

Supporting Information:

Direct Synthesis of Hierarchical Zeolite from a Natural Layered Material

Jie Zhu, Yu Cui, Yao Wang, and Fei Wei*

Beijing Key Laboratory of Green Reaction Engineering and Technology
Department of Chemical Engineering, Tsinghua University
Beijing 100084 (P. R. China)

Experimental Section

1. Preparation

In a typical synthesis of the hierarchical SAPO-34 zeolite, kaolin clay (10.9 g, pretreated by calcining at 1023 K for 2 h, from China Kaolin Clay Company, S-1 type, with size of 1–2 μm) and triethylamine (18.7 g, TEA, 99 wt%, as the micropore template) were mixed with orthophosphoric acid (18.6 g, H_3PO_4 , 85 wt%). Deionized water (50.0 g) was then added. After stirring for 2–4 hours and left for different times (0–24h) at room temperature for aging, the mixture was transferred into a stainless-steel autoclave lined with polytetrafluoroethylene (PTFE). The autoclave was heated at 458 K for 72 h under autogeneous pressure. The products were filtrated, washed, and dried at 383 K. Then the sample was calcined at 873 K for 4.5 h to remove the template. For comparison, the conventional SAPO-34 zeolites were prepared by the same procedure other than using pseudoboehmite (73 wt% Al_2O_3) as aluminum source and silica sol (40 wt% SiO_2) as silicon source.

The hierarchical zeolites were hydrothermally treated at 1073 K for 17 h in flowing 100% steam with a weight hourly space velocity (WHSV) of 1 h^{-1} as the steaming treatment to test zeolites hydrothermal stability.

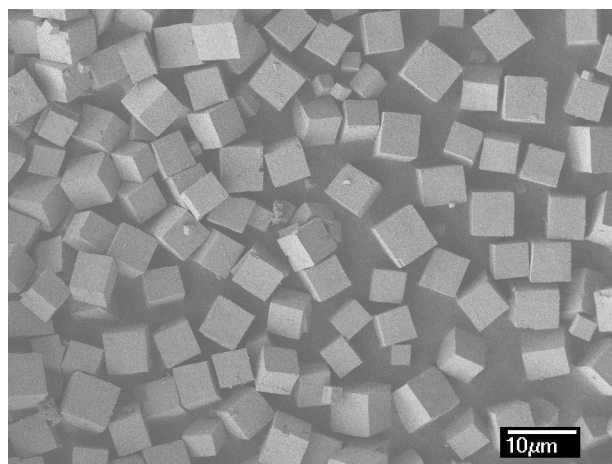
2. Characterization

X-ray diffractions (XRD) were performed on a Rigaku D/Max-rB diffractometer with Cu $K\alpha$ radiation, 40 kV voltage and scan range 5–45°. Samples for XRD were prepared by compressing

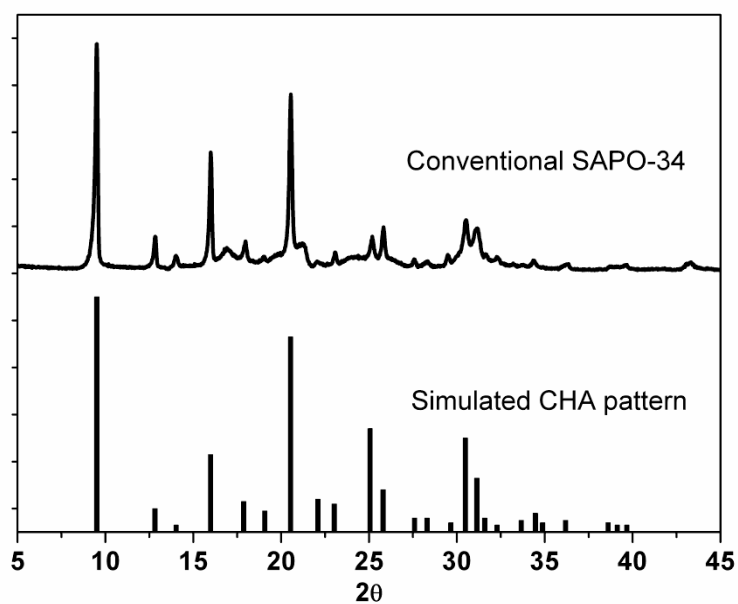
into a disk of 2 cm diameter by 0.25 cm thickness. SEM images were obtained by a high-resolution scanning electron microscope (JEOL, JSM-7401). TEM experiments were performed on a high-resolution transmission electron microscope (JEOL, JEM-2010, excited at 120 kV) equipped with energy dispersive X-ray spectroscopy (EDS, Oxford) and selected area electron diffraction (SAED). The sample pore size distribution was estimated using nitrogen adsorption/desorption isotherms measured on an ASAP-2010 apparatus.

3. *Catalytic Activity Testing*

DME conversions and selectivities were measured in a packed bed reactor (8.0 mm i.d) equipped with a thermocouple held in a concentric thermowell (1.6 mm) aligned along the tube center. Catalyst samples (0.03 g, 150–250 μm aggregates) were activated in flowing nitrogen (30 ml/min) for 2 h at 773 K and cooled to reaction temperature (723 K) before reaction. The reaction pressure was 0.12 MP. The feed pulses of pure DME were injected by a six way valve. The volume of each feed pulse was 0.445 ml. The product gas was introduced to the gas chromatograph and analyzed using an Al_2O_3 column and a flame ionization detector.



(a)



(b)

Fig. S1 SEM image (a) and XRD pattern (b) of the conventional SAPO-34 zeolites. The particle sizes of the conventional and hierarchical SAPO-34 were both 4–8 μ m. Simulated CHA XRD pattern was collected from the reference (M.M.J. Treacy, J.B. Higgins, Collection of Simulated XRD Powder Patterns for Zeolites (fifth), Elsevier, 2007.)

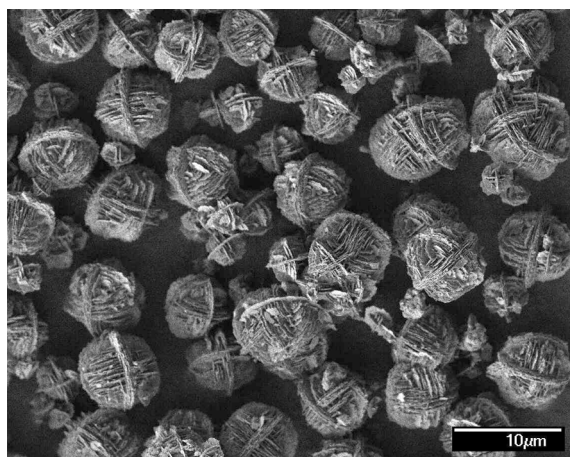


Fig. S2 SEM image of hierarchical SAPO-34 after hydrothermal steaming treatment (at 1073 K, 17 h, 100% steam). The nearly unchanged morphology showed the superior hydrothermal stability of hierarchical SAPO-34.

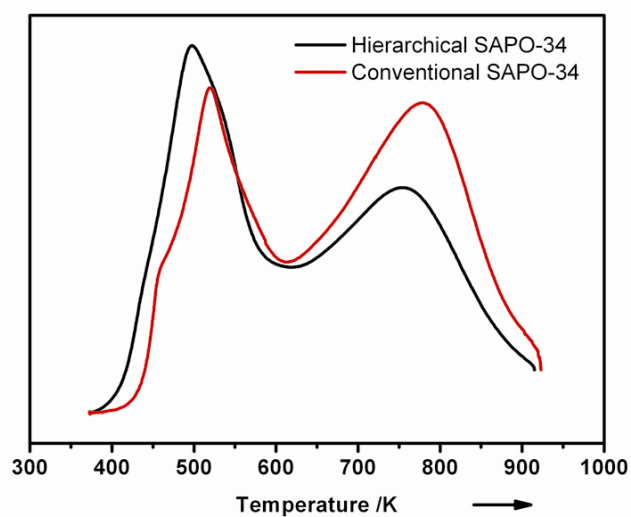


Fig. S3 NH₃ Temperature Programmed Desorption (TPD) spectra of various SAPO-34. The integral areas of the spectra for hierarchical SAPO-34 and conventional SAPO-34 are 3027 and 3259, respectively. This indicated that the hierarchical SAPO-34 had the similar acid strength and acid amount with the conventional SAPO-34.

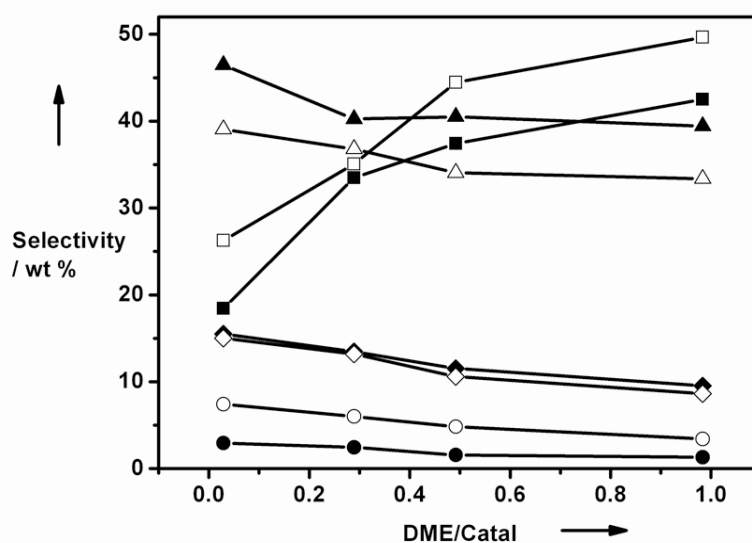


Fig. S4 Olefins and propane selectivities with various zeolites as a function of DME feed (reaction temperature: 723 K; reaction pressure: 0.12 MP, weight hourly space velocity (WHSV): 390 h^{-1}). Ethene selectivity on hierarchical SAPO-34 (■); Ethene selectivity on conventional SAPO-34 (□); propene selectivity on hierarchical SAPO-34 (▲); propene selectivity on conventional SAPO-34 (△); butenes selectivity on hierarchical SAPO-34 (◆); butenes selectivity on conventional SAPO-34 (◇); propane selectivity on hierarchical SAPO-34 (●); propane selectivity on conventional SAPO-34 (○).

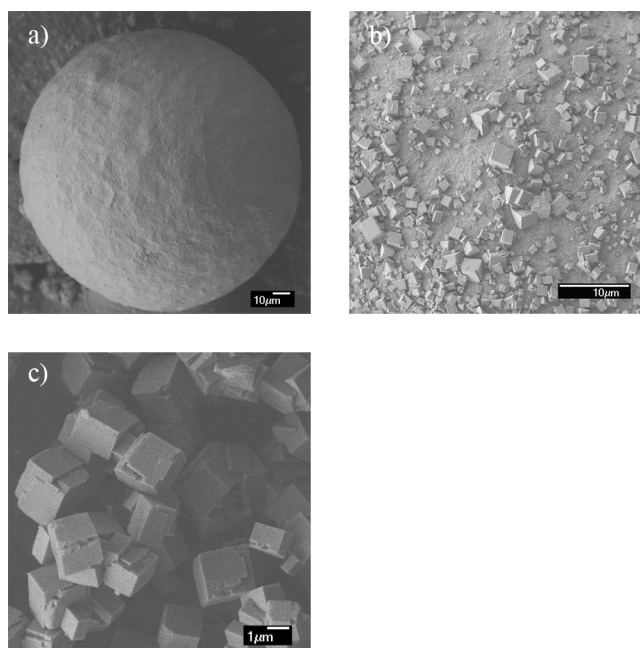


Fig. S5 SEM images of a) Kaolin microsphere fully covered with a silica sol layer, b) synthesized zeolites on the sphere surface, and c) synthesized zeolites in the solution. The synthesized zeolites are both cubic morphology, showing that the Kaolin layered structures play dominant roles in the hierarchical zeolites growth.

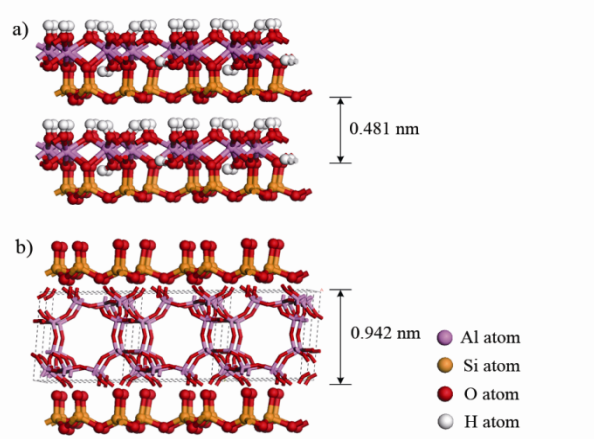
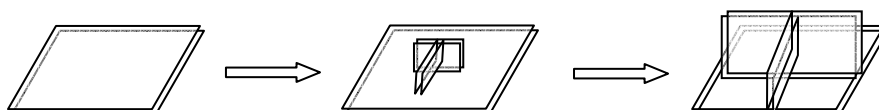


Fig. S6 Schematic representations of a) Kaolin structure and b) zeolite formed in the nano-confined environment. Illustrating the supposed mechanism of zeolite first growth along the $\langle 001 \rangle$ orientation.



Scheme S1. Illustration of the hierarchical zeolite growth mechanism. The zeolite preferentially grow up from one orientation to the three orientations of $\langle 001 \rangle$ crystal orientation group.