Electronic Supplementary Information (ESI)

Fluoride etching opens the access for bulky molecules to active sites in microporous Ti-Beta zeolite

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1. Experimental Section

Chemicals and materials

The reagents used in this work include tetraethylorthosilicate (TEOS) (Beijing Chemical Works), tetraethyl orthotitanate (TEOT) (35%, Sinopharm), tetrapropylammonium hydroxide (25 wt.%, Sinopharm), hydrogen peroxide (H_2O_2, 30% Beijing Chemical Works), hydrofluoric acid (HF, 40 wt.%, Beijing Chemical Works), ammonium fluoride (NH_4F, Beijing Chemical Works) and distilled water, tert-butyl hydroperoxide (TBHP) (65%, Sinopharm Chemical Reagent Co.). Ceric sulfate and 1-octane were purchased from Beijing Chemical Works. Pentadecane (99%), chlorobenzene (99%), 2-cyclohexen-1-one (97%), norbomene (99%), cyclooctene (95%) and methyl oleate (94%), dibenzothiophene (DBT) (98%) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) (99%) were purchased from Aladdin Biochemical Technology Co..

2. Supplementary Figures and Tables

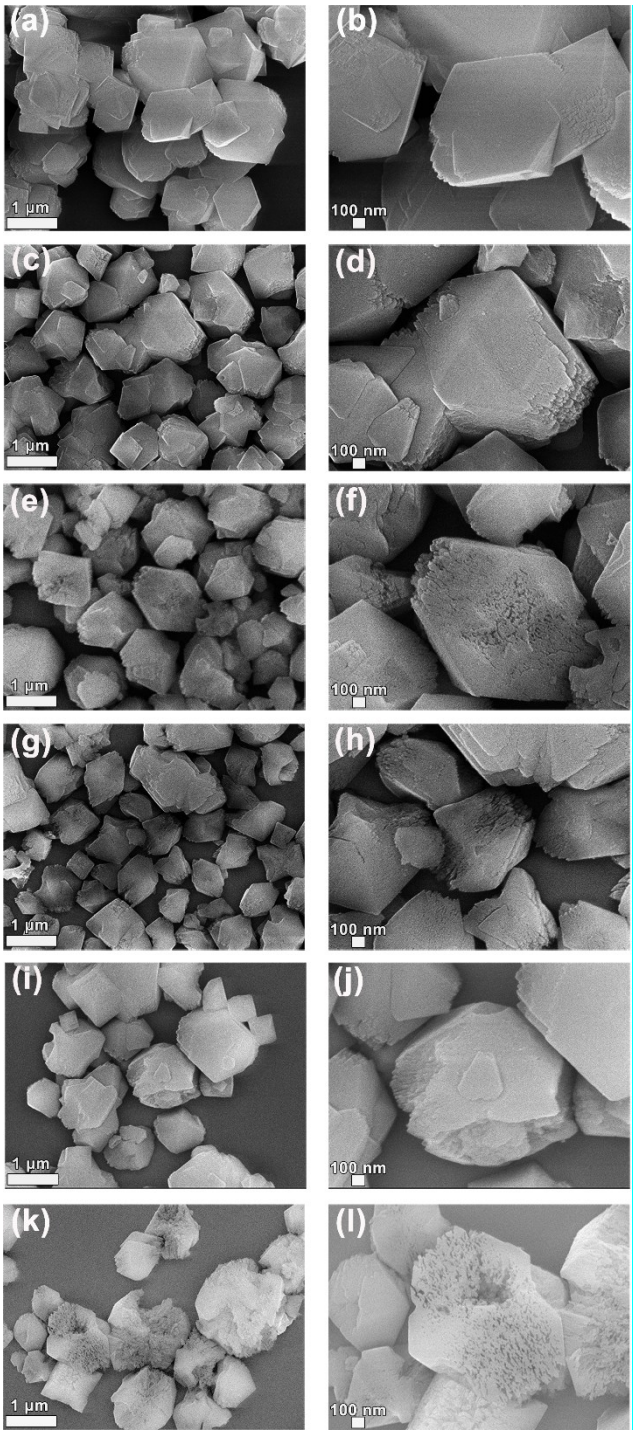

Fig. S1 SEM images of the prepared Ti-Beta samples, (a) and (b) TB-Parent, (c) and (d) TB-$HF_{0.1}/AF_0$, (e) and (f) TB-$HF_{0.1}/AF_{0.5}$, (g) and (h) TB-$HF_{0.1}/AF_2$, (i) and (j) TB-$HF_{0.05}/AF_{0.5}$, (k) and (l) TB-$HF_{0.25}/AF_{0.5}$.

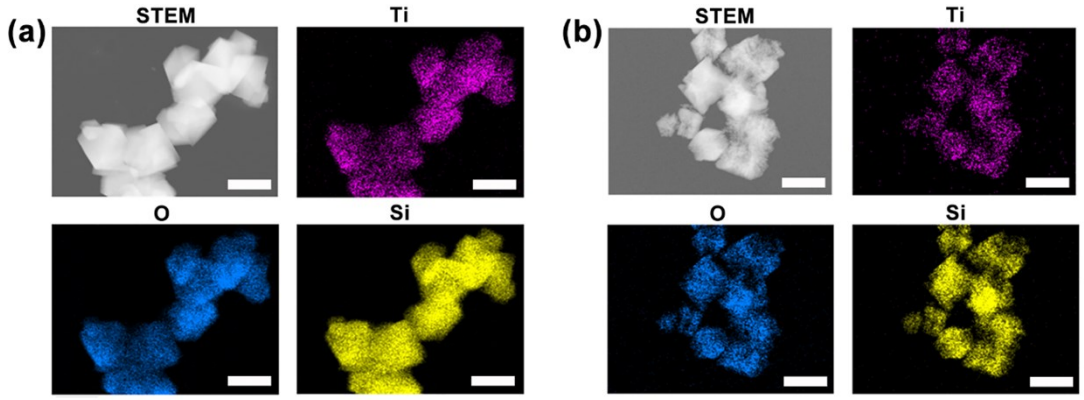

Fig. S2 STEM-energy-dispersive X-ray spectrometry (EDX) analysis for the prepared Ti-Beta samples, (a) TB-Parent, (b) TB-$HF_{0.25}$/$AF_{0.5}$.

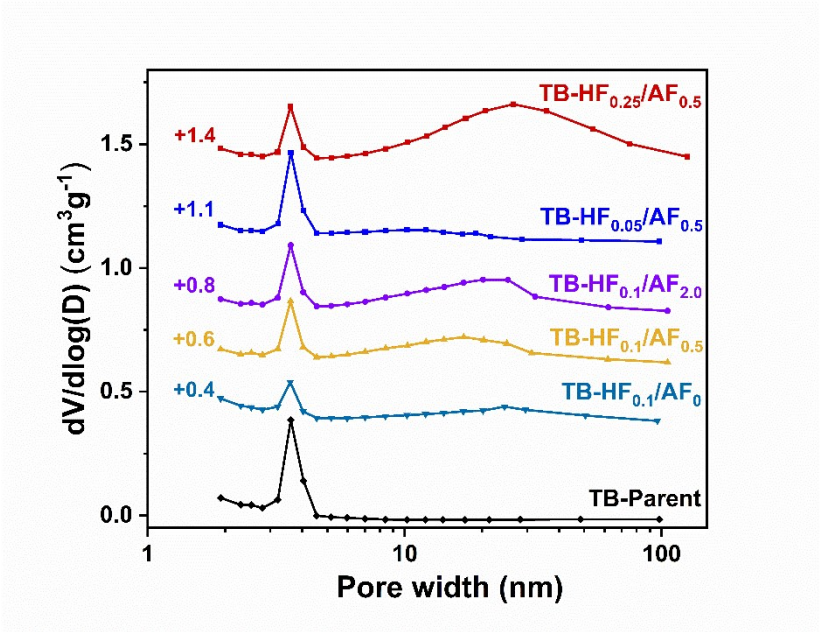

Fig. S3 Pore size distributions of the prepared Ti-Beta samples.

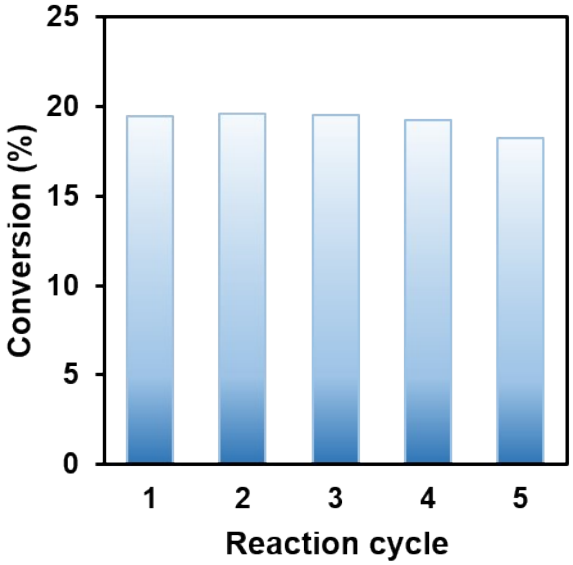

Fig. S4 Recycle tests in the epoxidation of methyl oleate over TB-$HF_{0.25}$/$AF_{0.5}$. Reaction condition: 2.5 mmol of methyl oleate with 3.5 mmol H_2O_2, in 5mL acetonitrile, at 333 K for 2 h over 50 mg of catalysts.

Table S1 Chemical composition of fluoride medium solution, relative yield and crystallinity of as-synthesized Ti-Beta samples

Sample	$Mass_{TB}$ (g)	H_2O (g)	HF (M)	NH_4F (wt.%)	Yield (%)[a]	Crystallinity(%)[b]
TB-Parent	0.6	36	0	0	100	100
TB-$HF_{0.1}$/AF_0	0.6	36	0.1	0	86	89
TB-$HF_{0.1}$/$AF_{0.5}$	0.6	36	0.1	0.5	78	91
TB-$HF_{0.1}$/AF_2	0.6	36	0.1	2.0	72	74
TB-$HF_{0.05}$/$AF_{0.5}$	0.6	36	0.05	0.5	88	93
TB-$HF_{0.25}$/$AF_{0.5}$	0.6	36	0.25	0.5	73	88

[a] Yield refers to the mass ratio of individual sample to the TB-Parent sample; [b] Crystallinity is calculated based on the relative peak (2θ = 7.5–7.6, 22.36°) intensity in XRD pattern.

Table S2 Oxidative desulfurization of DBT and 4,6-DMDBT over Ti-Beta samples.[a]

Sample	Ti (wt.%)[b]	DBT oxidation		4,6-DMDBT oxidation	
		$Con._{DBT}$ (%)[c]	TON[d]	$Con._{4,6\text{-}DMDBT}$(%)[c]	TON[d]
TB-Parent	1.24	24.8	2.1	9.8	0.8
TB-$HF_{0.1}/AF_0$	1.00	21.8	2.3	10.0	1.1
TB-$HF_{0.1}/AF_{0.5}$	0.98	36.7	3.9	29.1	3.1
TB-$HF_{0.1}/AF_2$	1.00	29.5	3.1	20.3	2.1
TB-$HF_{0.05}/AF_{0.5}$	1.19	31.9	2.8	20.2	1.8
TB-$HF_{0.25}/AF_{0.5}$	1.00	70.4	7.4	52.0	5.5

[a] Reaction conditions: 10 mL 500 ppm model fuels, 50 mg of catalyst, n(TBHP)/n(sulphide) is 2, for 30 min of the reaction at 60 °C. [b] Measured by ICP-OES. [c] Conversion (Conv.) = mole of converted reactant/mole of initial reactant × 100%. [d] Turnover number is defined as moles of the converted substrate at per mole of Ti sites for 30 min of reaction.

Table S3 Catalytic epoxidation activities of TB-$HF_{0.25}/AF_{0.5}$ and TB-Parent for bulky molecules containing C=C bonds with various molecule sizes.[a]

Substrates	TB-$HF_{0.25}/AF_{0.5}$			TB-Parent		
	Conv.[b] (%)	Sele.[c] (%)	TON[d]	Conv.[b] (%)	Sele.[c] (%)	TON[d]
2-cyclohexen-1-one	50	98	118	39	97	76
Norbornene	66	92	157	49	90	95
Cyclooctene	35	99	84	20	98	39
Methyl oleate	19	99	46	10	98	18

[a] Reaction conditions: 2.5 mmol of bulky substrates with 3.5 mmol H_2O_2, in 5 mL acetonitrile, at 60 °C for 30 min over 50 mg of catalysts. [b] Conversion (Conv.) = mole of converted reactant/mole of initial reactant × 100%. [c] Selectivity (Sele.) refers to the selectivity of the main product, i.e., (mole of epoxide)/(mole of all products) × 100%. [d] Turnover number (TON) is defined as moles of the converted substrate at per mole of Ti sites for 2 h of the reaction.

Table S4 Comparison of the catalytic activity of some representative titanosilicate catalysts with the prepared TB-$HF_{0.25}/AF_{0.5}$ for the epoxidation reaction of bulky molecules.

Substrate	Catalysts	Temp.(K)	Time(h)	Substrate (mmol)	Cat.(mg)	Conversion (%)	Rate(mmol/g/h)[a]	Reference
norbornene	Ti-Beta	333	2	2.5	50	66.0	16.5	This work
	Ti-Beta	333	4	5.3	50	54.3	14.4[b]	1
cyclooctene	Ti-Beta	333	2	2.5	50	35.0	5.0	This work
	Ti-Beta	333	4	4.0	60	14.0	2.3[b]	1
2-cyclohexen-1-one	Ti-Beta	333	2	2.5	50	50.0	12.5	This work
	Ti-Beta	343	5	5.0	100	51.6	5.2[b]	2
Methyl Oleate	Ti-Beta	333	2	2.5	50	18.0	4.5	This work
	TS-1	323	5	0.3	150	92.0	0.4[b]	3
	TS-1	363	9	0.06	10	75.8	0.5[b]	4
	TS-1	353	24	0.3	150	93.0	0.1[b]	5
	Ti-MCM-41	323	8	1	30	26.7	1.1[b]	6
	Ti-Beta	323	8	1.0	30	45.3	1.9[b]	6

[a] Rate refers to millimole of the converted substrate at per gram of catalyst for certain hours of the reaction. [b] Rate value is calculated based on the reported data in the literature.

3. References

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