Electronic Supplementary Material (ESI) for Chemical Communications

Defect-Less, Layered Organo-Titanosilicate with Superhydrophobicity and Its Catalytic Activity in Room-Temperature Olefin Epoxidation

Supporting Information

Hui Zhou, Liping Xiao[a], Xiaonao Liu, Sha Li, Hisayoshi Kobayashi, Xiaoming Zheng and Jie Fan[b]

Experimental

Synthesis of LOTS (Ti/Si mole ratio = 0.07) materials: Layered organo-titanosilicate (denoted as LOTS) is prepared by a facile and one-step method. In a typical synthesis, 10 mmol of phenyltrimethoxysilane (PTMS), 0.7 mmol of titanium n-butoxide (TBOT), 12 mmol hydrochloric acid (37 wt%) and 40 mmol acetic acid (HAc) were added to 30 ml of ethanol solutions with a PTMS/TBOT/HCl/HAc/EtOH/H_2O molar ratio of 1:0.07:1.2:4:53:4.1. The mixture was stirred vigorously for 2 hours to ensure the complete dissolution. Then the mixture was transferred into a Petri dish (diameter 125 mm). A transparent viscous liquid was formed after evaporating of ethanol solvent at 65 ^oC for 24 hours. The viscous liquid sample was further aged at 250 ^oC to ensure full condensation of titanosilicate frameworks. The final LOTS materials were obtained in the form of solid powder after grinding.

Synthesis of m-TS (Ti/Si mole ratio = 0.07) materials: Mesoporous titanosilicate (denoted as m-TS) as a reference, is synthesized by AcHE process[1]. In a typical synthesis, 0.7 mmol of TBOT, 10 mmol of tetraethyl orthosilicate (TEOS), 40 mmol of HAc, 12 mmol of HCl, and 1.6 g of F_{127} ($EO_{106}PO_{70}EO_{106}$, MW=12600 g/mol) were dissolved in 30 mL of ethanol. The mixture was stirred vigorously for 2 hours and transferred into a Petri dish (diameter 125 mm). The ethanol was evaporated at 40°C. After 6 hours, a transparent membrane was formed, and transferred into a 65 °C oven and aged for an additional 24 h. The as-synthesized m-TS samples were calcined at 450 °C for 6 hours in air to remove organic templates.

Olefin epoxidation: The catalytic activity of LOTS was assessed in the epoxidation

of cyclohexene (CHE) at room temperature (25 ^{o}C) using 30 % H_2O_2 aqueous as oxidant and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as solvent. In a typical test, 40 mg Catalyst was dispersed in 6 mL HFIP and the temperature was maintained at 25 ^{o}C. Then, 120 umol CHE and 240 umol H_2O_2 were added into the solution and the epoxidation was started. After each 15 min, 100 uL reaction solution was taken out, and mixed with 200 uL 0.2 % v/v n-octane (internal standard substances) in acetonitrile for GC-FID analysis. The residual H_2O_2 concentration is measured by colorimetric determination[2]. 100 uL reaction solution was mixed with 2 mL water and 600 uL $Ti(SO_4)_2$ solution (10 g $Ti(SO_4)_2$ and 98 g H_2SO_4 desolved in 1 L water), finally a clear yellow solution is obtained. The amount of cyclohexene (CHE), and epoxy cyclohexane (ECHA) in the result mixture was analyzed by GC-FID; and the amount of H_2O_2 was analyzed by the spectrophotometric analysis of the resultant yellow solution at λ = 420 nm. The conversion of CHE, yield of ECHA and utilization of H_2O_2 are calculated as the following equations:

(1) Conversion of CHE = Consumed CHE amount / Initial CHE amount × 100 %;

(2) Yield of ECHA = Final ECHA amount / Initial CHE amount × 100 %;

(3) Utilization of H_2O_2 = Consumed H_2O_2 amount for CHE oxidation[a] / Consumed total H_2O_2 amount × 100 %.

[a]: Consumed H_2O_2 amount for CHE oxidation = total amount of (7-Oxabicyclo[4.1.0]heptanes + 2-Cyclohexen-1-ol + 1,2-Cyclohexanediol) + 2 * the amount of 2-Cyclohexen-1-one.

Catalyst regeneration: After the catalysis procedure of CHE epoxidation on LOTS, the LOTS catalyst was filtered, washed with ethanol, and air dried at 150 ^{o}C for 6 h.

Characterization

The low-angle and wide-angle X-ray diffraction (XRD) spectroscopy was collected on a Bruker D8 diffractometer using a CuKa radiation.

The Fourier transform infrared (FT-IR) spectra of the samples were recorded on a Thermo Nicolet 380 spectrometer.

The high resolution transmission electron microscopy (HR-TEM) images and energy dispersive X-ray (EDX) element mapping were recorded on a JEM-2010(HR) transmission electron microscope operating at 200K eV with Oxford Instruments energy disperse X-ray spectrometer. Nitrogen sorption analysis was carried out at 77 K using a Micrometrics TriStar 3000 system.

The X-ray photoelectron spectroscopy (XPS) analysis was performed in a VG Scientific ESCALAB Mark II spectrometer equipped with two ultra-high vacuum (UHV) chambers. All binding energies were referenced to the C1s peak at 284.6 eV of the surface adventitious carbon.

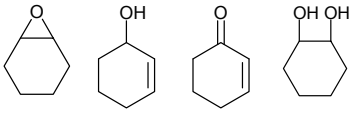
The thermogravimetric analysis (TGA) was carried out on a STA409PC TG-DTA/DSC analyzer (ramp rate: 5 ^{o}C/min). The hydrophobicity of material was measured by goniometry on a Shanghai Zhongchen JC2000D contact angle measuring instrument.

The solid ^{29}Si NMR and ^{13}C NMR experiments were carried out at 9.4 T on a Varian Infinity Plus-400 spectrometer operating at 79.5 and 100.6 MHz, respectively. Samples were packed in either a 5 mm (^{29}Si) or a 4mm (^{13}C) probe and spun at a spinning frequency of 8 and 12 kHz, respectively. For ^{29}Si MAS NMR, pulse width ($\pi/2$) of 4.5 μs with a recycle delay of 20 s was used. For ^{13}C MAS NMR, pulse width ($\pi/2$) of 4.25 μs with a recycle delay of 2s was used. The ^{29}Si NMR and ^{13}C NMR chemical shift was externally referenced to kaolin and hexa-methyl benzene, respectively.

The ICP-MS measurements were carried out on a Thermo Electron XSENIES ICP-MS instrument with a quadrupole mass spectrometer. Firstly, 10 mg of sample was dissolved by 0.5 mL HF. After HF was removed by the addition of HNO_3 and heat treatment, the resulted clear solution was diluted to be ca. 100 ppb, and the Ti

content was measured by ICP-MS measurement.

Table S1. The physical property and catalytic performance of different titanosilicates

Cat.	Ti/Si mole ratio	Ti Cont.[a] (wt%)	Surface Area (m^2/g)	Conv. of CHE (%)	Selectivity[b] 				Util. of H_2O_2 (%)	TON[c]
LOTS	0.07	2.25	6.80	98.8	98.1	0.23	0.60	1.09	76	6.32
LOTS[d]	0.07	2.25[e]	----	93.0	93.5	0.51	1.04	4.99	66	5.95
m-TS	0.07	3.55	423	30.2	75.1	14.1	8.54	6.81	21	1.23
TS-1	0.025	3.00	339	12.2	89.5	2.87	6.53	1.15	70	0.59
Blank	----	----	----	5.19	96.5	0	0	3.47	58	----

Reaction condition: 40 mg Cat., 6 mL HFIP, 120 umol cyclohexene, 240 umol H_2O_2 (30% in water); 25 ^oC, reaction time is 2 h.

[a]: the Ti content is measured by ICP-MS.

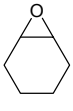
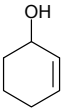
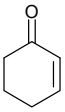
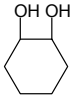
[b]: the distribution of products is identified by GC-MS.

[c]: TON is calculated when the catalysis is stopped when the reaction time is 2 h. TON = the Converted CHE amount / the Ti atom amount.

[d]: LOTS recycled after four runs of catalysis; the catalytic result is the fourth run.

[e]: The Ti content in LOTS after four reaction cycles keeps the same as the fresh one, indicating the leaching of Ti during reaction process is negligible.

Table S2. The epoxidation activity of different titanosilicates using methanol or acetonitrile as solvents

Cat.	Ti/Si mole ratio	Ti Cont. (wt%)	Solvent	Conv. of CHE (%)	Selectivity				Util. of H_2O_2 (%)	TON [a]
										
LOTS	0.07	2.25	MeOH	24.7	50.9	2.15	37.7	9.35	35	105
m-TS	0.07	3.55	MeOH	17.3	0.38	0.23	48.8	50.6	19	47
TS-1	0.025	3.00	MeOH	9.76	43.8	22.2	24.8	9.18	33	31
Blank	----	----	MeOH	2.73	5.60	21.3	27.3	48.5	42	----
LOTS	0.07	2.25	MeCN	15.2	52.5	7.22	36.4	3.91	36	65
m-TS	0.07	3.55	MeCN	11.8	2.17	3.70	65.0	29.2	22	32
TS-1	0.025	3.00	MeCN	6.11	42.7	15.1	38.3	3.90	14	20
Blank	----	----	MeCN	1.47	39.3	12.4	32.7	15.5	8	----

Reaction condition: 25 mg Cat., 5 mL solvent, 5 mmol cyclohexene, 10 mmol H_2O_2 (30% in water); 60 ^{o}C, reaction time is 6 h. The reaction condition is in accordance with that in the literatures[3, 4].

[a]: TON is calculated when the catalysis is stopped when the reaction time is 6 h. TON = the converted CHE amount / the Ti atom amount.

Figure S1. Energy dispersive X-ray (EDX) element mapping of a single LOTS particle aging at 250 ^{o}C

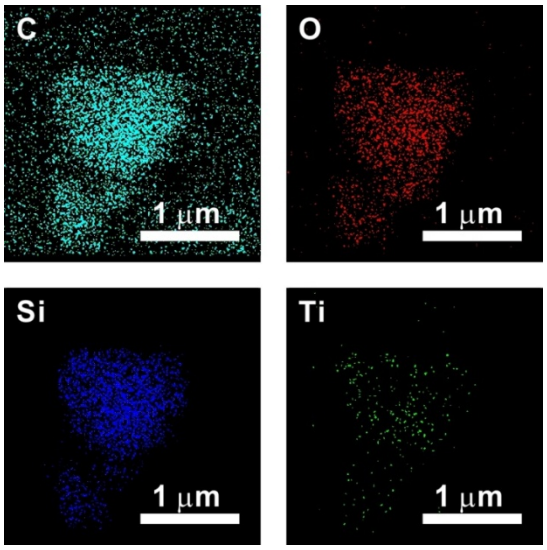


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Figure S2. FT-IR spectra of LOTS with different Ti/Si mole ratio

There is no vibration band in the range of 920-970 cm^{-1} for the sample of Ti/Si = 0. In contrast, for all the Ti-containing samples (Ti/Si ratio from 0.01 to 0.07) do display a new band at 926 cm^{-1} and the intensity of this band increases with the Ti/Si ratio. These results suggest that the band at 926 cm^{-1} may indeed be assigned to the Ti-O-Si linkage.

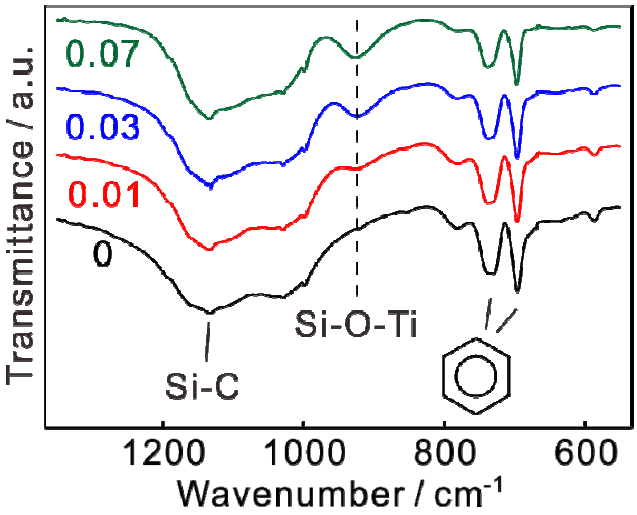


Figure S3. X-ray photoelectron spectroscopy (XPS) of different catalysts

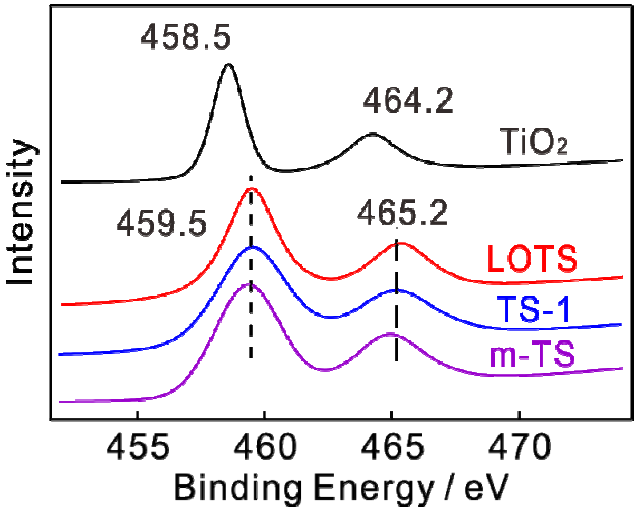


Figure S4. The XRD patten (A), FT-IR spectra (B) and DRUV-vis spectra (C) for commercial TS-1 (Si/Ti = 40)

The strong peaks in XRD pattern (Figure S5A) show the typical MFI structure with high purity[5]. The vibration band at 975 cm^{-1} in FTIR spectra (Figure S5B) is the characteristic vibration peak of Ti-O-Si linkage[5]. The band located at 206 nm in DRUV-vis spectroscopy (Figure S5C) gives a strong proof of tetra-coordinated Ti species in TS-1[6].

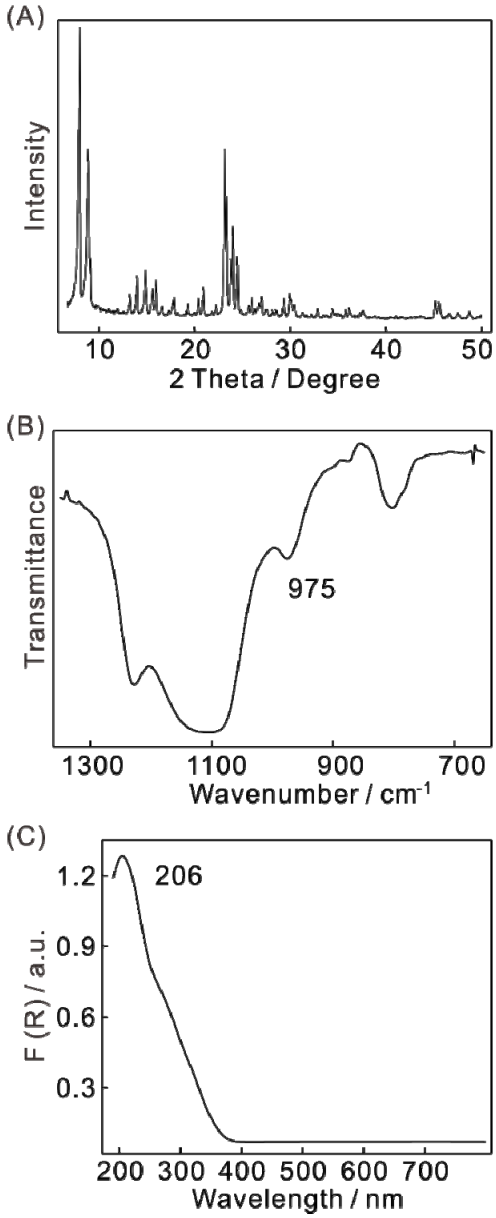


Figure S5. The small angle XRD pattern (A), TEM image (B), DRUV-vis spectra (C) and TG curve (D) of m-TS calcinated at 450 ^{o}C

The small angle XRD pattern and the TEM image confirmed that the m-TS has an well-ordered 2D hexagonal mesoporous structure (Figure S7A, S7B). The band located at 226 nm in DRUV-vis spectroscopy (Figure S7C) confirmed of the tetra-coordinated Ti species in m-TS[7]. The result from TG analysis of m-TS calcined at 450 ^{o}C confirmed that the organic templates have been totally removed by calcinations.

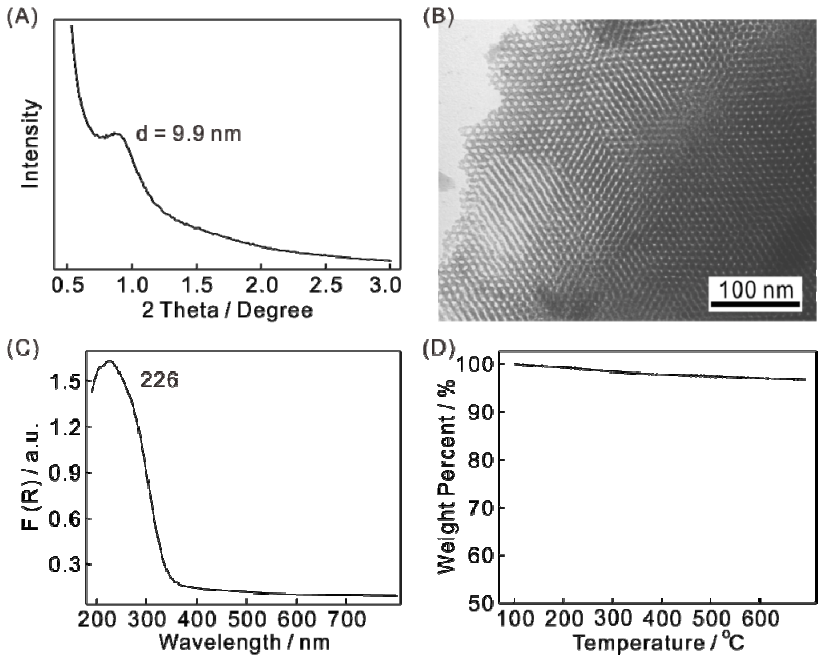


Figure S6. The repeated experiments of epoxidation of cyclohexene on LOTS

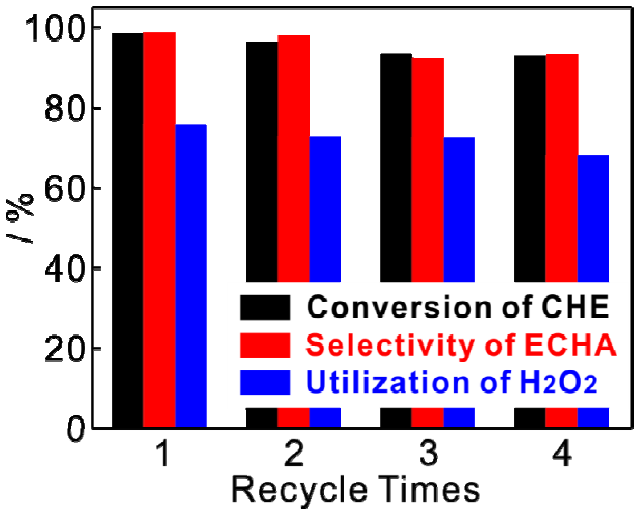
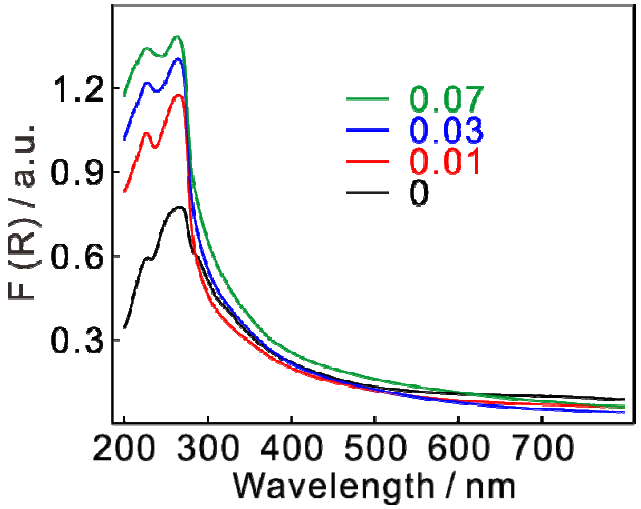


Figure S7. The DRUV-vis spectra of LOTS with different Ti/Si mole ratio

All the samples with different Si/Ti show two different signals located at 226 and 265 nm even if when there is no titanium n-butoxide added (Ti/Si = 0), indicating that the phenyl groups in LOTS can also give a strong absorbance in the range of 200-400 nm. So the Ti coordination environment in LOTS is somewhat difficult to be evaluated by DRUV-vis spectra. The intensity of the band at 226 nm increases semi-quantitatively with the Ti/Si ratio (from 0 to 0.07), implying that the Ti species have been incorporated into the framework in tetra-coordinated state.



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