Electronic Supplementary Information (ESI)

for

Intensified interzeolite transformation: ultrafast synthesis of active and stable Ti-Beta zeolites without solvents

Zhiguo Zhu,[ab] Hao Xu,*[a] Bowen Wang,[a] Jinpeng Yin,[a] Jingang Jiang,[a] Hongying Lü[b]
and Peng Wu*[a]

Corresponding Address:

[a] *Shanghai Key Laboratory of Green Chemistry and Chemical Processes, college of Chemistry and Molecular Engineering, East China Normal University, North Zhongshan Rd. 3663, Shanghai 200062, China*

E-mail address: pwu@chem.ecnu.edu.cn (P. Wu); hxu@chem.ecnu.edu.cn (H. Xu)

[b] *Green Chemistry Centre, College of Chemistry and Chemical Engineering, Yantai University, 30 Qingquan Road, Yantai 264005, Shandong, China*

Experimental section

Material preparation

Preparation of Ti-MWW-DeB sample. Ti-MWW precursor (Si/Ti = 43, Si/B = 73， detected by ICP analysis) was commercially available from Zhejiang Taide New Material Co., Ltd., which was synthesized using fumed silica, tetrabutyl orthotitanate, boric acid, and deionized water, with piperidine as the structure-directing agent according to previous literature.[1] It was hydrothermally treated by deionized water with a solid-to-liquid ratio of 1 g : 20 mL in a Teflon-lined autoclave at 413 K for 6 h. The dried sample (Si/Ti = 44, Si/B = 603), denoted as Ti-MWW-DeB, was employed as the silica and titanium sources for synthesizing the following Ti-Beta zeolite.

Besides, for comparison, a nearly pure silica MWW sample was also prepared. B-MWW precursor was hydrothermally synthesized using piperidine as the structure directing agent (SDA).[1] The resultant gel with a molar composition of 1.0 SiO_2 : 1.4 PI : 0.67 B_2O_3 : 19 H_2O was transferred into a Teflon-lined autoclave and heated with a rotatory rate of 10 rpm at 443 K for 7 days. After crystallization, the product was washed with deionized water, dried, and calcined at 823 K for 6 h to remove residual SDA. Then it was treated by 2 M HNO_3 solution at 373 K for 10 h with a solid-to-liquid ratio of 1 g : 50 mL to extract B, giving rise to a nearly pure silica MWW sample (Si/B = 713, designated as DeB-MWW).

Preparation of siliceous Beta seeds. The siliceous Beta seeds were prepared by acid-assisted dealuminaton of commercially available H-Beta aluminosilicate (Si/Al = *ca.* 11, Shanghai Xinnian Petrochemical Additives Co., Ltd). First, the H-Beta sample was refluxed in the HNO_3 solution (65 wt %) at a solid-to-liquid ratio of 1 g : 50 mL for 8 h, resulting in a siliceous zeolite with a Si/Al ratio over 1900, which was used as Beta seeds.

Synthesis of Ti-Beta via interzeolite transformation. Ti-Beta zeolite was hydrothermally crystallized using Ti-MWW-DeB zeolite as silica and titanium sources with the addition of Beta seeds under solvent-free conditions. In a typical synthesis, Ti-MWW-DeB powder and Beta seeds of 10 wt % with respect to silica source were added into tetraethylammonium hydroxide (TEAOH) (25 wt %) aqueous solution at the room temperature under stirring for about 5 min. Subsequently, ammonium fluoride (NH_4F) was also blended with this mixture, resulting in a gel composition of 1.0 Ti-MWW-DeB : 0.3 TEAOH : 0.5 NH_4F. After stirring for 5 min, they were put into an oven at 353 K for 40 min, giving a dried gels ($H_2O/SiO_2 < 1.0$). Then, the dried powder was transferred into a Teflon-lined autoclave without adding any other reagents and heated at 463 K for different times under static conditions. Afterwards, the as-synthesized Ti-Beta product was calcined at 873 K for 6 h to remove the occluded organic species, designated as Ti-Beta-DT.

Additionally, all-silica Beta, designated as Beta-DT, was also hydrothermally synthesized via interzeolite transformation with the DeB-MWW as the silica source following the same procedures as the synthesis of Ti-Beta-DT zeolite.

Synthesis of other titanosilicates. For controlling experiment, Ti-Beta obtained by seeding method (Ti-Beta-OH),[2] fluoride-assisted route (Ti-Beta-F),[3] and post-synthesized approach (Ti-Beta-PS),[4] as well as Ti-MOR[5] and TS-1[6] were prepared in our laboratory according to well-established procedures reported in the literatures. Note that Ti-Beta-F was synthesized utilizing ammonium fluoride as the fluorine source. Moreover, Ti-Beta-PS was post-synthesized by solid-gas reaction between highly dealuminated Beta with $TiCl_4$ vapor, during which isomorphous substitution of Ti ions in the framework was realized. Experimental details of the synthesis procedures have been described elsewhere.[2–6]

Characterizations

The X-ray diffraction (XRD) patterns were recorded using a Rigaku Ultima IV X-ray diffractometer (35 kV, 25 mA) with the Cu-Kα radiation (λ=1.5405 Å). UV-Raman spectra were obtained with a 244 nm excitation line using a spectral resolution of 2 cm^{-1} on a Jobin-Yvon T6400 triple-stage spectrograph. Scanning electron microscopy (SEM) images were performed on a Hitachi S-4800 microscopy. The N_2 adsorption-desorption isotherms were determined on a BELSORP-MAX instrument at the temperature of 77 K after activating the samples at 573 K at least for 5 h under vacuum conditions. The sample composition was measured with inductively coupled plasma (ICP) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer. UV–visible (UV–vis) diffuse reflectance spectra were performed on a Shimadzu UV-2700 spectrophotometer using barium sulfate as the reference background. X-ray photoelectron spectroscopic (XPS) data were collected on a Kratos Axis Ultra spectrometer (Kratos Analytical, UK) equipped with a monochromatized aluminum X-ray source. FT-IR spectra for zeolites in the framework regions were carried out on a Nicolet Nexus 670 FT-IR spectrometer with a spectral resolution of 2 cm^{-1} in absorbance mode using potassium bromide (KBr) as the background.

Catalytic reaction

The epoxidation of cyclohexene with H_2O_2 was evaluated in a 25 mL flask linked to a water condenser under appropriate stirring. In a typical run, catalyst (50 mg), cyclohexene (10 mmol), H_2O_2 (10 mmol, 30 wt %), and CH_3CN (CH_3OH for TS-1) (10 mL) were stirred in the flask at 333 K for 2 h. After reaction, this system was cooled down immediately by ice bath, and then the catalyst was removed from the reaction system by centrifugation. The reaction mixture was analyzed using a gas chromatograph (Shimadzu GC-14B, FID detector) equipped with a 30 m DB-1 capillary column to obtain the conversion and selectivity. The products were identified using a GC-MS (Agilent-6890GC/5973MS). The amount of residual H_2O_2 was determined by standard titration method using a 0.05 M $Ce(SO_4)_2$ solution. The utilization efficiency of oxidant was calculated depended on the amounts of desired product of cyclohexene oxide and converted H_2O_2.

Results and discussion

Table S1 Textural properties of various Ti-Beta zeolites.

Sample	Time[a]	Crystal size (nm)	Si/Ti ratio		V_{micro}[c] ($cm^3\ g^{-1}$)	SSA ($m^2\ g^{-1}$)	
			Gel	Product[b]		S_{BET}[d]	S_{ext}[e]
Ti-Beta-DT	2 h	150-250	48	53	0.21	543	91
Ti-Beta-F	8 d	4000-5000	50	65	0.20	515	55
Ti-Beta-OH	14 d	150-250	50	51	0.21	550	95
Ti-Beta-PS	-	80-110	-	52	0.20	591	131

[a] The time required for realizing a full crystallization of *BEA structure.

[b] Determined by ICP analysis.

[c] Determined from the N_2 adsorption amount at $P/P_0 = 0.99$.

[d] Specific surface area (S_{BET}), determined from the N_2 adsorption isotherms at 77 K by BET method.

[e] Calculated by *t*-plot method.

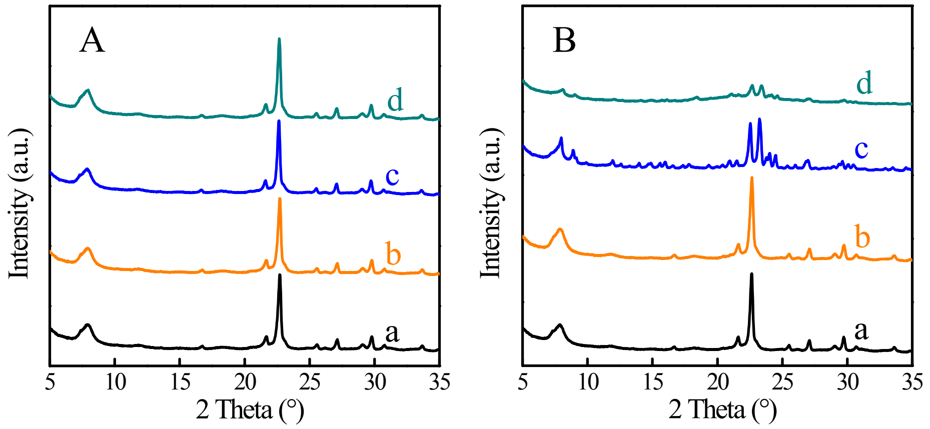

Fig. S1 XRD patterns of solid products during the crystallization of Ti-Beta-DT (A) at the temperature of 413 K (a), 433 K (b), 443 K (c), and 463 K (d), (B) with the TEAOH/SiO_2 molar ratio of 0.4 (a), 0.3 (b), 0.2 (c), 0.1 (d). Other crystallization conditions: (A) TEAOH/SiO_2 = 0.4; (B) temp., 463 K. Beta seeds/SiO_2, NH_4F/SiO_2, and crystallized time were 0.1, 0.5, and 1 d, respectively, for all cases.

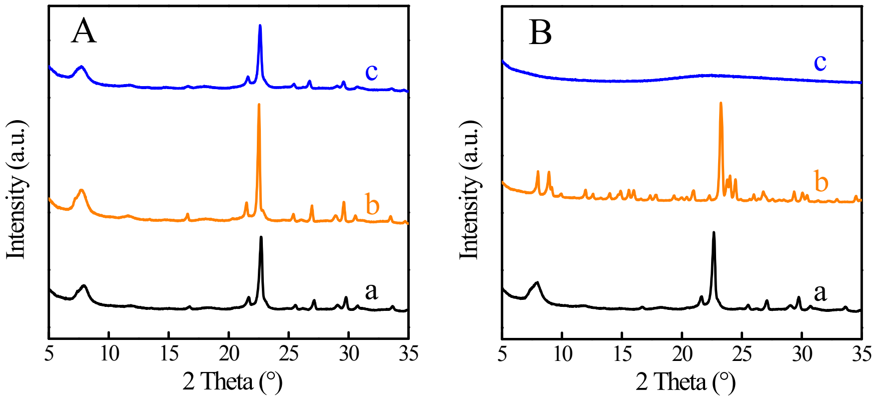

Fig. S2 XRD patterns of solid products obtained at the temperature of (A) 413 K and (B) 463 K for Ti-Beta-DT (a), Ti-Beta-F (b), and Ti-Beta-OH (c).

The crystallization processes of Ti-Beta zeolite for intensified interzeolite transformation, seeding route, and fluoride-assistant synthesis were all capable to proceed at 413 K (Fig. S2A). Whereas, once the crystallized temperature was increased from 413 K to 463 K for conventional methods, the seeding route and fluoride-assisted synthesis both failed to obtain the Ti-Beta zeolites (Fig. S2B). The fluoride method led to a MFI phase, whereas the fluoride-free seeding method resulted in an amorphous one. Undoubtedly, this fact verified that this intensified interzeolite transformation route could be capable to expand the temperature window for the hydrothermal synthesis of Ti-Beta, especially to higher temperature region.

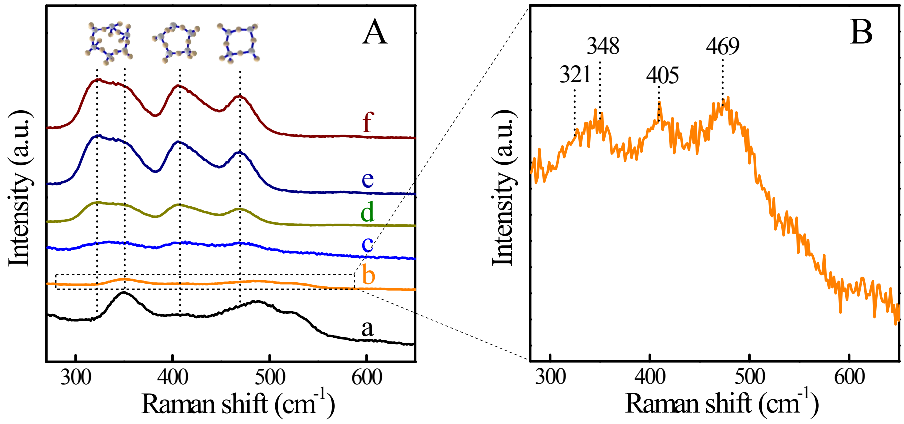

Fig. S3 (A) UV Raman spectra of calcined solid products during the crystallization of Ti-Beta-DT for 0 h (a), 0.5 h (b), 1 h (c), 1.5 h (d), 2 h (e), 1 d (f), and (B) magnified UV Raman spectrum of Ti-Beta-DT prepared for 0.5 h. Crystallization conditions: TEAOH/Ti-MWW = 0.3; NH_4F/Ti-MWW = 0.5; Beta seeds, 10 wt %; temp., 463 K.

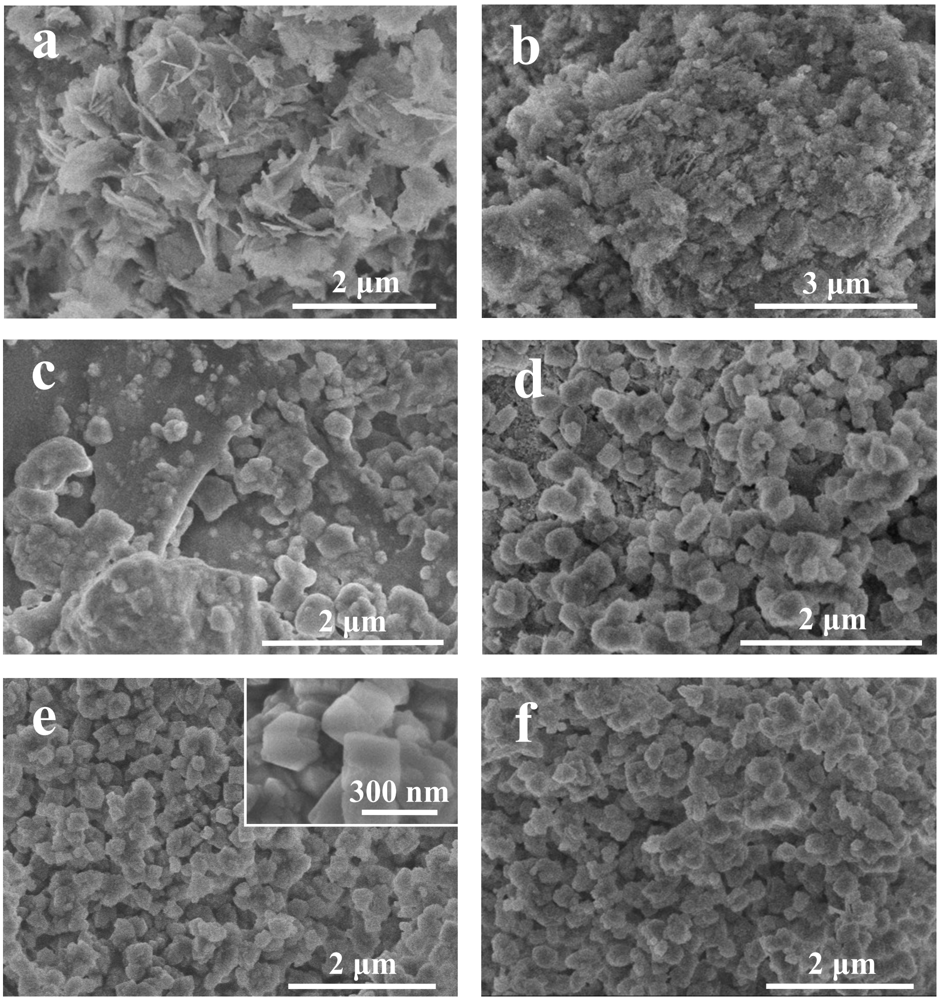

Fig. S4 SEM images of Ti-MWW (a) and Ti-Beta-DT samples crystallized for 0.5 h (b), 1 h (c), 1.5 h (d), 2 h (e), and 1 d (f). Other crystallization conditions: see Fig. S3.

Prior to hydrothermal synthesis, the parent Ti-MWW crystals appeared as thin platelets, in good consistent with previous reports.[1] *After 0.5 h of hydrothermal treatment at 463 K, the parent crystals were converted into amorphous phase completely (Fig. S4b), indicating a great structural degradation. When the crystallization time was extended to 1 h, some nanoparticles appeared with the co-existence of amorphous gels in the whole region. At 1.5 h, the nanosized crystals became dominant at the expanse of amorphous phase. At 2 h, irregular nanosized crystals with a diameter of 150−250 nm were formed in the whole region (Figure S4e)* *and their morphology and size almost didn't change hereafter, implying Ti-Beta-DT zeolite was completely crystallized within 2 h at 463 K.*

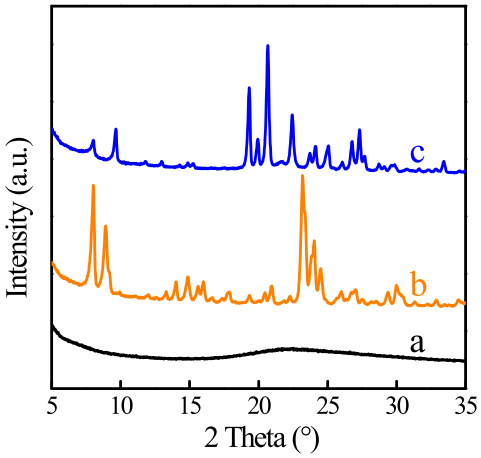

Fig. S5 XRD patterns of solid products synthesized from TEOS (a), silicalite-1 (MFI) (b), all-silica NON zeolite (c). Crystallization conditions: TEAOH/SiO_2 = 0.3; TiO_2/SiO_2 = 0.02; NH_4F/SiO_2 = 0.5; Beta seeds, 10 wt %; temp., 463 K; time, 1 d.

*To confirm the specific structural connection between the MWW and *BEA structures, three other silica sources of tetraethyl orthosilicate (TEOS), MFI-type silicalite-1, and all-silica NON zeolite were also employed to synthesize Ti-Beta zeolite under the same crystallization conditions. During the experiment section for these preparation, tetraethyl orthosilicate (TBOT) was used as the titanium source. However, after hydrothermal treatment, the corresponding topology structures were not changed for MFI and NON zeolite. An amorphous phase was obtained with TEOS (Fig. S5). At this point, it could be inferred that the framework structure similarity between MWW and *BEA-type zeolite was an indispensable factor in the crystallization of the Ti-Beta-DT zeolite, which was similar to the findings in the synthesis of all-silica Beta and Sn-Beta zeolite by our group previously.*[7,8]

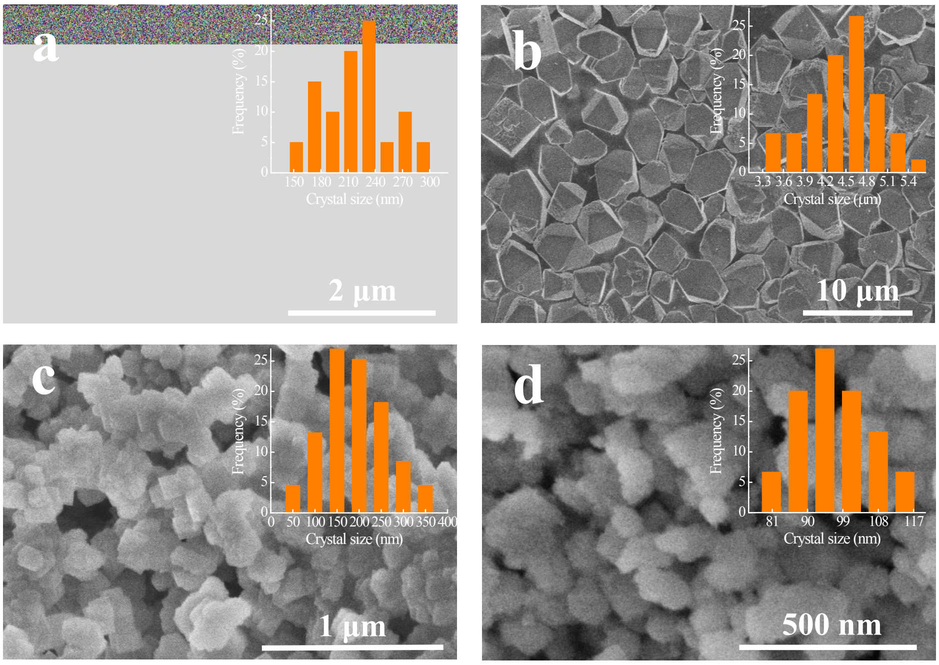

Fig. S6 Scanning electron micrograph images of Ti-Beta-DT (a), Ti-Beta-F (b), Ti-Beta-OH (c), and Ti-Beta-PS (d) samples.

As illustrated in Fig. S6, Ti-Beta-DT and Ti-Beta-OH zeolites exhibited comparable irregular nanosized crystal with a diameter of 150−250 nm. An obvious increase in particle size (4–5 μm) for Ti-Beta-F was observed (Fig. S6b). The crystal of Ti-Beta-PS was composed of nanosized particles, the size of which ranged from 80 to 110 nm. Hence, the crystal sizes for Ti-Beta-DT and Ti-Beta-OH (nanometer order) were remarkably smaller than Ti-Beta-F (micrometer order), resulting in higher BET surface area and external surface area for Ti-Beta-DT and Ti-Beta-OH (Table S1).

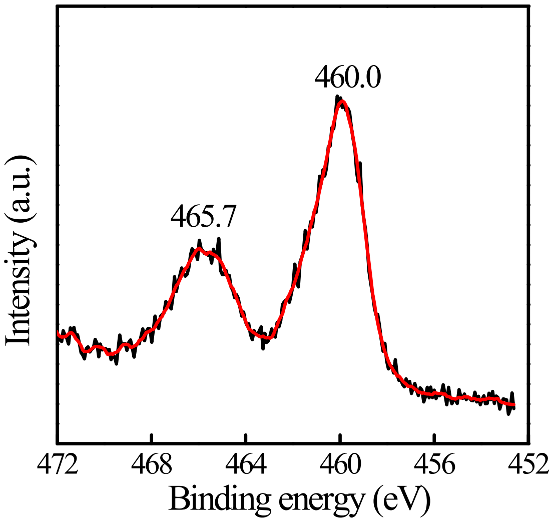

Fig. S7 Ti 2p XPS spectrum of dehydrated Ti-Beta-DT sample.

XPS spectroscopy is an effective technique for investigating the coordinate states of transition metal ions in metallosilicates.[8,9] *Thus, it was also adopted here to explore the Ti coordination state of the Ti-Beta-DT sample. Fig. S7 shows the Ti 2p XPS spectrum of dehydrated Ti-Beta-DT sample in the 2p region. Two signal bands at about 460.0 and 465.7 eV, associated with* $2p_{1/2}$ *and* $2p_{3/2}$ *photoelectrons of tetrahedrally coordinated Ti species in the zeolite framework,*[9] *were obviously observed, implying that the Ti species existed as isolated ones in the *BEA framework. Additionally, no signals related to octahedrally coordinated Ti species were found in this spectrum. The XPS results were in line with the results from the UV–vis spectra (Fig. 2).*

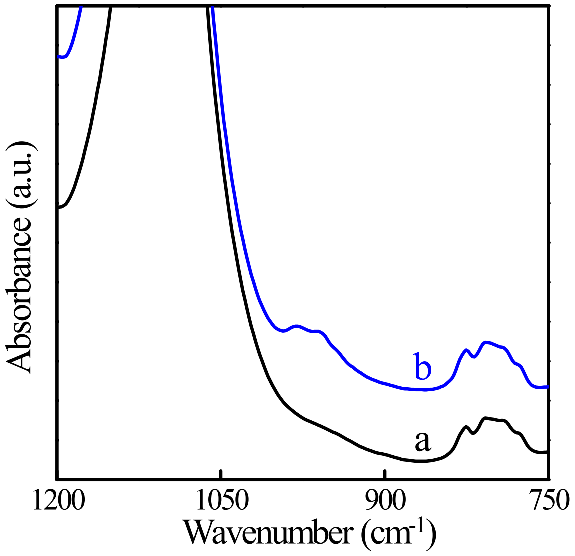

Fig. S8 FT-IR spectra in the region of framework vibration for all-silica Beta-DT (a), and Ti-Beta-DT (b) samples.

Compared to all-silica Beta-DT zeolites also synthesized by intensified interzeolite transformation, Ti-Beta-DT showed a minor vibration signal at approximate 965 cm^{-1}*, generally assigned to the presence of isolated Ti species in the framework (Fig. S8).* [10] *In combination with UV-vis and Ti 2p XPS analyses, the conclusion could be made that the Ti species in Ti-Beta-DT zeolite were tetrahedrally coordinated in the *BEA framework.*

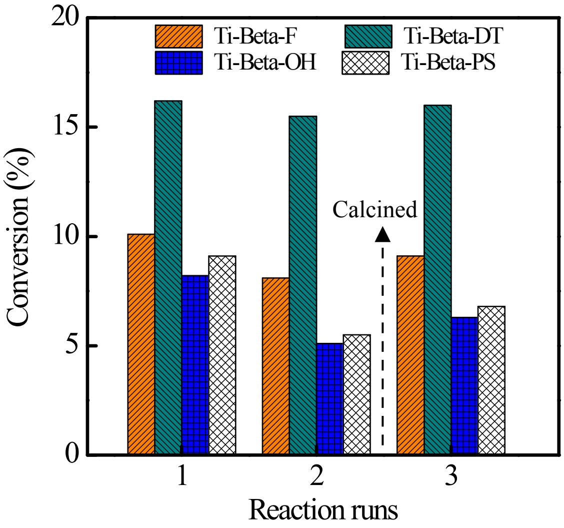

Fig. S9 Reusability of Ti-Beta zeolites in the selective oxidation of cyclohexene with hydrogen peroxide. Reaction conditions: cat, 50 mg; cyclohexene, 10 mmol; H_2O_2 (30 wt %), 10 mmol; CH_3CN, 10 mL; temp., 333 K; time, 2 h.

As shown in Fig. S9, the conversion of Ti-Beta catalysts decreased when the catalyst was only washed with CH_3CN *after the first reaction cycle. Note that the decrease degree of Ti-Beta-DT was minimum (4.3 %) among other three ones (Ti-Beta-F, 19.8 %; Ti-Beta-OH, 37.8 %; Ti-Beta-PS, 39.6 %). After regenerating by calcination in air, the activity for Ti-Beta-DT was almost restored to the initial level, whereas others could not. The framework structures for all Ti-Beta zeolites were well retained after the second run (Fig. S10) and the Ti contents were nearly the same as the initial values according to ICP analysis. In combination with UV-vis spectra (Fig. 2), these results indicated that the* Ti^{4+} *sites within Ti-Beta-DT framework were stable under the present reaction conditions.*

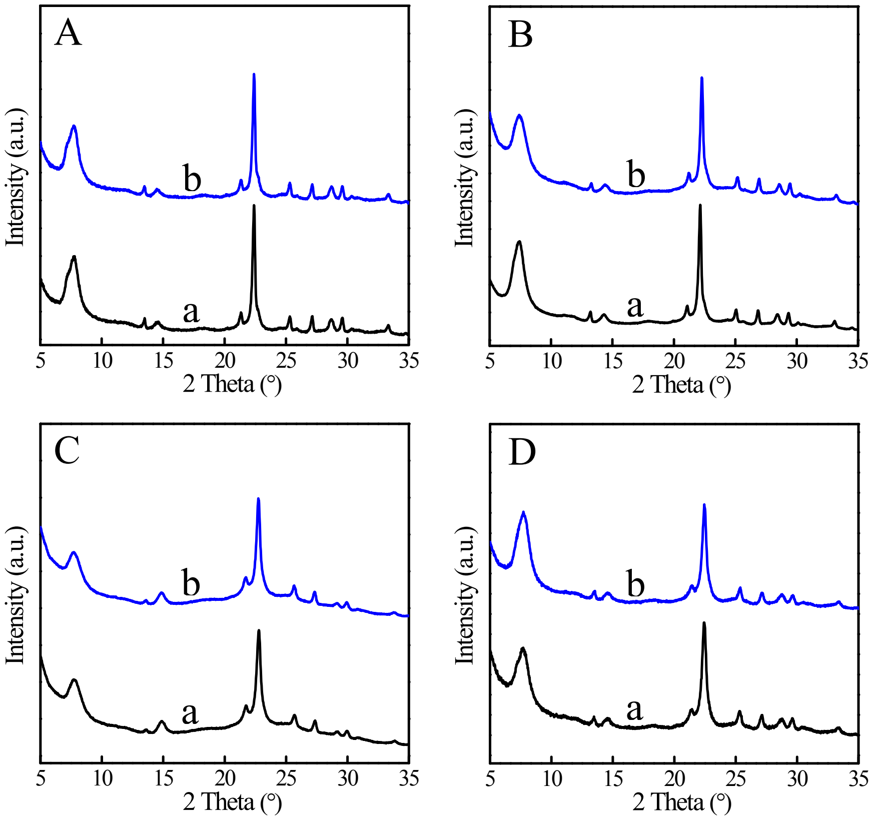

Fig. S10 XRD spectra of (A) Ti-Beta-DT, (B) Ti-Beta-F, (C) Ti-Beta-OH, and (D) Ti-Beta-PS samples in fresh (line a) and used (line b) states. The used catalyst indicates the calcined sample after the second run in the selective oxidation of cyclohexene with hydrogen peroxide.

As demonstrated in Fig. S10, the framework structures for all Ti-Beta zeolites were well retained after the second run.

References

1 P. Wu, T. Tatsumi, T. Komatsu and T. Yashima, *J. Phys. Chem. B*, 2001, **105**, 2897.

2 M. A. Camblor, M. Costantini, A. Corma, L. Gilbert, P. Esteve, A. Martínez and S. Valencia, *Chem. Commun.*, 1996, 1339.

3 T. Blasco, M. A. Camblor, A. Corma, P. Esteve, A. Martínez, C. Prieto and S. Valencia, *Chem. Commun.*, 1996, 2367.

4 J. Nogier, Y. Millot, P. P. Man, T. Shishido, M. Che, S. Dzwigaj, *J. Phys. Chem. C*, 2009, **113**, 4885.

5 Y. Yang, J. Ding, C. Xu, W. Zhu, P. Wu, *J. Catal.*, 2015, **325**, 101.

6 M. Taramaso, G. Perego, B. Notari, U.S. Patent 4410501, 1983.

7 Z. Zhu, H. Xu, J. Jiang, H. Wu and P. Wu, *ACS Appl. Mater. Interfaces*, 2017, **9**, 27273.

8 Z. Zhu, H. Xu, J. Jiang, Y. Guan and P. Wu, *J. Catal.*, 2017, **352**, 1.

9 V. Smeets, C. Boissière, C. Sanchez, E. M. Gaignaux, E. Peeters, B. F. Sels, M. Dusselier and D. P. Debecker, *Chem. Mater.*, 2019, **31**, 1610.

10 N. K. Mal, V. Ramaswamy, S. Ganapathy and A. V. Ramaswamy, *Appl. Catal. A: Gen.*, 1995, **125**, 233.