Supporting Information

Efficient post-synthesis of hierarchical SAPO-34 zeolites via organic amine etching under hydrothermal conditions and their enhanced MTO performance

Yingying Pan[a], Guangrui Chen[a], Guoju Yang[a,b], Xiaoxin Chen*[a,c] and Jihong Yu*[a,b]

[a]State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, People's Republic of China.

[b]International Center of Future Science, Jilin University, Changchun 130012, People's Republic of China.

[c]Ministry-of-Education Key Laboratory for the synthesis and Application of Organic Functional Molecules, Hubei University, People's Republic of China.

E-mail: chenxiaoxin@jlu.edu.cn, jihong@jlu.edu.cn.

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A. Experimental Section

Chemical and materials:

Phosphoric acid (85 wt%, Beijing Chemical Works), pseudoboehmite (Al_2O_3, 62.5 wt%, Vists Company), triethylamine (TEA, 99%, Tianjin Fuyu Company), fumed silica (Changling Chemical Company), Ultra-pure water (Merck Milli-Q Ultra Pure Water System).

Synthesis of parent SAPO-34 catalysts and hierarchical SAPO-34 catalysts:

The parent SAPO-34 samples (S0) were prepared in a reaction mixture with molar composition of $1.0Al_2O_3$: $1.0P_2O_5$: $0.4SiO_2$: 4.7TEA: $70H_2O$ under hydrothermal conditions for 24 hours at 180 °C. The crystallized SAPO-34 sample was washed with distilled water and dried at 80 °C for 12 h. Then, 0.9 g of parent solid samples were mixed in 5 mL TEA and 5 mL distilled water at 100 °C and 140 °C for 36 h and the products were named of S1-100 (36 h) and S2-140 (36 h), respectively. The solid samples at 180 °C for 24 h, 36 h, 48 h were named of S3-180 (24 h), S3-180 (36 h) and S3-180 (48 h), respectively. All of the samples were calcined at 600°C for 6 h.

Post-synthesis of calcined SAPO-34 catalysts (100-36h-cal, 140-36h-cal, 180-24h-cal, 180-36h-cal, 180-48h-cal):

The crystallized SAPO-34 sample (S0) was calcined at 600°C for 6 h, then washed with distilled water and dried at 80 °C for 12 h. The sample by calcination was named S0-cal. The post-treatment synthetic process was same as that of hierarchical SAPO-34 catalysts. 0.9 g of parent solid samples (S0-cal) were mixed in 5 mL TEA and 5 mL distilled water at 100 °C and 140 °C for 36 h and the products were named of 100-36h-cal and 140-36h-cal, respectively. The solid samples post-treated at 180 °C for 24h, 36h, 48h were named of 180-24h-cal, 180-36h-cal and 180-48h-cal, respectively. All of the samples were calcined at 600 °C for 6 h.

B. Characterizations

The crystallinity and phase purity of the samples were characterized by Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku diffractometer equipped with a graphite monochromator using Cu Kα radiation (= 1.5418 Å) operated at 40 kV and 30 mA in steps of 0.02. Scanning electron microscope (SEM) images were recorded with the electron microscope JSM-7800F (JEOL) to perform the morphology of SAPO-34 and the crystal size. Chemical compositions were analyzed by inductively coupled plasma (ICP) using Perkin-Elmer Optima 3300 DV ICP instrumen. Nitrogen adsorption/desorption measurements were carried out on a Micromeritics 2020 analyzer at 77.35 K after the samples were degassed at 350 °C under vacuum. The Brunauer-Emmett-Teller (BET) surface area was calculated from the linear part of the BET plot in accordance with IUPAC recommendation. A Micromeritics AutoChem II 2920 automated chemisorption analysis unit was used on recording temperature programmed desorption of ammonia (NH_3-TPD) experiments to characterize the acidity of samples. Thermo-gravimetric (TG) analysis was performed on a TA company TGA Q 500 unit in air at a heating rate of 10 °C min^{-1} from room temperature to 800 °C in air. The NMR experiments were performed on a Varian Infinity plus 400WB spectrometer with BBO MAS probe operating at a magnetic field strength of 9.4 T. The resonance frequencies in this field strength were 161.9, 104.2 and 79.5 MHz for ^{31}P, ^{27}Al, and ^{29}Si, respectively.

Chemical shifts were referenced to 1.0 M $Al(NO_3)_3$ for ^{27}Al, 85% H_3PO_4 for ^{31}P, and 2,2-dimethyl-2-ilapentane-5-sulfonate sodium salt (DSS) for ^{29}Si. The spinning rates of the samples at the magic angle were 4, 10, and 6 kHz for ^{29}Si, ^{27}Al, and ^{31}P, respectively.

C. MTO Catalytic Tests and Carbon Deposit Analyses

The MTO reaction was carried out in a quartz tubular fixed bed steel reactor with a length of 30 cm and an inner diameter of 6 mm under atmospheric pressure. 0.30 g (40-60mesh) catalyst of calcined SAPO-34 was packed in the center of quartz wools. The sample was pretreated in a N_2 flow of 30 mL/min at 773 K for 1 h and then the temperature of reactor was adjusted to 673 K. The reactant methanol was fed by passing the carrier gas (N_2, 15 mL/min) through a saturator containing methanol at 313 K, which gave the weight hourly space velocity (WHSV) of 2.0 h^{-1}.The analysis of the reaction products was performed by using an on-line gas chromatograph (Agilent GC 7890N) equipped with flame ionization detector (FID) and Plot-Q capillary column (Agilent J &WGC Columns, HP-PLOT/Q19091P-Q04, 30 m × 320 μm × 20 μm). The conversion and selectivity were calculated on CH_2 basis.

The amount of generated coke in SAPO-34 catalysts after the MTO reactions was determined by thermal analysis (TG) on a TGA Q500 at a heating rate of 10 °C min^{-1} from room temperature to 800 °C under air flow. To analyze the coke species in the deactivated SAPO-34 catalysts, the deactivated catalysts were etched by HF solution for 24 h, and then extracted by $CHCl_3$. Subsequently, the obtained solutions were analyzed by GC-MS. (Thermo Fisher Trace ISQ, equipped with TG-5MS column, 60 m × 320 μm × 25 μm).

D. Supplementary Tables and Figures

Table S1 Post-treated conditions of the hierarchical samples.

Sample	Post-treatment temperature (°C)	Post-treatment time (h)
S0	—	—
S1-100 (36h)	100	36
S2-140 (36h)	140	36
S3-180 (24h)	180	24
S3-180 (36h)		36
S3-180 (48h)		48

Table S2 The yields of SAPO-34 catalysts (180-24h-cal, 180-36h-cal, 180-48h-cal).

Sample	Yield*(%)
S0-cal	100.0
180-24h-cal	82.8
180-36h-cal	81.4
180-48h-cal	80.6

*Yield = M2/M1, wherein M1 is the mass of the initial sample, M2 is the mass of the samples after post-treatment.

Table S3 MTO catalytic results of the parent SAPO-34 sample (S0) and hierarchical SAPO-34 catalysts (S1-100 (36h), S2-140 (36h), S3-180 (24h), S3-180 (36h), S3-180 (48h)).

Sample	TOS*(min)	Selectivity (%)							
		CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4	C_5^+	$C_2^=+C_3^=$
S0	46	0.9	29.8	1.1	41.5	7.3	15.6	3.9	71.3
S1-100 (36h)	66	0.8	31.4	1.0	41.9	6.2	15.0	3.7	73.3
S2-140 (36h)	66	0.8	31.3	1.0	42.0	6.0	15.1	3.8	73.3
S3-180 (24h)	106	0.8	33.3	0.8	43.6	4.39	13.9	3.3	76.9
S3-180 (36h)	186	0.9	35.3	0.8	42.5	4.3	13.2	3.0	77.8
S3-180 (48h)	106	0.8	33.6	0.8	43.6	4.0	14.0	3.2	77.2

Experimental conditions: WHSV=$2h^{-1}$, T=673K, catalyst weight=300 mg.

*Lifetime: the reaction duration with > 99.9% conversation of methanol.

Table S4 MTO catalytic results of the parent SAPO-34 sample (S0-cal) and SAPO-34 catalysts (180-24h-cal, 180-36h-cal, 180-48h-cal).

Sample	TOS*(min)	Selectivity (%)							
		CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4	C_5^+	$C_2^=+C_3^=$
S0-cal	46	0.9	29.8	1.1	41.5	7.3	15.6	3.9	71.3
180-24h-cal	66	0.8	34.2	0.5	42.1	3.0	15.3	3.2	76.3
180-36h-cal	126	0.8	35.9	0.5	42.0	2.4	14.3	3.1	77.9
180-48h-cal	146	0.9	36.4	0.5	42.0	2.7	14.7	3.2	78.4

Experimental conditions: WHSV=2h^{-1}, T=673K, catalyst weight=300 mg.

*Lifetime: the reaction duration with > 99.9% conversation of methanol.

Table S5 The rates of coke formation in methanol conversion over parent SAPO-34 sample (S0) and hierarchical SAPO-34 catalysts (S3-180 (36h) and S3-180 (48h)).

Catalysts	S0	S3-180 (36h)	S3-180 (48h)
Coke (%,g/g Cat.)[a]	19.98	21.69	21.01
TOS (min)[b]	46	186	106
R_{coke} (mg/min)[c]	1.303	0.350	0.595
P_{coke} (g/gMeOH)[d]	0.130	0.035	0.060

a. Coke weight percent with > 99.9% methanol conversion;

b. The reaction duration with > 99.9% methanol conversion;

c. R_{coke} (mg/min) = coke amount (mg)/reaction time (min);

d. P_{coke} (g/gMeOH) = coke amount (g)/methanol feedstock (g).

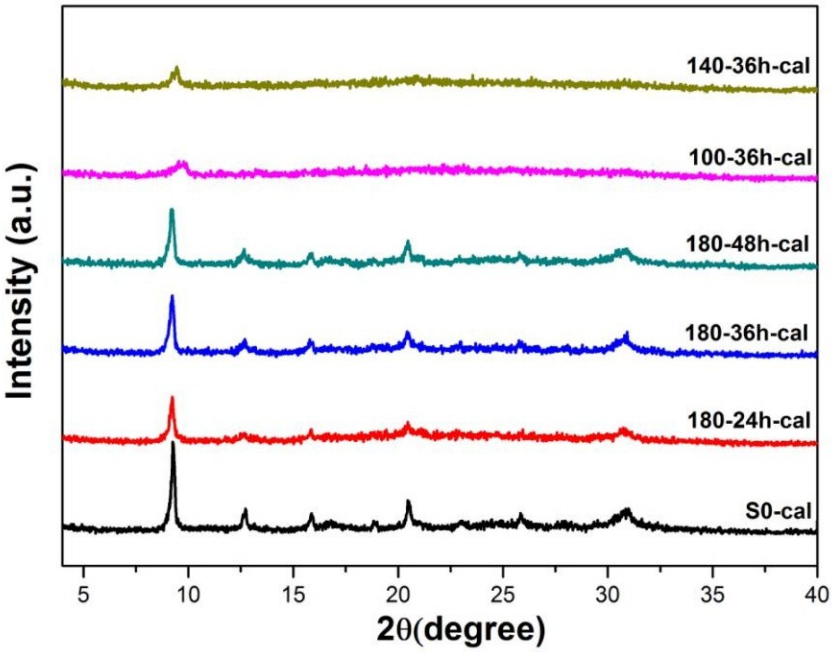

Figure S1 XRD patterns of the parent SAPO-34 sample (S0-cal) and the post-treated SAPO-34 samples (180-24h-cal, 180-36h-cal, 180-48h-cal, 100-36h-cal, 140-36h-cal).

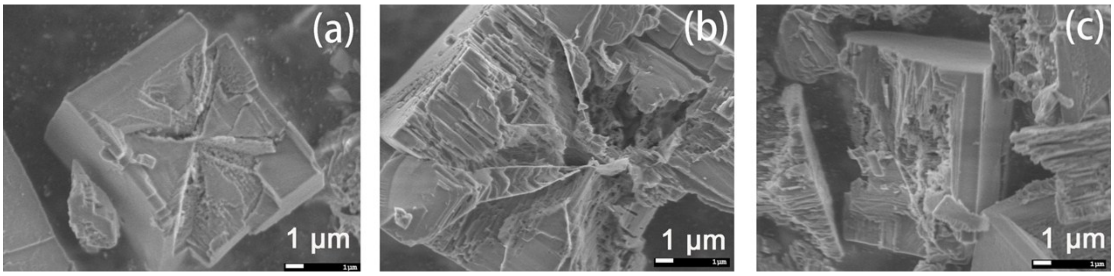

Figure S2 SEM images of the hierarchical samples (S3-180 (24h) (a), S3-180 (36h) (b), S3-180 (48h) (c)).

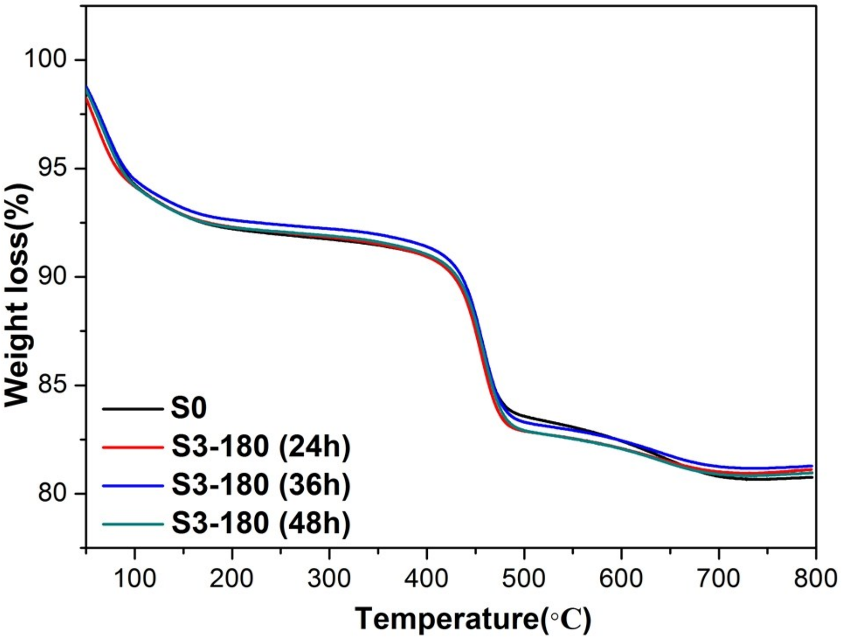

Figure S3 TG curves of the parent sample SAPO-34(S0) and post-treated hierarchical SAPO-34 (S3-180 (24h), S3-180 (36h), S3-180 (48h)) catalysts.

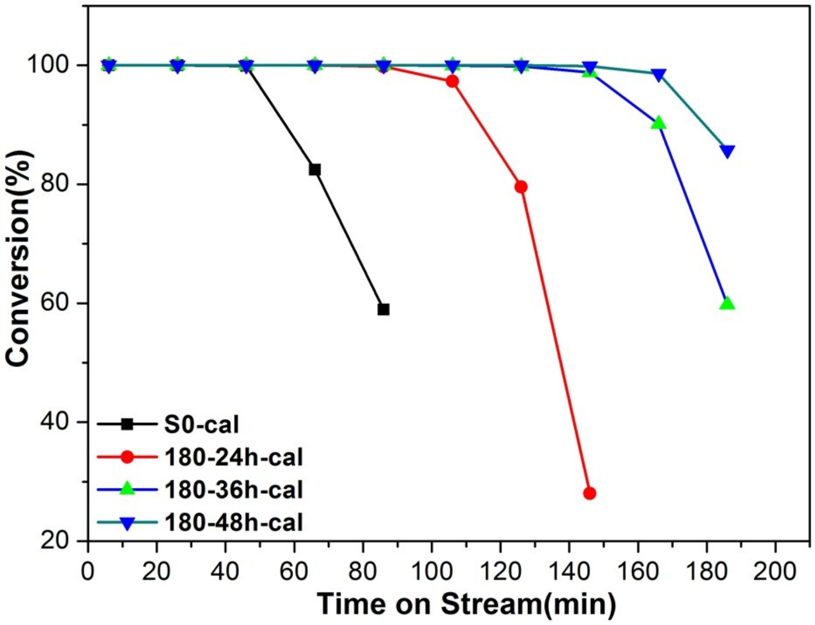

Figure S4 Lifetime of the parent SAPO-34 sample (S0) calcined at 600 °C and the post-treated SAPO-34 samples (180-24h-cal, 180-36h-cal, 180-48h-cal) after calcination at 600 °C.

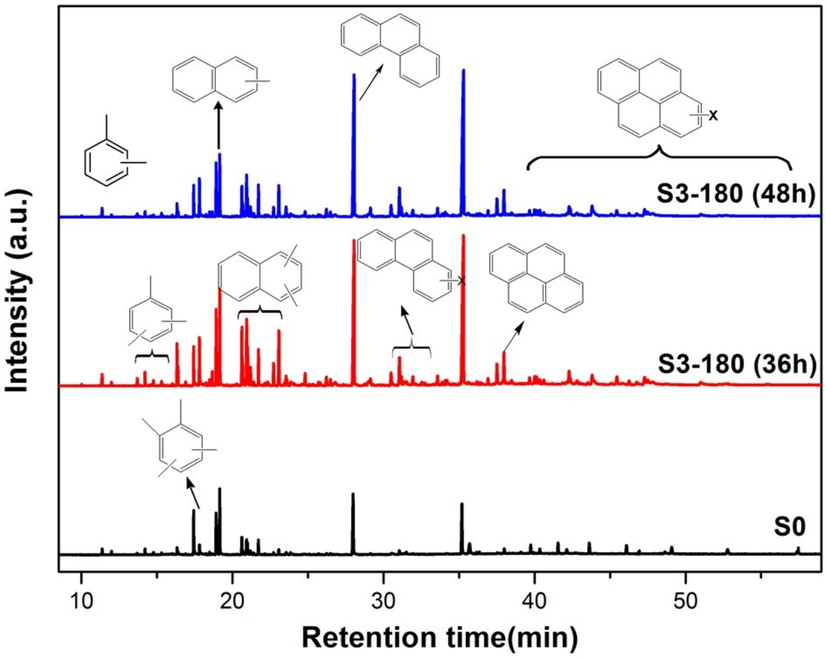

Figure S5 GC-MS of occluded organic species retained in the SAPO-34 catalysts after methanol conversion at 673K. The structures annotated onto the chromatograms are peak identifications in comparison with the mass spectra of those in the NIST database.