1-nano (d).

The IR spectra were recorded using KBr technique after evacuating the samples at

723 K for 2 h.

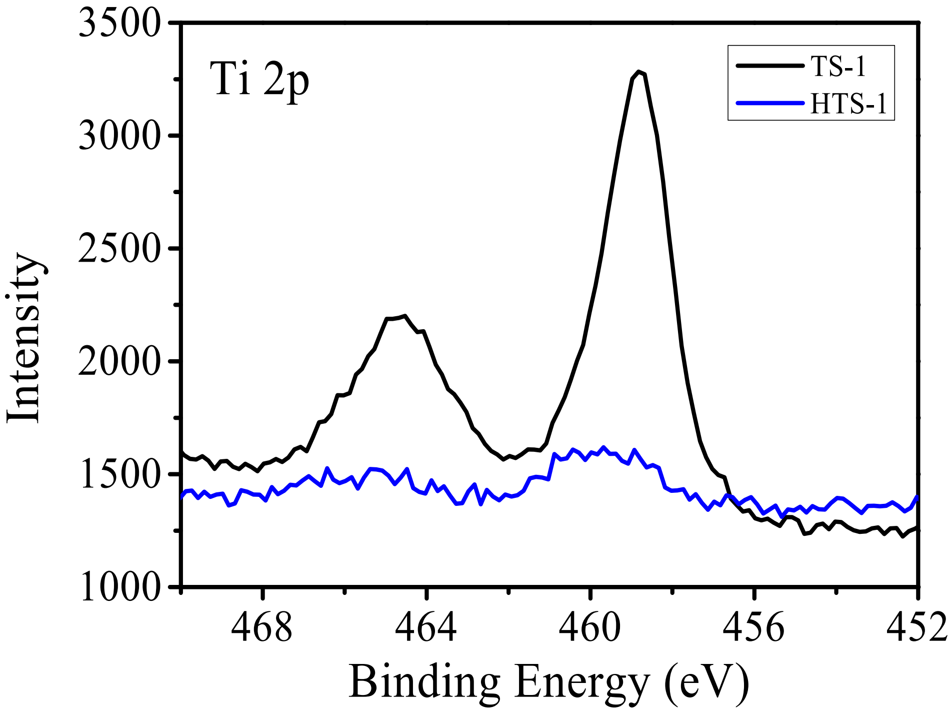


Fig. S7 Ti 2p XPS spectra of TS-1 and HTS-1.

Table S1. Surface and bulk elemental composition of titanosilicates measured by XPS and ICP analyses.

	XPS			ICP
	Si (wt.%)	Ti (wt.%)	Si/Ti molar ratio	Si/Ti molar ratio
TS-1	26.1	1.76	25	46
HTS-1	27.0	0.24	193	50.0

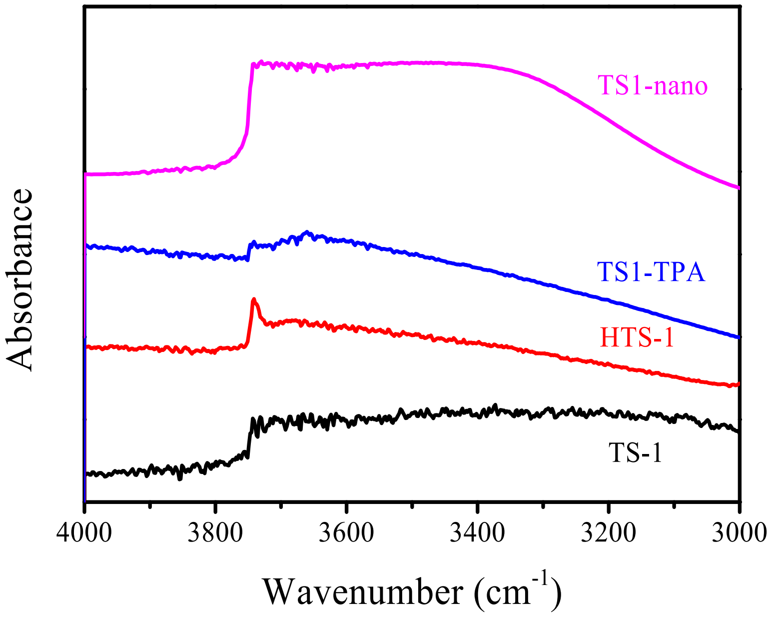


Fig. S8 FT-IR spectra of different titanosilicates in the hydroxyl stretching region. The spectra were all collected using self-supported wafer after evacuation at 723 K for 2 h.

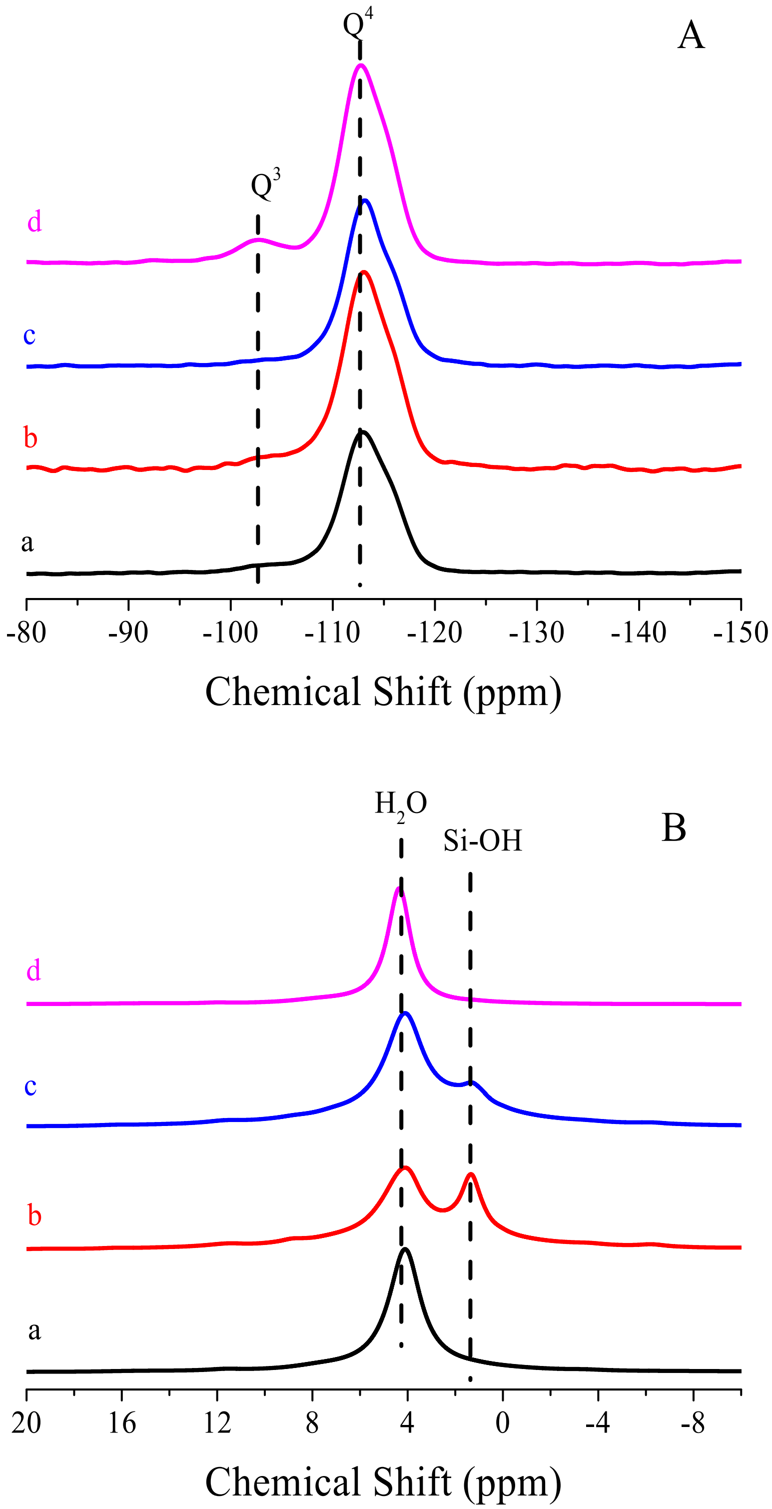


Fig. S9 ^{29}Si-NMR spectra (A) and ^{1}H-NMR spectra (B) of TS-1 (a), HTS-1(b), TS-1-TPA (c)and TS-1-nano (d).

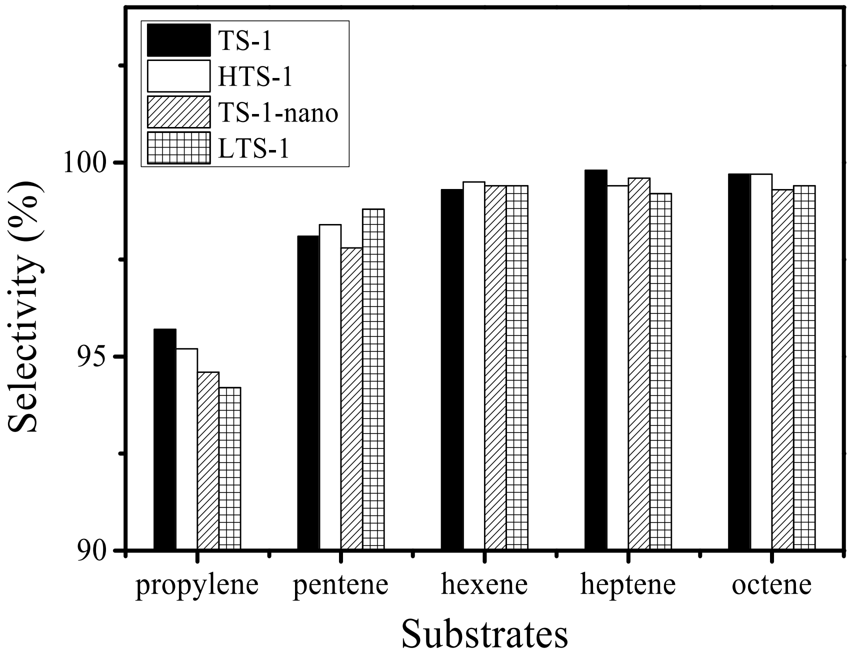


Fig. S10 Epoxide selectivity in the epoxidation of various linear alkenes with different chain length over titanosilicates. Reaction conditions: alkene, 10 mmol (for propylene, 0.4MPa was charged); H_2O_2, 10 mmol; methanol, 10 mL; cat., 50 mg; temp., 333 K; time, 2 h.

Table S2. Catalytic performance of TS-1-TPA and TS-1-TPAOH in the epoxidation of 1-hexene

	Conv.(%)	Oxide sel. (%)
TS-1-TPA	22.8	98.6
TS-1-TPAOH	23.4	99.3

Reaction condition: alkene, 10 mmol; H_2O_2, 10 mmol; methanol, 10 mL; cat., 50 mg; temp., 333 K; time, 2 h.

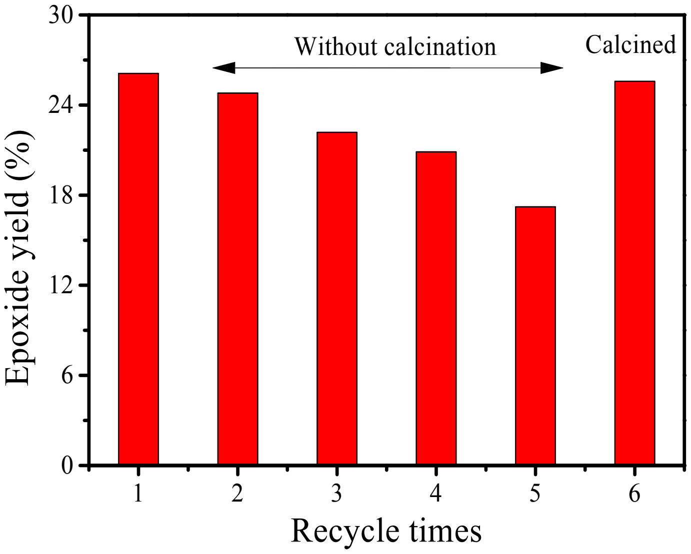


Fig. S11 The reuse of HTS-1 in the expoxidation of 1-hexene.

Reaction condition: alkene, 10 mmol; H_2O_2, 10 mmol; methanol, 10 mL; cat., 50 mg; temp., 333 K; time, 2 h.

After each reaction, the liquid-phase reaction removed by centrifugation. Then, the reaction was restarted by charging under the same conditions. After the fifth time of recycling, the catalyst was calcined under 823 K for 5 h in air with purpose to eliminate the organic residue occluded inside zeolite channels.

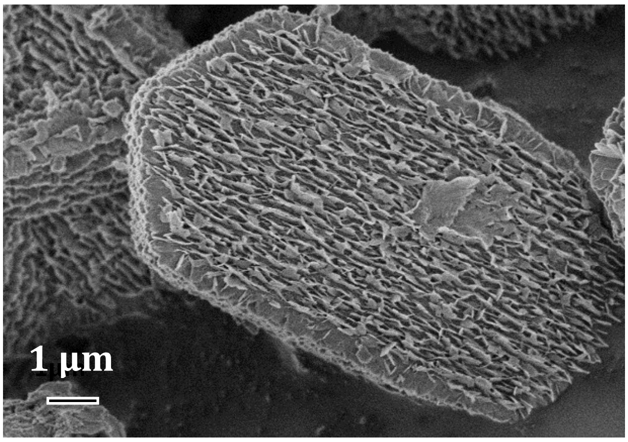


Fig. S12 SEM image of HTS-1 after the epoxidation of 1-hexene for six times.

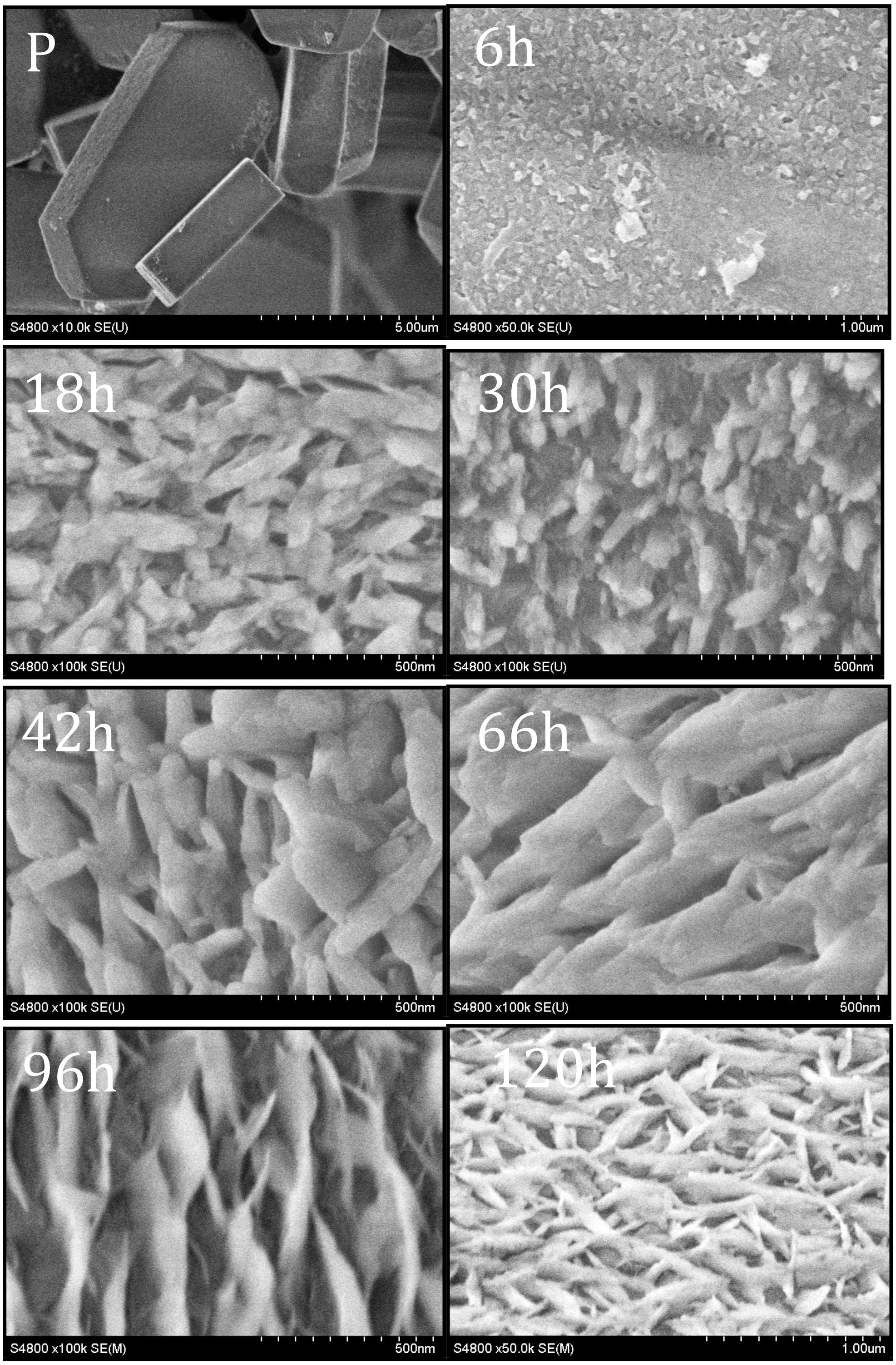


Fig. S13 SEM images of HTS-1 synthesized by desilication-recrystallization procedure for a different period of time. P represents the pristine microsized TS-1 sample.

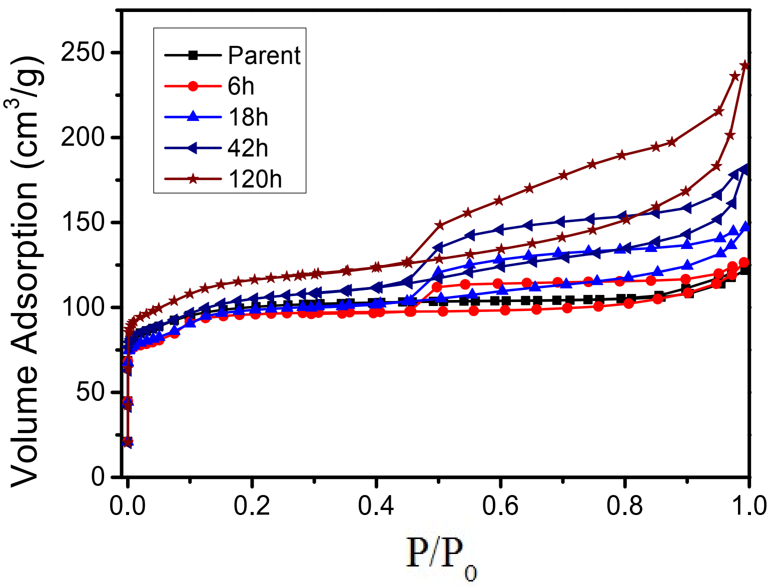


Fig. S14 N_2 adsorption/desorption isotherms of HTS-1 synthesized by desilication-recrystallization procedure for a different period of time.

Table S3. Physiochemical properties of HTS-1 collected at different time.

Catalyst	Si/Ti[a]	S_{BET}[b] (m^2 g^{-1})	V_{micro}[c] (m^3 g^{-1})	V_{meso}[d] (m^3 g^{-1})	V_{total}[b] (m^3 g^{-1})	$S_{external}$[c] (m^2 g^{-1})
Parent	46.3	268	0.154	0.02	0.17	14
6h	45.5	278	0.144	0.05	0.19	15
18h	42.6	291	0.133	0.09	0.22	25
30h	43.1	295	0.127	0.12	0.25	24
42h	43.7	303	0.125	0.16	0.28	32
66h	44.4	326	0.121	0.17	0.29	38
96h	44.1	315	0.129	0.17	0.30	41
120h	44.0	339	0.133	0.24	0.37	60

[a] Measured by ICP-AES.

[b] Calculated from N_2 adsorption/desorption measurement with BET method.

[c] Calculated from N_2 adsorption/desorption measurement using *t*-plot method.

[d] $V_{meso}=V_{total}-V_{micro}$.

The time-dependent deslication-recrystallization (DR) process for synthesizing HTS-1 was traced. The SEM invetigation showed the morphology changed greatly during the whole process (ESI, Fig. S10). The desilication on the crystal surface appeared at 6 h of treatment, but no signs of recrystallization were observed. After the DR treatment for 18 h, randomly distributed rod-like crystals occurred and covered the etched surface of zeolite crystals. With further prolonged recrystallization time to 66 h, the rod-like crystals transformed into ordered lamellar structure. A longer treatment for 96 - 120 h led to a completely crystalized layered shell structure on the core crystals. A recrystallization took a relatively long time, zeolitic shell, especially with a unique lamellar MFI structure, was not likely formed within 18 h. Thus, it is likely that the rod-like crystals in the early stage were the mesophase assembled from the Si species dissolved out the bull crystals. A similar phenomenon was reported previously in direct hydrothermal synthesis of lamellar MFI zeolite using Gemini-type SDA (K. Na, M. Choi, W. Park, Y. Sakamoto, O. Terasaki and R. Ryoo, *J. Am. Chem. Soc.*, 2010, *132*, 4169).The recrystallization of lamellar MFI crystal experienced a mesophase intermediate. The N_2 adsorption measurement was in agreement to the observed structure transformation (ESI, Fig. S11). During the whole process of treatment, the material presented a typical change from microporous zeolites to hierarchical materials according to surface area and pore volume statistics. The hysteresis loop occurred in the early stage of treatment. The mesopore volume of the material gradually increased from 0.02 to 0.24 $cm^3 g^{-1}$ (ESI, Table S2). Along with the generation of mesopores, the external surface was enlarged by four times, from 14 $m^2 g^{-1}$ in beginning TS-1 to 60 $m^2 g^{-1}$ in final HTS-1 product. The mesoporous shell structure contributed mostly the whole mesoporosity of HTS-1.