Electronic Supplementary Information (ESI)

Synthesis of Two Titanosilicates with Distinct Interlayer Connections from Similar Gels

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Experimental Section

Chemicals

Dowex Monosphere 550A UPW hydroxide resin was purchased from Supelco. Cab-O-Sil M5 fumed silica (97% SiO_2) was purchased from Cabot. Hexamethyleneimine (>98%, HMI), piperidine (>98%, PI) and tetrabutyl titanate (TBOT, >98%) were purchased from Shanghai Shangsi chemical corporation. Cyclohexylamine (>99%), toluene (>99%), paraformaldehyde (>95%), hydrobromic acid (40 wt. % aqueous solution), glyoxal (40 wt. % aqueous solution), $KHCO_3$ (>99%), diethyl ether (>99%), activated carbon, chloroform (>99%), $MgSO_4$ (>99%), HNO_3 (65 wt. % aqueous solution), H_3BO_3 (>99%), cyclohexanone (>99%), acetonitrile (>99%), hydrogen peroxide (30 wt. % aqueous solution), 1-hexene (>99%), cyclohexene(>99%), H_2O_2 (30%) and CH_3CN (>99%) were purchased from TCI. All chemical were used as received without further purification. Ti-MWW (HTS) with a Si/Ti ratio of 41 was purchased from Zhejiang TWRD New Materials Co., Ltd., China as a commercial catalyst.

Preparation of SDA

1,3-Bis(cyclohexyl)imidazolium bromide (IMBr for short) was prepared according to literature [1] and exchanged to the hydroxide form using hydroxide resin, the final 1,3-Bis(cyclohexyl)imidazolium hydroxide (IMOH) concentration was determined by titration with potassium biphthalate to a phenolphthalein end point.

Synthesis of zeolites

All inorganic reactions were performed in 80 mL of poly (tetrafluoroethylene) stainless steel autoclaves. The typical synthesis of titanosilicate zeolites was conducted as follows. H_2O and TBOT was firstly added to the IMOH solution and then the mixture was stirred for 30 min to get complete hydrolysis of TBOT. Finally, fumed silica was added to the mixture gradually, followed by homogenization. The gel mixture was aged under 353 K for 6 hours and then transfer to autoclave under

rotation at 443 K for 4 - 6 days. The solid product was recovered by filtration, washing, and drying. For Ti-SSZ-70 zeolite, the synthetic gel composition was 1 SiO_2: 0 - 0.1 TBOT: 0.2 IMOH: 30 H_2O. In the case of Ti-ECNU-6, HMI was needed in the synthesis system and the gel composition was 1 SiO_2: 0~0.1 TBOT: 0.16 IMOH: (0.3~0.6) HMI: 30 H_2O.

The as-synthesized Ti-SSZ-70 and Ti-ECNU-6 samples were refluxed in HNO_3 aqueous solution at a solid to liquid ratio of 1 g to 50 mL under reflux conditions to extract extra-framework Ti, and were further calcined in air at 823 K for 5 hours to burn off organic species.

B-MWW sample (gel B_2O_3/SiO_2 = 0.75) using hexamethyleneimine (HMI) as SDA was prepared to our previous work.[2] For a better description, the samples were denoted as sample-A as acid-treated and sample-AC as acid-treated and further calcined.

Characterizations

The X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV X-ray diffractometer using Cu-Kα radiation (λ = 1.5405 Å) at 35 kV and 25 mA. Scanning electron micrographs (SEM) were performed on a Hitachi S-4800 microscopy. The nitrogen adsorption isotherms were performed at 77 K on a BELSORP-MAX instrument after activating the samples at 573 K under vacuum at least for 5 h. The Brunauer-Emmett-Teller (BET) analysis was carried out using the data in the relative pressure region of P/P_0 = 0.05 - 0.25, which provided the specific surface area. The amounts of Si, B and Ti were quantified by inductively coupled plasma (ICP) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer. UV–vis diffuse reflectance spectra were recorded on a Perkin Elmer Lamda 35 UV/VIS spectrometer using $BaSO_4$ as the reference after the samples were dehydrated at 673 K. The thermogravimetric and differential thermal analyses (TG-DTA) were performed on a METTLER TOLEDO TGA/SDTA 851 apparatus from 298 K to 1073 K at a heating rate of 10 K min^{-1} in air. The CHN chemical analysis was carried out

on Elementar Vario EL III. Bruke-300. The liquid ^{13}C NMR was recorded on a Bruker Avance 300 spectrometer with a frequency of 75.4 MHz and the solid ^{13}C MAS NMR was recorded on a Bruker DSX 300 spectrometer with a frequency of 75 MHz. The FT-IR spectra were recorded by a Nicolet Nexus 670 FT-IR spectrometer at a resolution of 2 cm^{-1} using a KBr technique.

Catalytic reactions

The liquid-phase oxidation of 1-hexene and cyclohexene with hydrogen peroxide was carried out in a round-bottom flask (20 mL) fitted with a condenser and a magnetic stirrer. For a typical run, a mixture of 0.05 g of catalyst, 10 mmol of 1-hexene or cyclohexene, 10 mmol of hydrogen peroxide (30 wt. % aqueous solution) and 10 mL of solvent (acetonitrile) was stirred vigorously at 333 K for 2 h. The reaction mixture was analyzed using a gas chromatograph (Shimadzu 14 B, FID detector) equipped with a 30 m DB-1 capillary column and with cyclohexanone as an internal standard.

Supplementary References

1. R. H. Archer, J. R. Carpenter, S.-J. Hwang, A. W. Burton, C.-Y. Chen, S. I. Zones, M. E. Davis, Chem. Mater. 22 (2010) 2563-2572.

2. P. Wu, T. Tatsumi, T. Komatsu, T. Yashima, J. Phys. Chem. B, 105 (2001) 2897.

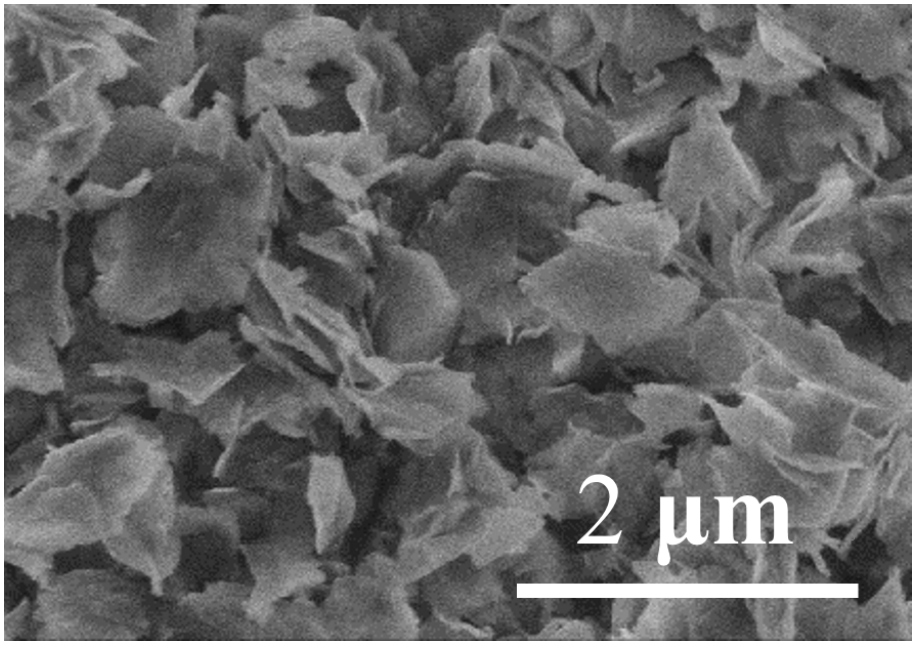

Fig. S1 SEM image of Ti-SSZ-70 as-synthesized at a gel Si/Ti ratio of 20.

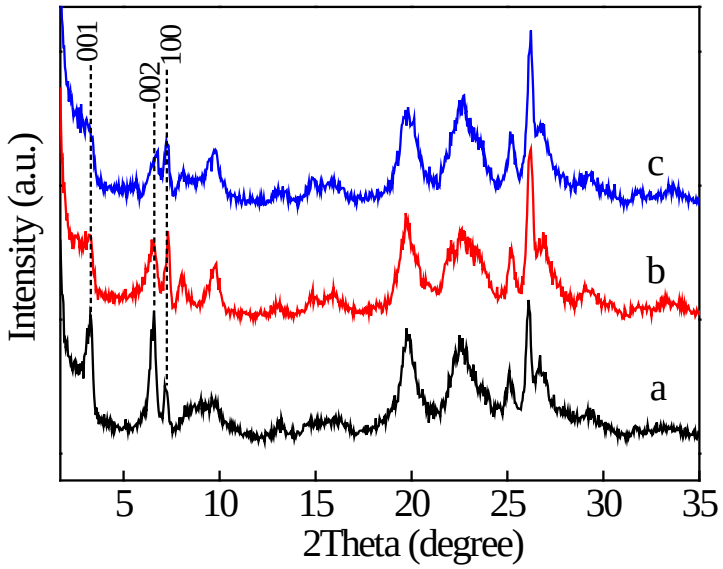

Fig. S2 XRD patterns of Ti-ECNU-6 as-synthesized at a HMI/SiO_2 ratio of 0 (a), 0.3 (b) and 0.6 (c). The detailed composition of the gel was: 1 SiO_2: 0.05 TBOT: 0.16 IMOH: *x* HMI: 30 H_2O.

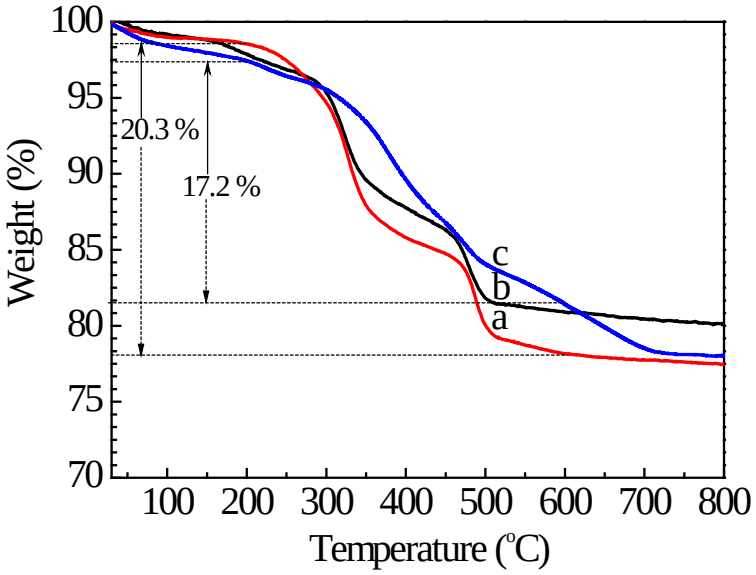

Fig. S3 TG curves of as-made Ti-SSZ-70 (a), Ti-ECNU-6 (b) and B-MWW (c). Ti-SSZ-70 and Ti-ECNU-6 were synthesized at gel Si/Ti ratio of 20.

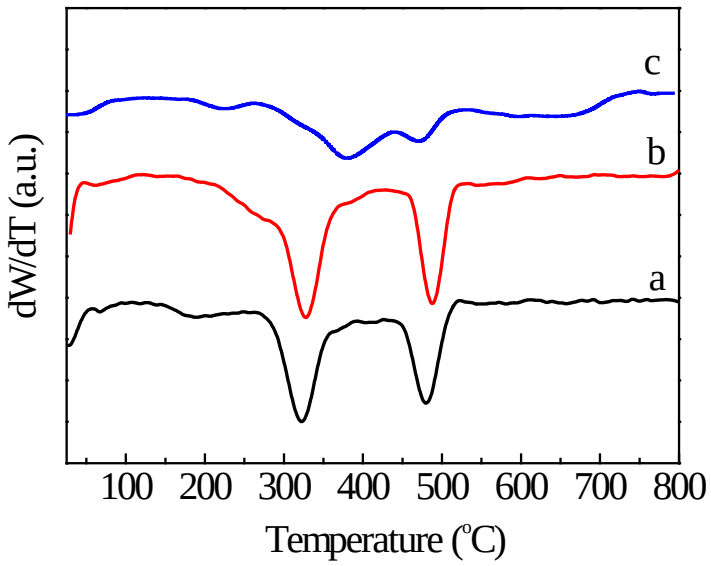

Fig. S4 DTG curves of as-made Ti-SSZ-70 (a), Ti-ECNU-6 (b) and B-MWW (c). Ti-SSZ-70 and Ti-ECNU-6 were synthesized at gel Si/Ti ratio of 20.

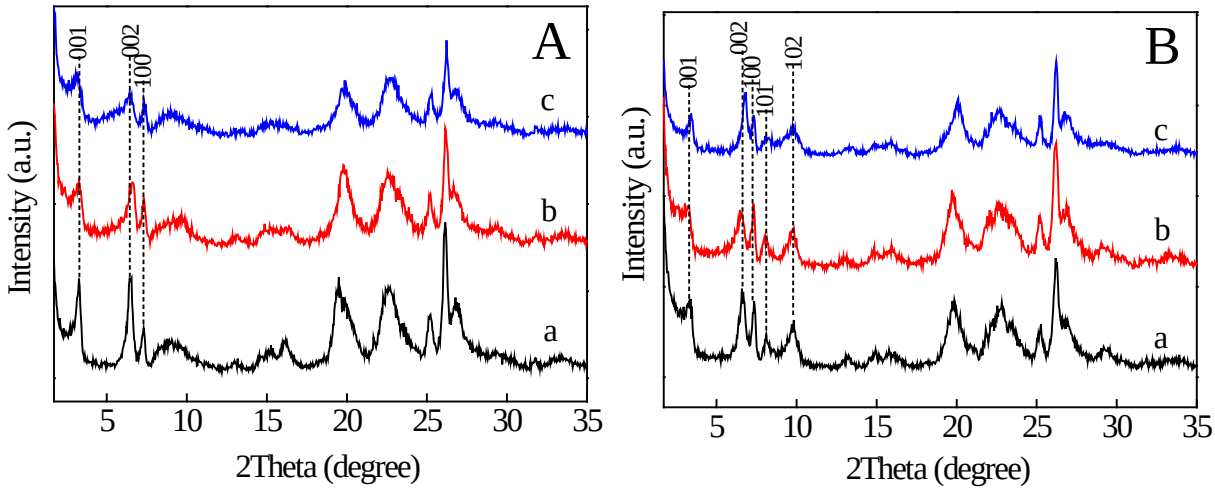

Fig. S5 XRD patterns of (A) Ti-SSZ-70 and (B) Ti-ECNU-6 as-synthesized at gel Si/Ti ratio at (a) 30, (b) 20 and (c) 10.

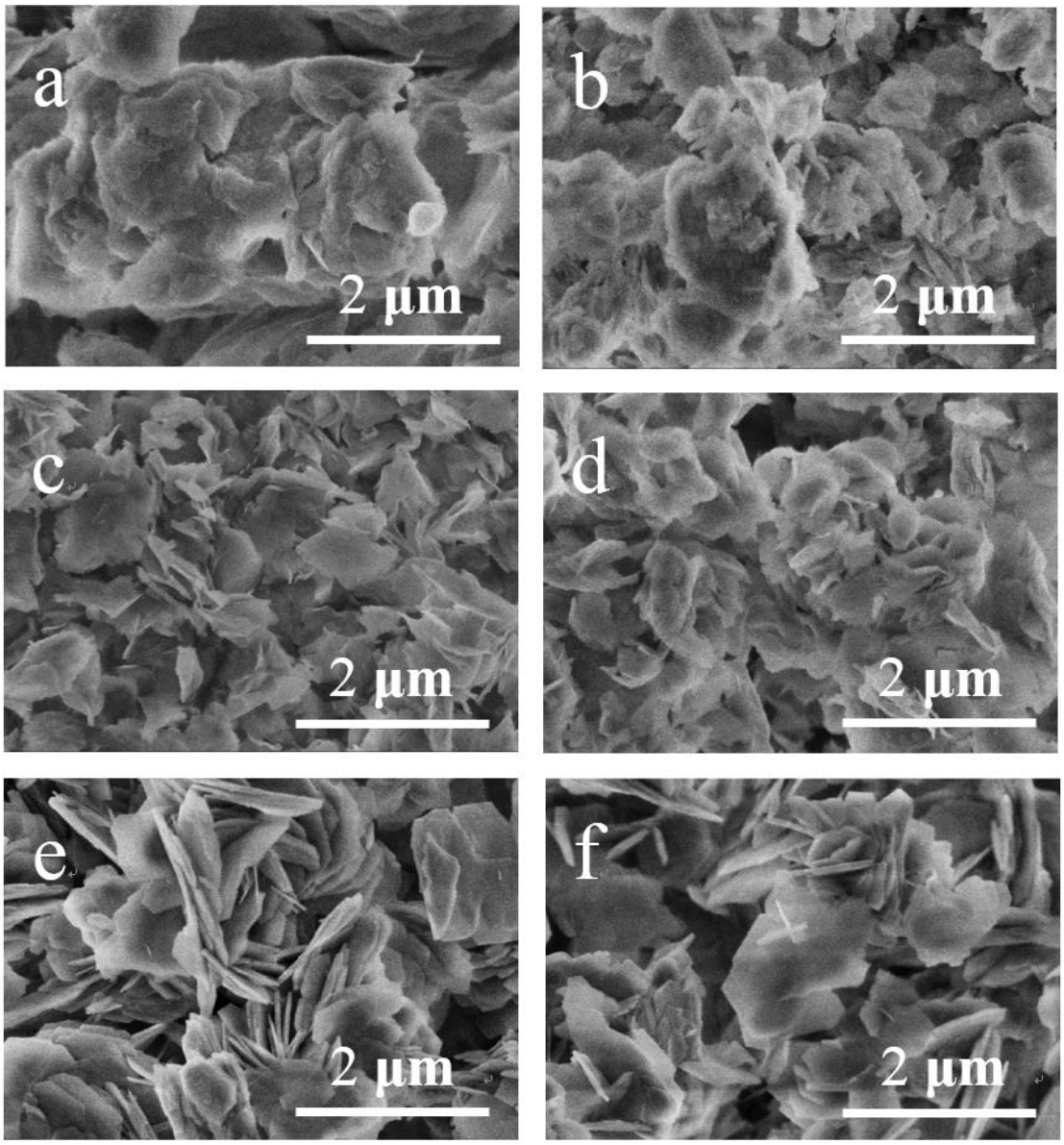

Fig. S6 SEM image of Ti-SSZ-70 synthesized at gel Si/Ti ratio of 10 (a), 20 (c) and 30 (e) and Ti-ECNU-6 synthesized at gel Si/Ti ratio of 10 (b), 20 (d) and 30 (f).

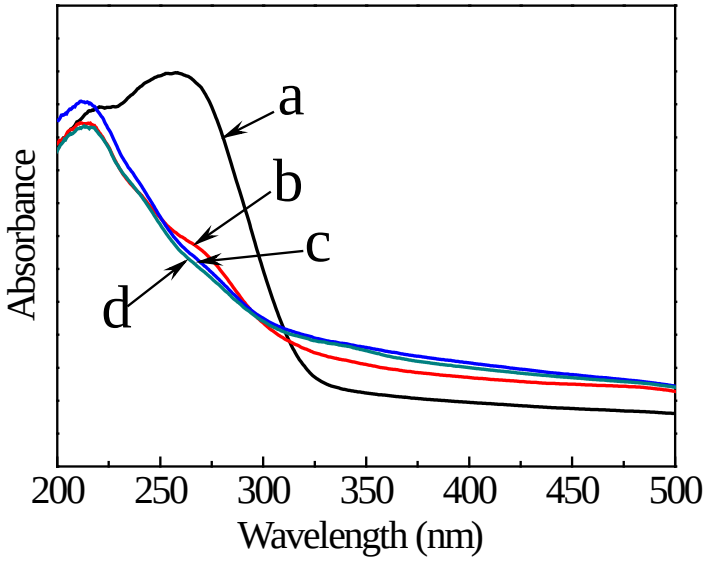

Fig. S7 UV-vis spectra of Ti-ECNU-6 (a) as- synthesized at Si/Ti = 20 and Ti-ECNU-6-A after acid-treatment with 1.0 M HNO_3 (b), 1.5 M HNO_3 (c) and 2.0 M HNO_3 (d). Acid treatment was performed at reflux condition for 2 h.

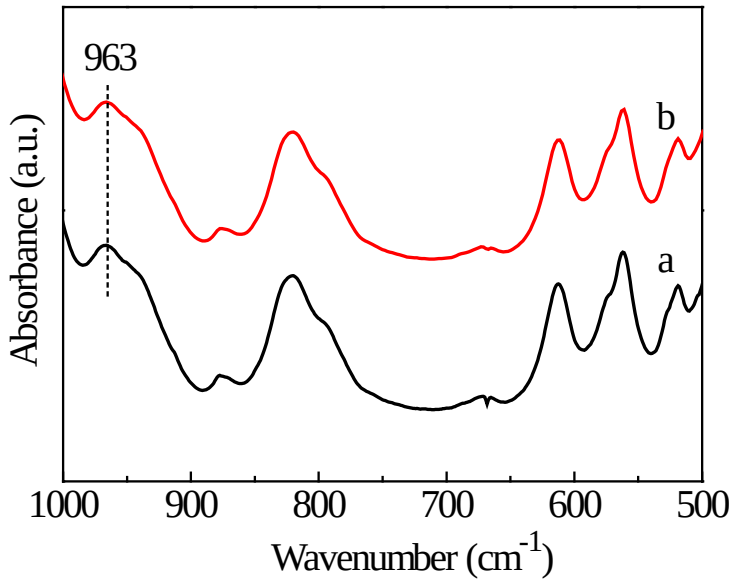

Fig. S8 IR spectra of Ti-SSZ-70-A (a) and Ti-ECNU-6-A (b). Ti-SSZ-70 (gel Si/Ti = 20) and Ti-ECNU-6 (gel Si/Ti = 20) were acid-treatment with 1.5 M HNO_3, and the samples were measured after evacuation at 723 K for 2 h.

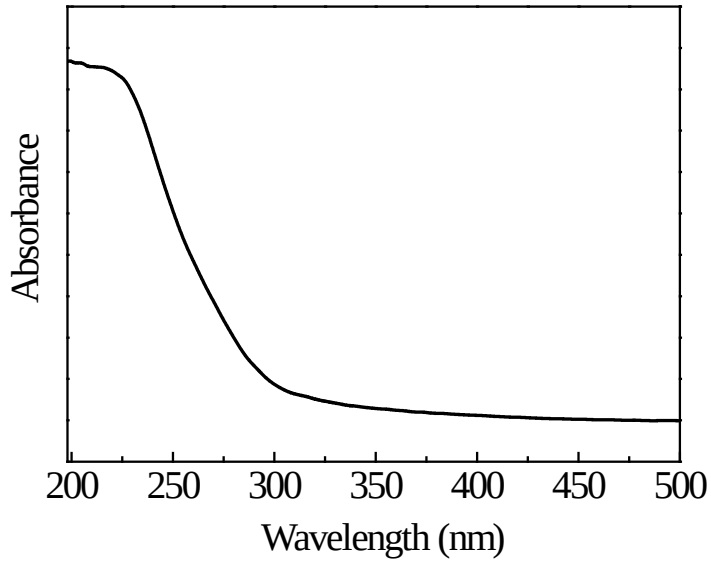

Fig. S9 UV-vis spectra of Ti-MWW (HTS).

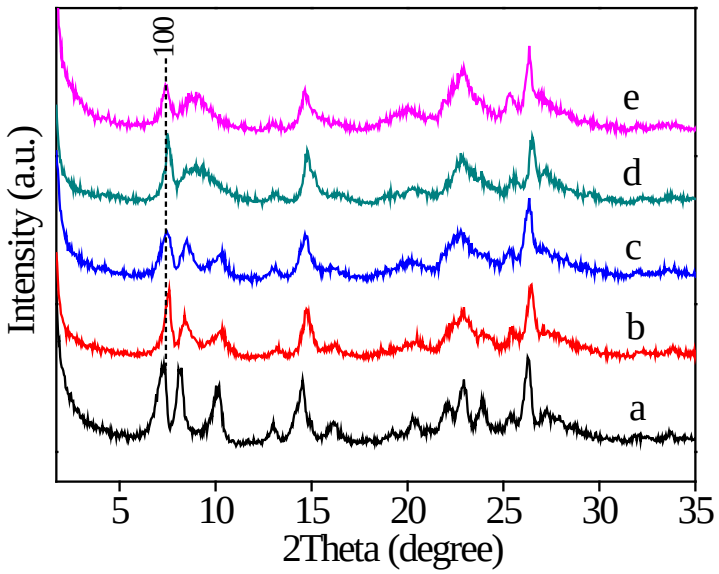

Fig. S10 XRD patterns of Ti-MWW (HTS) (a), Ti-ECNU-6-AC (gel Si/Ti = 30) (b), Ti-ECNU-6-AC (gel Si/Ti = 20) (c), Ti-SSZ-70-AC (gel Si/Ti = 30) (d) and Ti-SSZ-70-AC (gel Si/Ti = 20) (e). Ti-ECNU-6-AC and Ti-SSZ-70-AC were obtained by acid treatment with 1.5 M HNO_3 at reflux condition for 2 h and further calcined at 823 K for 6 h.

Table S1. Elementary analysis results of Ti-SSZ-70 and Ti-ECNU-6 samples [a]

Sample	N (wt. %)	C (wt. %)	H (wt. %)	Molar C/N	Orgainic species (wt. %)
Ti-SSZ-70	2.09	14.14	2.27	7.9	18.5
Ti-ECNU-6	1.95	11.88	2.05	7.1	15.9
Ti-SSZ-70-AT[b]	1.37	9.38	1.45	8.0	12.2
Ti-ECNU-6-AT[b]	1.22	7.94	1.24	7.6	10.4

[a] The samples were synthesized at gel Si/Ti ratio of 20, and the molecular formulas of IMOH and HMI are $C_{15}H_{26}N_2O$ and $C_6H_{13}N$, respectively; [b] The acid-treat (AT) condition: The as-made samples were treated with 1.5 M HNO_3 at reflux condition with a solid to liquid ratio of 1 g to 50 mL for 6 h.

Table S2. The catalytic results of epoxidation of 1-hexene and cyclohexene with H_2O_2 [a]

Zeolite	Si/Ti [b]	Si/Ti [c]	Acid Concentration（M）	Si/Ti [d]	1-Hexene		Cyclohexene	
					Conv. /%	TON [e]	Conv. /%	TON [e]
Ti-SSZ-70	10	26	2.0	31	22.7	87	-	-
			3.0	39	26.1	125	-	-
	20	34	1.0	41	34.5	174	5.3	27
			1.5	46	38.8	219	6.4	36
			2.0	58	31.4	222	4.2	30
	30	43	1.5	63	35.7	274	4.8	38
Ti-ECNU-6	10	29	2.0	33	25.4	104	-	-
			3.0	38	29.3	137	-	-
	20	36	1.0	43	37.6	199	4.6	24
			1.5	48	42.9	252	5.1	30
			2.0	55	35.4	238	3.9	26
	30	47	1.5	67	38.4	317	4.1	33
Ti-MWW(HTS)	-	-	-	41	49.5	248	5.6	28

[a] Reaction conditions: cat., 50 mg; 1-hexene or cyclohexene, 10 mmol; H_2O_2, 10 mmol; CH_3CN, 10 mL; temp., 333K; time, 2 h; [b] In gel; [c] In direct-calcined product by ICP analysis; [d] In samples after acid washing and further calcination by ICP analysis; [e] Mol (mol-Ti)$^{-1}$.

Table S3. The recycling experiment in epoxidation of 1-hexene with H_2O_2[a]

Cycle	Ti-SSZ-70		Ti-ECNU-6	
	Conversion of 1-hexene /%	Si/Ti	Conversion of 1-hexene /%	Si/Ti
1	38.8	46	42.9	48
2	36.8	48	41.0	49
3	37.5	46	40.6	50
4	37.1	49	39.9	49

a. Reaction conditions: cat., 50 mg; 1-hexene, 10 mmol; H_2O_2, 10 mmol; CH3CN, 10 mL; temp., 333K; time, 2 h; The Si/Ti ratio was calculated by ICP analysis and the regeneration was conducted by calcination at 823 K for 6 h.