

## Hierarchical Ti-Beta with a three-dimensional ordered mesoporosity for catalytic epoxidation of bulky cyclic olefins

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### Synthesis of TS-1 zeolite

For the control experiment, the conventional titanium-substitution Silicalite-1 (TS-1) was hydrothermally synthesized as follow. Briefly, 9.52 g aqueous solution of TPAOH (40 wt%) and 9.70g deionized water were successively added into 11.25 g LUDOX (40 wt%) with stirring. 0.51g TBOT was quickly added into 1.12g ethanol, and then mixed with the above solution with stirring. After aging at room temperature for 12 h, the synthesis gel with a composition of  $\text{SiO}_2 : 0.25 \text{ TPAOH} : 0.02 \text{ TiO}_2 : 16.44 \text{ H}_2\text{O} : 0.32 \text{ ethanol}$  was transferred into a 50ml stainless steel autoclave with Teflon liner and heated at 135 °C for 4 days. The obtained solid was collected by filtration, fully washed with deionized water and dried at 353 K for 12 h, and then calcined at 823 K for 6 h in air to remove the organic structure-directing agent.

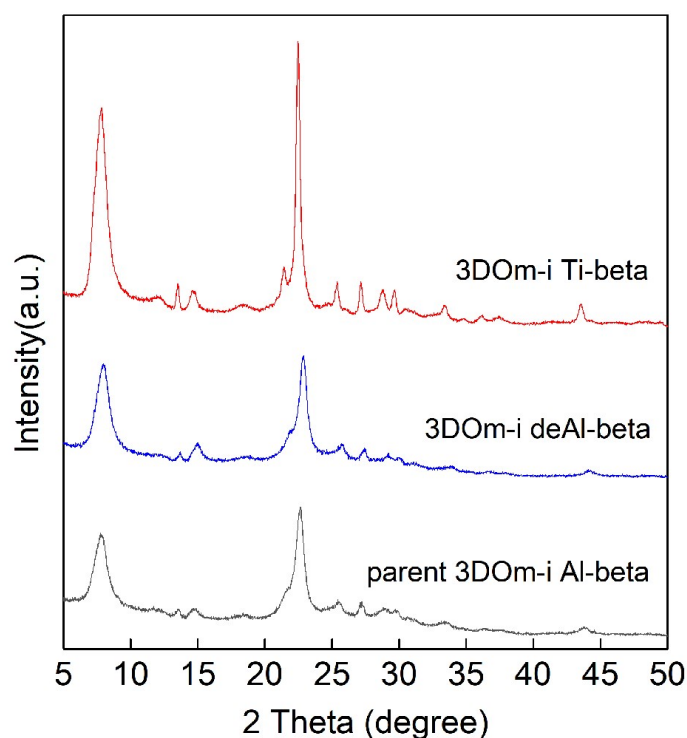


Figure S1. XRD patterns of the parent 3DOM-i Al-beta, 3DOM-i deAl-beta and 3DOM-i Ti-beta.

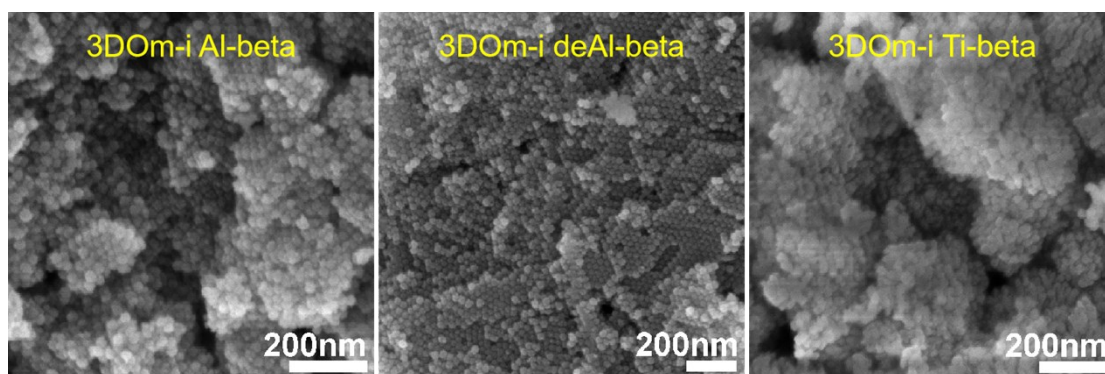


Figure S2. SEM images of the parent 3D Om-i Al-beta, 3D Om-i deAl-beta and 3D Om-i Ti-beta.

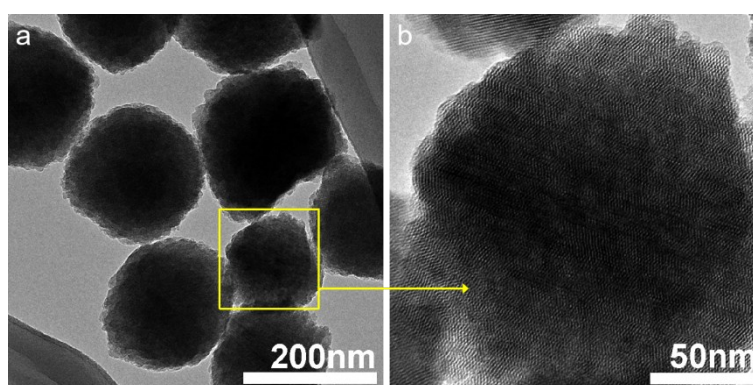


Figure S3. (a) TEM image of N\_Ti-beta, and (b) the corresponding high-magnification TEM image of the selected area in a.

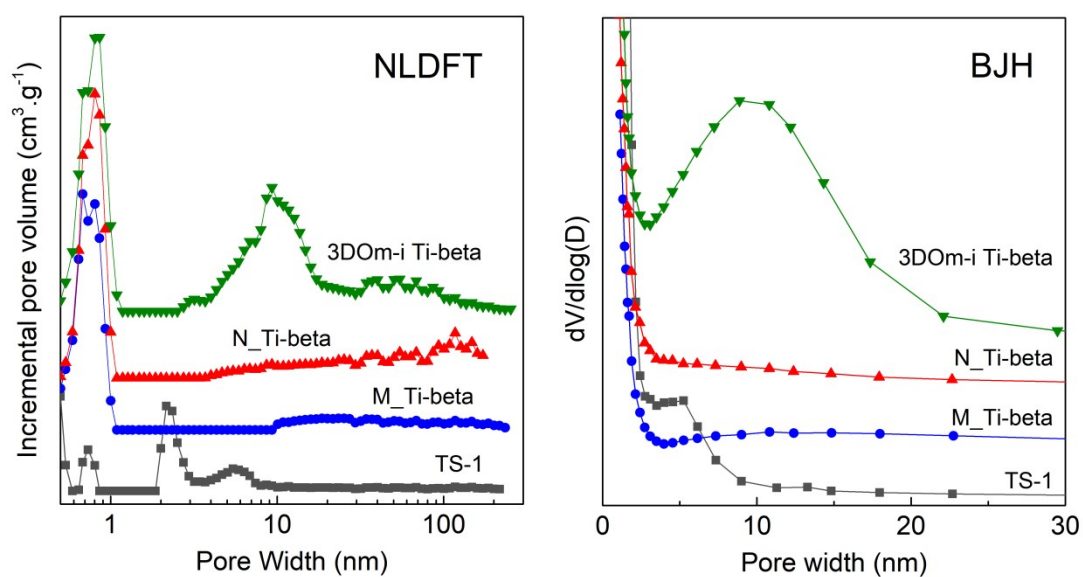


Figure S4. NLDFT and BJH pore size distributions of various titanasilicate zeolites.

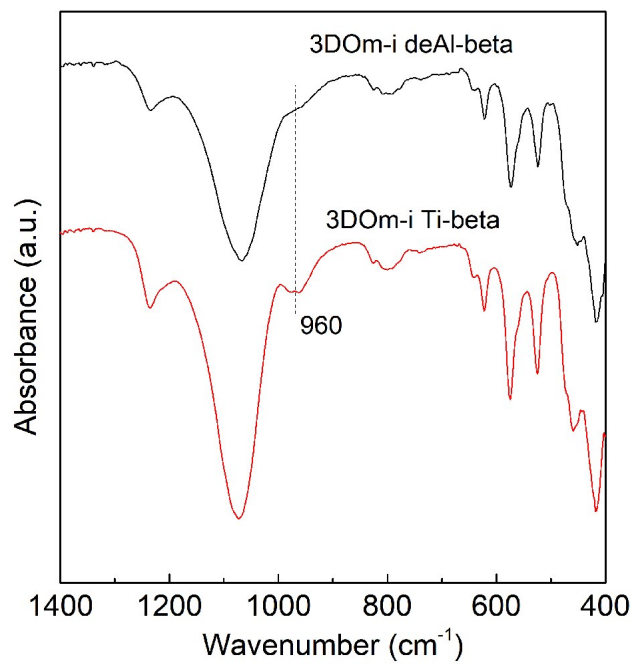


Figure S5. FT-IR spectra of the 3DOM-i deAl-beta and 3DOM-i Ti-beta samples.

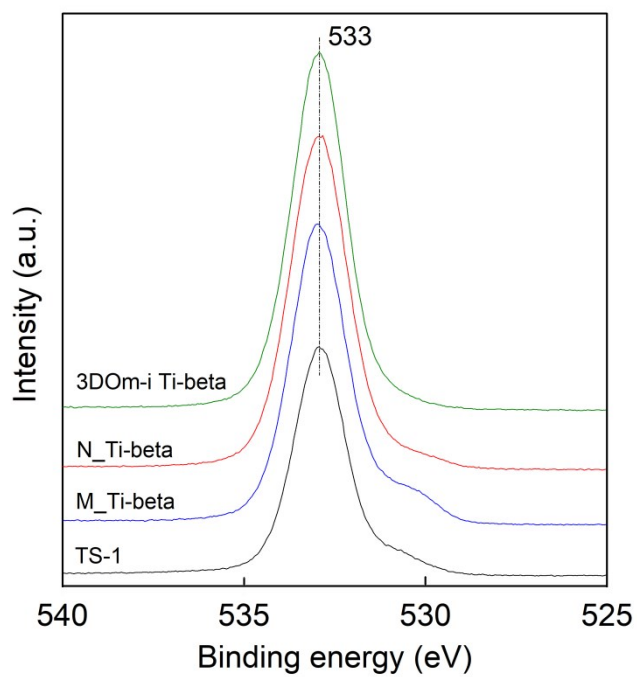


Figure S6. O 1s XPS spectra of the TS-1, M\_Ti-beta, N\_Ti-beta and 3DOM-i Ti-beta samples.

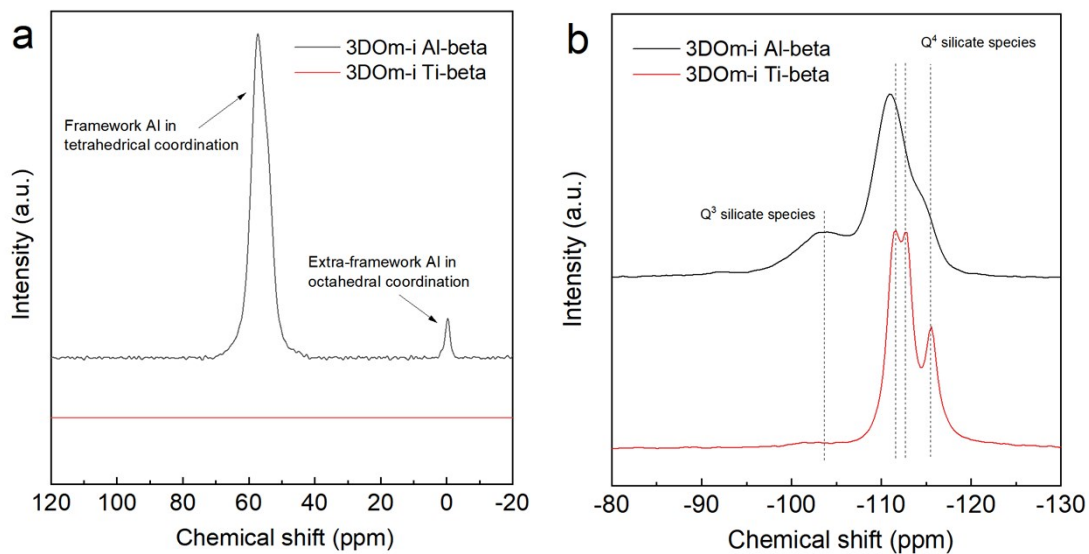


Figure S7. (a)  $^{27}\text{Al}$  and (b)  $^{29}\text{Si}$  MAS NMR spectra of the parent 3DOM-i Al-beta and 3DOM-i Ti-beta samples.

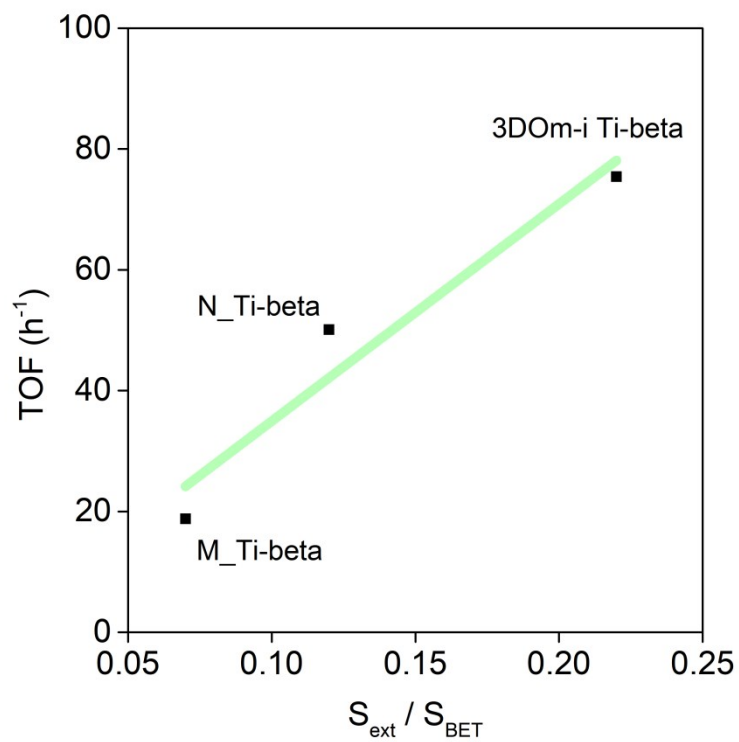


Figure S8. Correlation between the conversion of cyclooctene and the proportion of external surface area to overall surface area ( $S_{\text{ext}}/S_{\text{BET}}$ ).

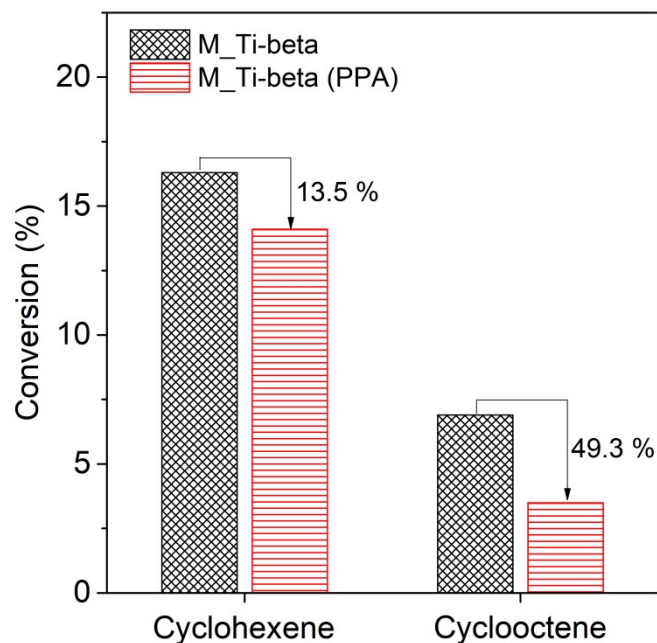


Figure S9. Conversions of cyclohexene and cyclooctene over the M\_Ti-beta catalyst with and without PPA poisoning.

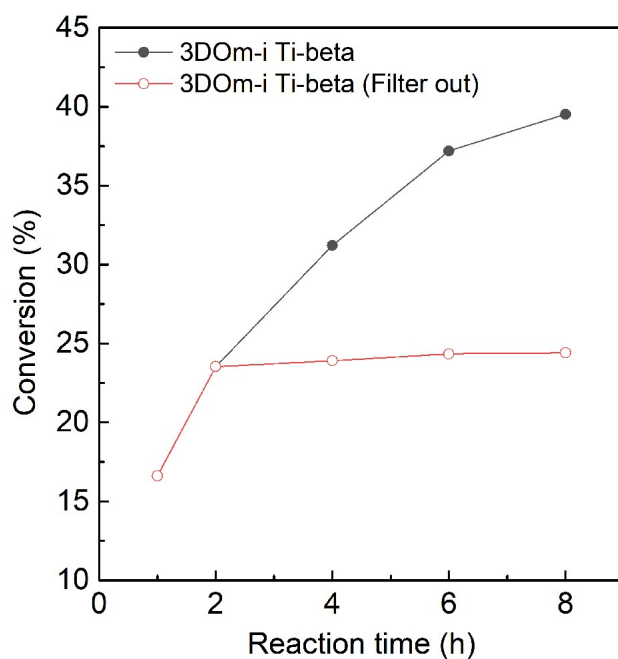


Figure S10. The leaching test of 3DOM-i Ti-beta. It was found that the conversion of cyclooctene almost stopped after the catalyst was filtered out at 2 hours, and the Ti content of the sample after leaching was  $261 \mu\text{mol.g}^{-1}$  determined by ICP-OES, closed to the value ( $265 \mu\text{mol.g}^{-1}$ ) of the fresh sample, indicating that the leaching of Ti active sites in 3DOM-i Ti-beta was effectively suppressed.

Scheme S1. Schematic of postsynthetic treatment of successive dealumination and titanation.

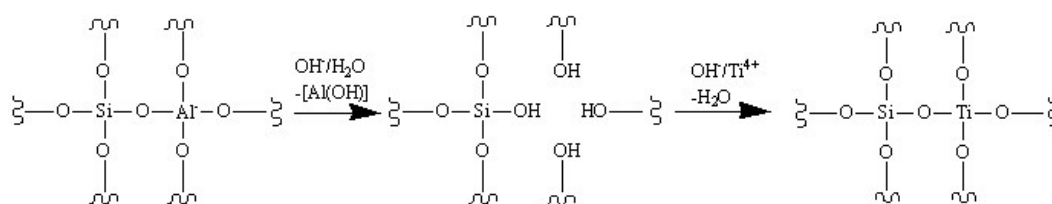


Table S1. Al Contents and Si / Al ratios of the dealuminated samples of M\_deAl-beta, N\_deAl-beta and 3DOm-i deAl-beta.

Sample	Al Content ( $\mu\text{mol.g}^{-1}$ ) <sup>a</sup>	Si / Al
M_deAl-beta	5.7	2122
N_deAl-beta	2.9	5421
3DOm-i deAl-beta	4.3	3225

<sup>a</sup> Ti content in the catalyst detected by ICP-OES.

Table S2. Conversions of cyclohexene and cyclooctene over M\_Ti-beta and 3DOm-i Ti-beta catalyst with and without PPA poisoning.

Catalysts	Cyclohexene				Cyclooctene	
	Conversion (%)	Selectivity (%) <sup>a</sup>			Conversion (%)	Selectivity <sup>b</sup> (%)
		Epoxide	Diol	Others		
M_Ti-beta	16.3	53.5	39.6	6.9	6.9	>99
M_Ti-beta (PPA) <sup>c</sup>	14.1	46.3	50.7	4.0	3.5	>99
3DOm-i Ti-beta	20.3	44.3	52.9	2.8	23.5	>99
3DOm-i Ti-beta (PPA) <sup>c</sup>	11.7	41.9	55.6	2.5	2.8	>99

<sup>a</sup> Epoxide: epoxycyclohexane. Diol: 1, 2-cyclohexanediol. Others: cyclohexen-1-one and 2-cyclohexen-1-ol as dominant and other products undetected by GC. <sup>b</sup> Selectivity of epoxycyclooctane. <sup>c</sup> The poisoning of sample was conducted by adding 10 mmol of phenylphosphonic acid (PPA) into the reaction mixture.

Table S3. Recyclability of 3DOm-i Ti-beta in the epoxidation of cyclooctene <sup>a</sup>.

Run Number <sup>b</sup>	Conversion (%)	Selectivity <sup>c</sup> (%)
1	21.0	>99
2	17.8	>99
3	14.5	>99
4	10.6	>99
5	20.5	>99
6	17.1	>99

<sup>a</sup> Reaction conditions: 50 mg catalyst, 10 mmol cyclooctene, 10 ml CH<sub>3</sub>CN, 10 mmol H<sub>2</sub>O<sub>2</sub> (30 wt%), 60 °C, 2 h. <sup>b</sup> After the first four runs, the used catalysts were collected by filtration, simply washed by acetonitrile and then carried on the next run of reaction. After the fifth run, the used catalysts were calcined in air at 773 K for 6 h. <sup>c</sup> Selectivity of epoxycyclooctane.