Supporting information

for

Preparation of hierarchical SAPO-34 crystals by post-synthesis fluoride medium etching

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Experimental section

Sample preparation

The following chemicals were used in the synthesis of SAPO-34 zeolite: colloidal silica Ludox HS-30 (SiO_2, 30 wt. % suspension in H_2O, Aldrich), tetraethyl orthosilicate (TEOS, 98 wt%, Aldrich), aluminum isopropoxide ($Al(OPri)_3$, 98 wt%, Fluka), phosphoric acid (H_3PO_4, 85 wt%, Aldrich), tetraethylammonium (TEA) hydroxide solution (35 wt%, Aldrich) and distilled water.

Micron-sized SAPO-34 synthesis

The conventional synthesis of micron-sized SAPO-34 zeolite with Ludox HS-30 as silica source was performed from a gel with composition: 1.0 Al_2O_3 : 2.5 P_2O_5 : 0.6 SiO_2 : 2.5 TEA_2O : 92.0 H_2O. The final reaction gel was loaded into a stainless steel autoclave and heated at 170 °C for 15 hours in an oven.

Hierarchical crystals preparation

As-synthesized micron-sized SAPO-34 zeolite was used for the preparation of hierarchical materials. Hierarchical crystals were prepared by fluoride medium treatment using mixed HF-NH_4F aqueous solution. The etching solution was prepared by mixing 18 ml of 0.05 mol/L HF water solution with a mixture of 0.18 g NH_4F and 18 g H_2O. Then 0.3 g of as-synthesized SAPO-34 zeolite was dispersed in the solution and reacted at 25°C for 15 or 30 min under ultrasonic (US) radiation. The solid was separated by vacuum filtration and thoroughly washed with distilled water and dried at 60 °C over night. The treated materials were denoted SAPO-34 US15 and SAPO-34 US30. The organic template was removed by calcination in air atmosphere at 350°C for 3 hours and then 550°C for 8 hours.

Physicochemical characterization

Powder X-ray diffraction (XRD) patterns were obtained with a PANalytical X'Pert Pro diffractometer using Cu Kα radiation (λ = 1.5418 Å, 45 kV, 40 mA). All analyses were performed using ca.30 mg powder. The samples were studied in the 4 - 40° 2θ range with a scanning step of 0.0167 ° s^{-1}. Scanning electron micrographs were taken on a MIRA-LMH (TESCAN) scanning electron microscope (SEM) equipped with a field emission gun. Nitrogen adsorptions were performed with a Micromeritics ASAP 2020 automated gas adsorption analyzer. Prior to analysis, the samples were outgassed at 300°C for 12 h. Specific surface areas were determined from the BET equation. The total volume was calculated from the volume adsorbed at P/P_0= 0.99. The *t*-plot method was used to distinguish the micropores from the mesopores and to calculate the external surface areas. The thermogravimetric analysis (TGA) was carried out in an air atmosphere on a SETSYS instrument (SETARAM) using a heating ramp of 5°C/min. Elemental analysis were measured by inductively coupled plasma–atomic emission spectroscopy (ICP-AES) using an OPTIMA 4300 DV (Perkin–Elmer) instrument. The temperature programmed desorption of ammonia (NH_3-TPD) experiments were performed using a Micromeritics AutoChem II 2920 automated chemisorption analysis unit with a thermal conductivity detector (TCD) under helium flow.

Solid-state magic angle spinning nuclear magnetic resonance spectroscopy (MAS-NMR) was used to characterize the local ^{29}Si and ^{27}Al environments in the zeolite samples. All data were recorded on a Bruker Advance 500 MHZ spectrometer using 4 mm rotors. The ^{29}Si MAS NMR spectra were recorded at 99.325 MHz with a pulse length of 2.2 μs (30 flip angle), a spinning rate of 12 kHz and a repetition time of 20 s. The ^{27}Al MAS NMR spectra were recorded at 130.29 MHz with a p/12 pulse length of 0.77 μs, a spinning rate of 12 or 14 kHz and a recycle delay of 1 s. TMS was used as reference for chemical shifts of ^{29}Si and $Al(NO_3)_3$ (1 M) and H_3PO_4 0.1 M for ^{31}P.

Infrared spectra were recorded with a Nicolet-Magna 550-FT-IR spectrometer at 4 cm^{-1} optical resolution. Calcined samples were pressed into self-supporting discs (diameter: 16 mm, approx. 10 mg cm^{-2}) and pre-treated in the IR cell attached to a vacuum line at 100 °C (1.2 °C /min) for 1.5 h first and then at 450 °C (2 °C /min) for 2 h under 10^{-6} Torr. The adsorption of deuterated acetonitrile, hereinafter referred to as acetonitrile, was performed at room temperature. After establishing a pressure of 10 torr at equilibrium, in order to remove the physisorbed species, the cell was evacuated at room temperature. All spectra were normalized to 20 mg wafers. The amount of acetonitrile (CD_3CN) was determined using the molar absorption coefficients defined by following by FTIR spectroscopy adds of small well-known amounts of D3-acetonitrile. The molar extinction coefficient obtained for Lewis acid sites is 4,5 cm.μmol^{-1} and for Brønsted acid sites is 2,0 cm.μmol^{-1}. The number of Brønsted sites was calculated by the integrated area of the bands observed at 2294 and 2287 cm^{-1}. The number of Lewis sites was calculated by the integrated area of the bands at 2328 and 2318 cm^{-1}.

Catalytic test

The sample was pelletized, rushed and sieved into 400MIC particle size. 50 mg of sample were mixed with 200 mg SiC before introduced into the reactor. Flowing N_2 (20 ml/min) was bubbled in methanol at -3 °C, giving a WHSV = 1.0 h^{-1}. The sample after calcination was first activated with air flow of 40 ml/min for 2 h at 400 °C, and then the temperature was decreased to the reaction condition 350 °C.

Table S1. Ratio between framework cations, specific surface area and pore volume of parent and treated SAPO-34 samples.

Sample	Al:P:Si	$S_{BET}{}^{b}$ m^2g^{-1}	$V_{mic}{}^{c}$ cm^3g^{-1}	$S_{ext}{}^{c}$ m^2g^{-1}	$V_{meso}{}^{d}$ cm^3g^{-1}
Initial SAPO-34	6.7:6.9:1:0	616	0.29	21	0.12
SAPO-34 US15	9.5:9.2:1.0	544	0.24	66	0.22
SAPO-34 US30	11.5:11.2:1.0	488	0.21	72	0.24

^{a}ICP; ^{b}BET surface area; ^{c}t-plot; $^{d}V_{total} - V_{mic}$ (V_{total} : the volume adsorbed at $P/P_0 = 0.99$).

Table S2. Weight losses of parent SAPO-34 and hierarchical materials obtained after 15 and 30 min US treatment in a mixed HF-NH_4F solution.

Sample	25-250 (ºC)	250-500 (ºC)	500-800 (ºC)
Parent SAPO-34	1.7%	12.5%	2.0%
SAPO-34 US15	8.1%	10.8%	2.8%
SAPO-34 US30	11.2%	9.8%	2.9%

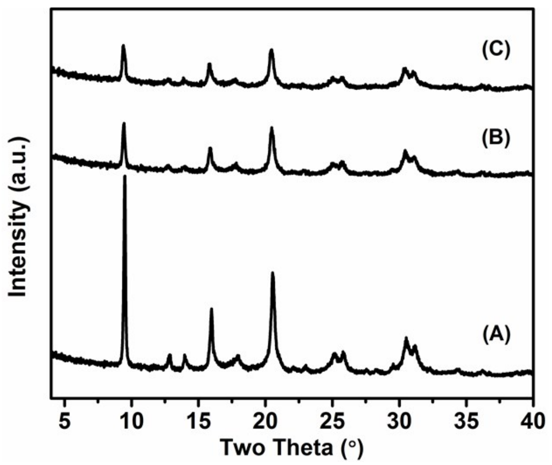

Fig. S1 XRD patterns of the initial SAPO-34 (A) and the samples the hierarchical materials obtained by fluoride treatment under ultrasonic radiation for 15 min (B) and 30 min (C).

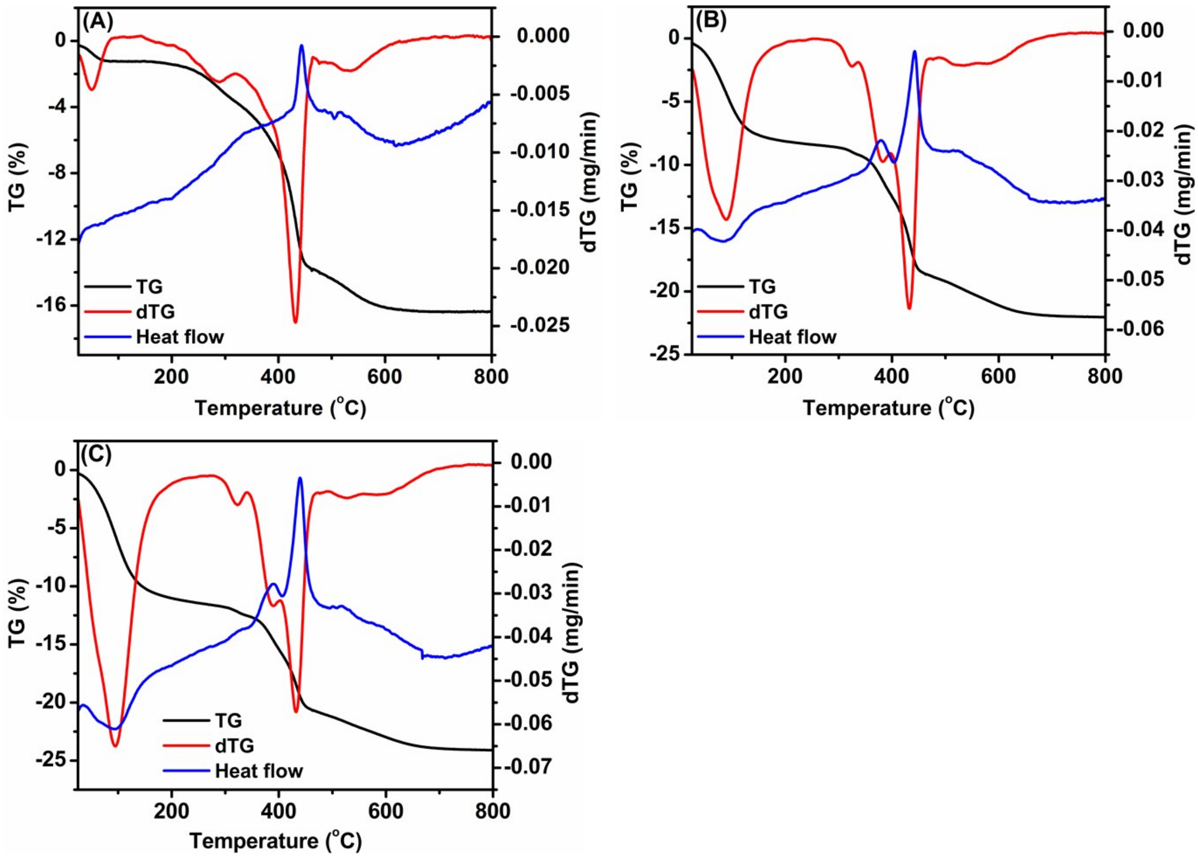

Fig. S2 Thermal analysis of SAPO-34 (A), SAPO-34 US15 (B) and SAPO-34 US30 (C).

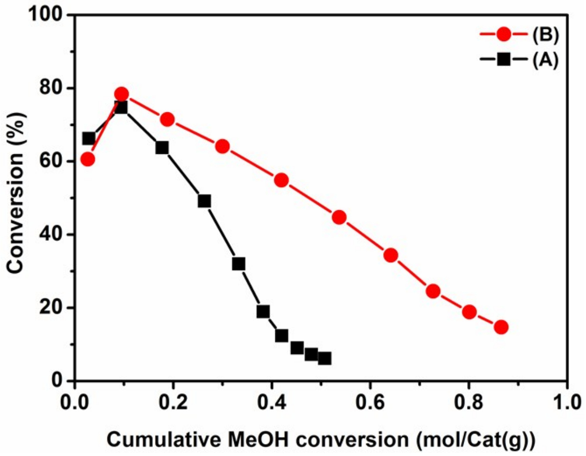

Fig. S3 Methanol conversion variation with cumulative methanol coversion ((mol/Cat (g)) over the conventional SAPO-34 (A) and 30 min treated (SAPO-34 US30) hierarchical material (B). Experimental conditions: WHSV=1 h^{-1}, T=623 K.