

Supplementary information

of

Fast synthesis of hierarchical Al-free Ti-BEA nanocrystals from low-templated dry gel via a steam-assisted conversion method

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Chemicals involved in the Ti-BEA synthesis

In the synthesis of Al-free Ti-BEA zeolites, the reagents used include fumed silica (Aerosil®200, Shanbo Co. Ltd., China), ammonium hexafluorotitanate ($\text{H}_8\text{F}_6\text{N}_2\text{Ti}$, AR, Maclin, Co. Ltd., China), sodium hydroxide (NaOH, AR, Xilong, Co. Ltd., China), aqueous tetraethylammonium hydroxide (TEAOH, 25 wt%, Xiya Reagent, China). All the reagents were invoked as purchased without any further purification.

Synthesis of pure Si-BEA seeds and its physicochemical property

Briefly, 0.64 g NaOH and 4.71 g TEAOH solution were dissolved in 60 g distilled water, and stirred until the formation of a clear solution. Then, 6.0 g silicon source was added to the clear solution and the resulting mixture was stirred vigorously for 20 min at room temperature to form a uniform gel with the molar composition of $\text{SiO}_2:0.16\text{NaOH}:0.08\text{TEAOH}:33\text{H}_2\text{O}$. Then the gel was heated at 70 °C for 24 h to form a dry gel and grinded into a fine powder. 5.0 g of obtained dry gel was weighed and transferred into a 10 mL small Teflon cup. The loaded Teflon cup was placed in a 40 mL Teflon-lined stainless-steel autoclave, and 1.25 g distilled water was added into the bottom of Teflon liner without contacting the dry gel. The autoclave was sealed and heated at 418 K for 24 h, then the as-prepared pure-Si BEA was obtained after washing and drying.

The detailed synthetic procedure and physicochemical property of the pure Si-BEA seeds were reported on our previous study (Y.L. Luo, Q.M. Huang, X.H. Chen, Micropor. Mesopor. Mater. DOI: 10.1016/j.micromeso.2019.109675).

Figures and Schemes

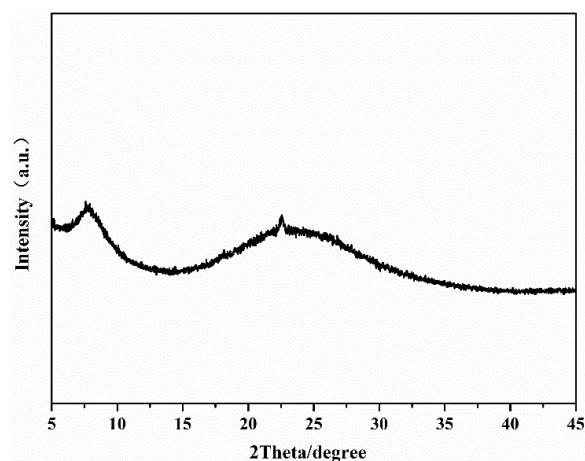


Fig.S1. XRD pattern of sample obtained without addition of Na^+ after 2 days at 145 °C. Only very weak reflections can be observed. They could originate from the seeds added in the gel.

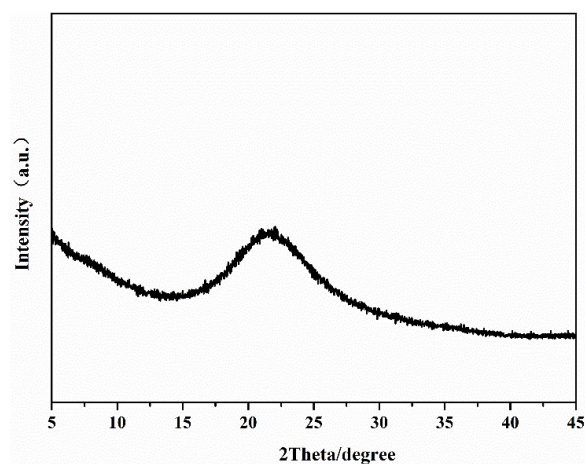


Fig.S2. XRD pattern of sample directly synthesized with NH_4NO_3 after 2 days at 145 °C. Only amorphous substances exist, indicating that ammonium ions added to the precursor cannot replace sodium ions.

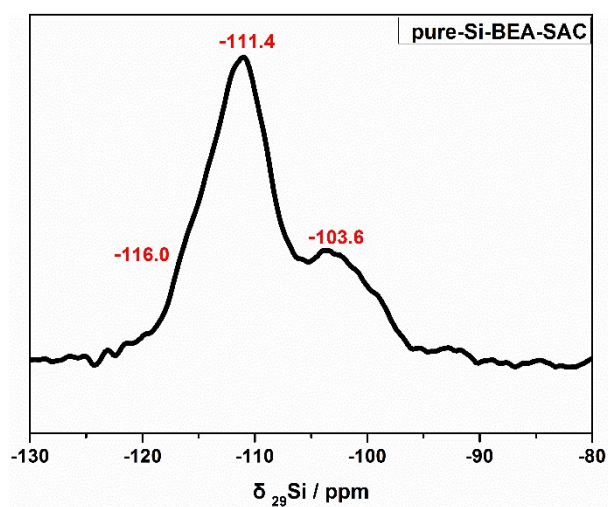


Fig.S3. ^{29}Si MAS NMR spectra of pure-Si-BEA-SAC sample.

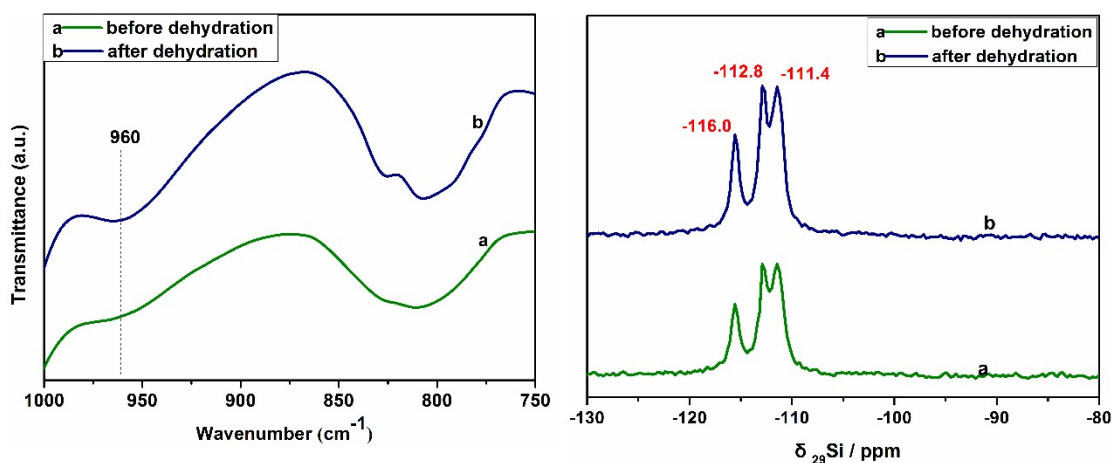


Fig.S4. DRIFT (left) and ²⁹Si MAS NMR (right) spectra of Ti-BEA-70 samples before dehydration (a) and after dehydration (b).

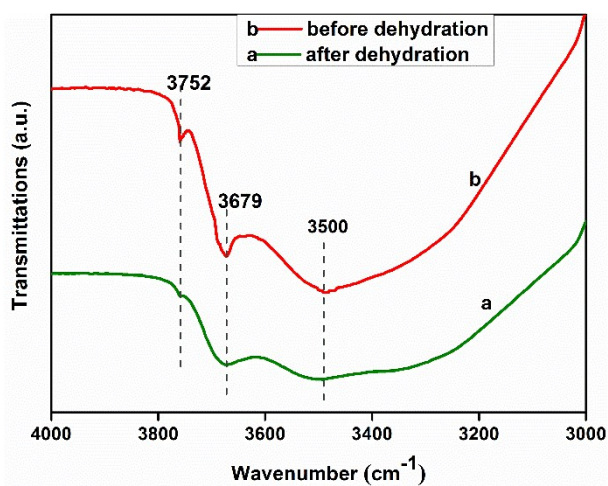


Fig.S5. DRIFT spectra of Ti-BEA-70 samples before and after dehydration: the stretching vibration of various silanol hydroxyl groups between 3000~4000 nm.

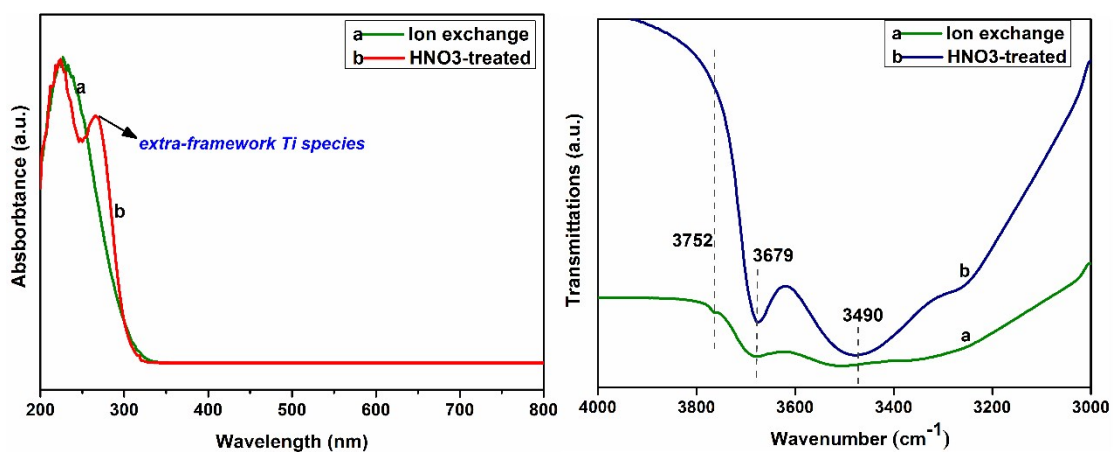


Fig.S6. UV-Vis (left) and DRIFT (right) spectra for Ti-BEA samples with different pretreatments: (a) ion exchange and (b) HNO₃ washing.

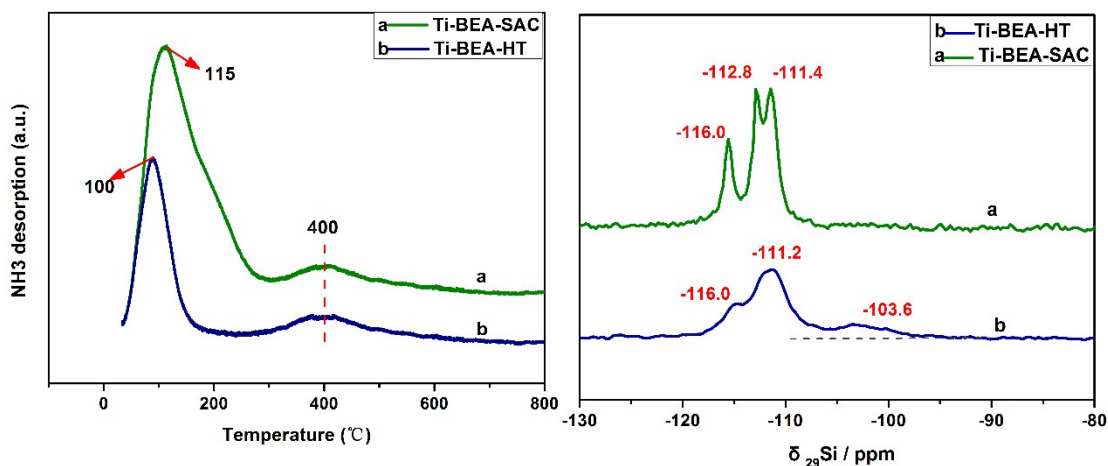


Fig.S7. NH₃-TPD curves (left) and ²⁹Si MAS NMR (right) spectra of Ti-BEA-SAC (a) and Ti-BEA-HT (b) with the same Si/Ti=70 in precursor.

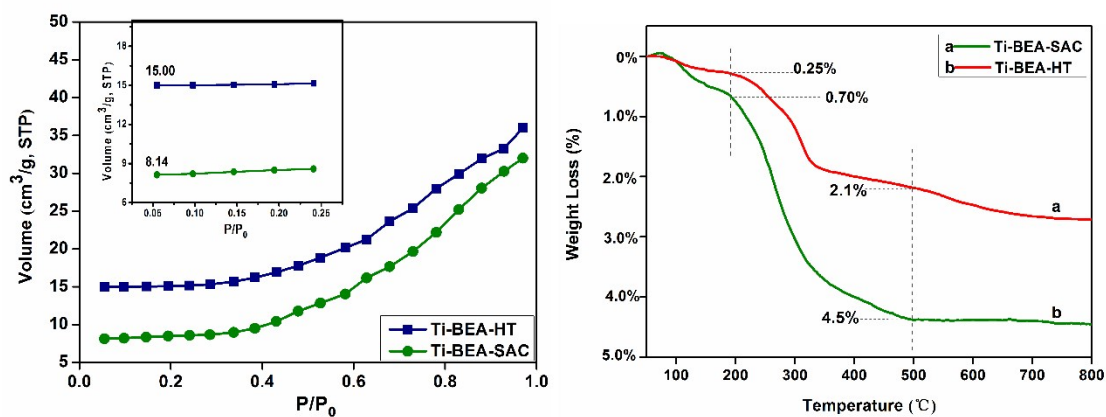
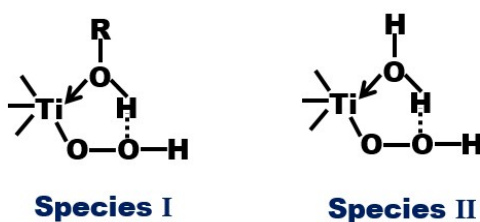
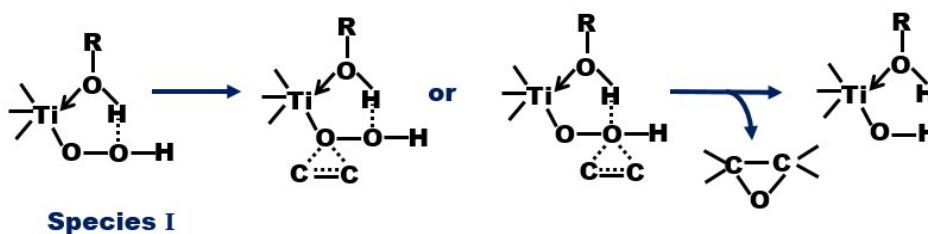


Fig.S8. Water adsorption isotherms (left) and TG curves (right) of Ti-BEA-SAC and Ti-BEA-HT samples.



Scheme S1. Two different intermediates Species I and Species II in protic and aprotic solvents in Ti active sites.



Scheme S2. Formation of cyclic species I and the coordination of cyclohexene to

the Ti-peroxo complex.

Tables related with catalytic performance

Table S1

Influence of solvents on cyclohexene epoxidation on Ti-BEA samples by SAC method ^a

| Solvent | Dielectric constants | Cyclohexene conversion (%) | Selectivity (%) | | |
|------------------|----------------------|----------------------------|-----------------|------|---------------------|
| | | | Epoxide | Diol | Others ^b |
| Acetonitrile | 37.5 | 59.5 | 55.7 | 21.3 | 23.0 |
| Acetone | 20.7 | 62.5 | 8.6 | 80.2 | 11.2 |
| Butanone | 18.5 | 71.6 | 7.8 | 79.8 | 12.4 |
| Methanol | 32.7 | 92.0 | 0.2 | 14.8 | 85.0 |
| Ethanol | 24.5 | 82.8 | 0.4 | 28.0 | 71.6 |
| Tertiary Butanol | 10.9 | 62.8 | 1.6 | 70.4 | 28.0 |

^a Reaction conditions: 30 mmol cyclohexene; 10 mmol H₂O₂; 50 mg catalysts with Si/Ti=36; reaction temperature, 323 K; duration, 2 h.

^b Mainly allylic oxidized products: 2-Cyclohexene-1-ol and 2-Cyclohexene-1-one.

Table S2

Cyclohexene epoxidation over various titanasilicate zeolites ^a

| Different zeolites | Si/Ti | Cyclohexene conversion (%) | Selectivity (%) | | |
|------------------------|-------|----------------------------|-----------------|------|---------------------|
| | | | Epoxide | Diol | Others ^b |
| TS-1 | 83 | 3.3 | 17.9 | 75.7 | 6.4 |
| Ti-MWW | 45 | 8.1 | 35.0 | 58.8 | 6.2 |
| Ti-MOR ^c | 92 | 9.0 | 55.0 | 39.1 | 5.9 |
| Ti-BEA-HT ^d | 60 | 16.5 | 78.4 | 18.6 | 3.0 |
| Ti-BEA-SAC | 36 | 44.8 | 53.8 | 23.7 | 22.5 |

^a Reaction conditions: 10 mmol cyclohexene; 10 mmol H₂O₂; 50 mg catalysts; Solvent, acetonitrile; reaction temperature, 323 K; duration, 2 h.

^b Mainly allylic oxidized products: 2-Cyclohexene-1-ol and 2-Cyclohexene-1-one.

^c It was post-synthesis by treating the dealuminated Al-BEA with TiCl₄ vapor. The reaction conditions are the same as others except for using 0.2 g catalyst.

^d It was prepared by direct hydrothermal synthesis. The reaction conditions are the same as others except for using 0.28 g catalyst.

Table S3

Recyclability of Ti-BEA zeolites prepared by SAC method in cyclohexene epoxidation ^a

| Sample ^b | Si/Ti molar ratio (product) ^d | Cyclohexene conversion (%) | Selectivity (%) | | |
|---------------------|--|----------------------------|-----------------|-------------------|---------------------|
| | | | Epoxide | Diol ^c | Others ^c |
| 1 st | 38 | 67.2 | 50.6 | 22.7 | 26.7 |
| 2 nd | 41 | 61.0 | 46.8 | 25.0 | 28.2 |
| 3 rd | 47 | 44.9 | 42.8 | 25.4 | 31.8 |
| 4 th | 50 | 30.6 | 42.7 | 23.9 | 33.4 |

5 th 50 20.9 38.5 24.8 36.7

^a Reaction conditions: 30 mmol cyclohexene; 10 mmol H₂O₂; 100 mg catalysts with Si/Ti=36; reaction temperature, 323 K; duration, 2 h.

^b After each run, the catalyst was washed with acetonitrile and then distilled water four times. The solid material was dried at 110 °C and then calcined at 550 °C for 6 h before the next run.

^c Mainly allylic oxidized products: 2-Cyclohexene-1-ol and 2-Cyclohexene-1-one.

^d Given by ICP.

Table S4

Catalytic performance of Ti-BEA-SAC in different catalytic reactions.

| Reactions | Si/Ti ^d | Conversion (%) | Selectivity (%) |
|---|--------------------|----------------|-----------------|
| 1-hexene epoxidation ^a | 70 | 10.1 | 98.0 |
| allyl chloride epoxidation ^b | 71 | 20.7 | 98.3 |
| cyclohexanone ammoximation ^c | 73 | 58.0 | 99.0 |

^a Reaction conditions: catalyst, 50 mg; 1-hexene, 10 mmol; H₂O₂ (30 wt.% aqueous solution), 10 mmol; solvent, 10 mL; temp., 333 K; time, 2 h

^b Reaction conditions: catalyst, 50 mg; allyl chloride, 10 mmol; H₂O₂ (30 wt.% aqueous solution), 10 mmol; solvent, 10 mL; temp., 333 K; time, 2 h

^c Reaction conditions: catalyst, 50 mg; cyclohexanone, 10 mmol; NH₃ (25 wt.%), 12 mmol; H₂O₂ (30 wt.% aqueous solution), 12 mmol; solvent, 10 mL; temp., 338 K; time, 2 h.

^d Given by ICP.