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Electronic Supplementary Information

Coke suppression in MTO over hierarchical SAPO-34 zeolites

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Experimental details

Preparation of parent and hierarchical SAPO-34

The parent SAPO-34 crystals were prepared by a hydrothermal synthesis method. The synthesis gel recipe in molar composition is 1 Al_2O_3:0.44 SiO_2: 1.1 P_2O_5:2.25 TEA: 35 H_2O. Before hydrothermal synthesis, synthesis gel and SAPO-34 crystal seeds with a mass ratio of 400:1 were mixed in a closed autoclave. Then the mixture was heated from room temperature to 165 ^oC in 7 h and kept for 33 h before cooling down. The solid product was filtered, washed and dried, followed by calcination at 600 ^oC for 5 h to remove template.

The hierarchical SAPO-34 was prepared by TEAOH etching treatment at 90 ^oC. In a typical post-treatment, 300 ml TEAOH aqueous solution (0.10 mol/l) was added into 3-neck flask and heated to 90 ^oC. 15 g parent SAPO-34 was mixed with TEAOH solution at 90 ^oC for 6 h with reflux. The treated SAPO-34 was then separated by filtration and carefully washing with deionized water for 5 times. Then the productes were dried at 110 ^oC before use. The etching conditions including TEAOH concentration (0.05-0.20 mol/l), treatment time (3-9 h) and the weight ratio of TEAOH solution to SAPO-34 (20-60) were investigated.

Characterizations

The morphology and elemental analysis of SAPO-34 was measured by a scanning electron microscope (SEM, Zeiss SUPRA 55 SAPPHIRE) equipped with an energy-dispersion X-ray spectrometer (EDS, Oxford X-max) at acceleration voltages of 2 kV and 20 kV, respectively.

High resolution picture and selected area electron diffraction patterns of SAPO-34 were obtained by transmission electron microscope (JEM-2100F, JEOL Ltd.) at an acceleration voltage of 200 kV.

Crystal structure of SAPO-34 was measured by X-ray diffractometer (XRD, Rigku, ultima IV) using a Cu Kα (0.154 nm) radiation under the conditions of 40 mA and 40

kV. The textural properties such as surface area (BET, DFT), micropore area (t-plot method), pore volume (BJH, DFT, and HK) and pore size distribution (BJH) of the samples were derived from N_2 adsorption–desorption measurements carried out at □-196 ^{o}C using an automatic micropore physisorption analyzer (Tristar 3020, USA) after the samples were degassed at 300 ^{o}C for at least 10 h under 0.133 Pascal pressure prior to each run. The macropore size was measured by mercury intrusion porosimetry (MIP, Micromeritics Autopore V 9620).

The acidity of the samples was determined using the stepwise temperature-programmed desorption of ammonia automated chemisorption analysis unit (NH_3-TPD, Tianjin Xianquan TP-5080) with a thermal conductivity detector (TCD) under nitrogen flow.

Fourier-transform infrared spectroscopy (FT-IR, Thermo Scientific, Nicolet 6700) was applied to detect the functional groups of SAPO-34.

Solid-state NMR experiments were performed with magic angle spinning (MAS) on a Bruker AVANCE 400 spectrometer operating at frequencies of 79.5, 104.22 and 161.9MHz for ^{29}Si, ^{27}Al and ^{31}P, respectively. Chemical shifts were referenced to tetramethylsilane (TMS) for ^{29}Si, 1 mol/L of $Al(NO_3)_3$ for ^{27}Al, and 85% H_3PO_4 for ^{31}P. The sample was spun at 5 kHz for ^{29}Si, ^{27}Al, and ^{31}P.

The near-surface chemical information of materials were analyzed by X-ray photoelectron spectroscopy (XPS, K-Alpha, Al Kα radiation, 1486.6 eV, 12 kV, 3 mA). XPS peak positions were calibrated with the help of the C 1s peak at 285.0 eV.

The composition of samples was analyzed by X-ray fluorescence (XRF, Bruker S4 PIONEER). The tableting was prepared by mixing boric acid and SAPO-34 with a weight ratio of 2:1.

The composition of samples was measured with Inductively Coupled Plasma (ICP, PerkinElmer Optima 8000). SAPO-34 zeolite solid was treated with 2 mol/l NaOH at 120 oC for 4 h to obtain liquid sample. Before ICP testing, the P, Si and Al in the liquid sample were diluted to ppm level.

Thermal degradation measurements were performed from room temperature to 1000 ^{o}C with a heating rate of 10 ^{o}C/min in air using a thermogravimetric analyzer (TG, NETZSCH, STA 449F3)..

Methanol to olefin reaction

The catalytic performance of SAPO-34 samples for MTO reaction were tested in a tubular fixed bed steel reactor with dimensions of 55 cm x I.D. 12 mm under atmospheric pressure. 3 g catalyst (20–40 mesh) was packed in the center of reactor. The mixture of methanol and water (mass ratio 1:1) was fed into the reactor by a HPLC pump. The feedstock was firstly vaporized at 150 ^{o}C before reaching reactor. The reaction temperature is 400 ^{o}C and weight hourly space velocity (WHSV) of methanol is 0.73 h^{-1}. The liquid products were collected by a cooling trap. The gaseous products were connected with an on-line gas chromatograph (GC 2014C, Shimadzu) equipped with a flame ionization detector (FID) and a HP-PLOT/Q capillary column (30m x 0.35 mm). The liquid products were analyzed by an off-line GC (GC-950, Haixin) equipped with a thermal conductivity detector (TCD) and packed column (PORAPAK T, 3 m x 3mm). The conversion and selectivity were calculated on CH_2 species. The product selectivity was expressed as mass percentages of each product among all the detected products except dimethyl ether (DME). The catalyst was reactivated in air at 600 ^{o}C for 12 h.

Figures

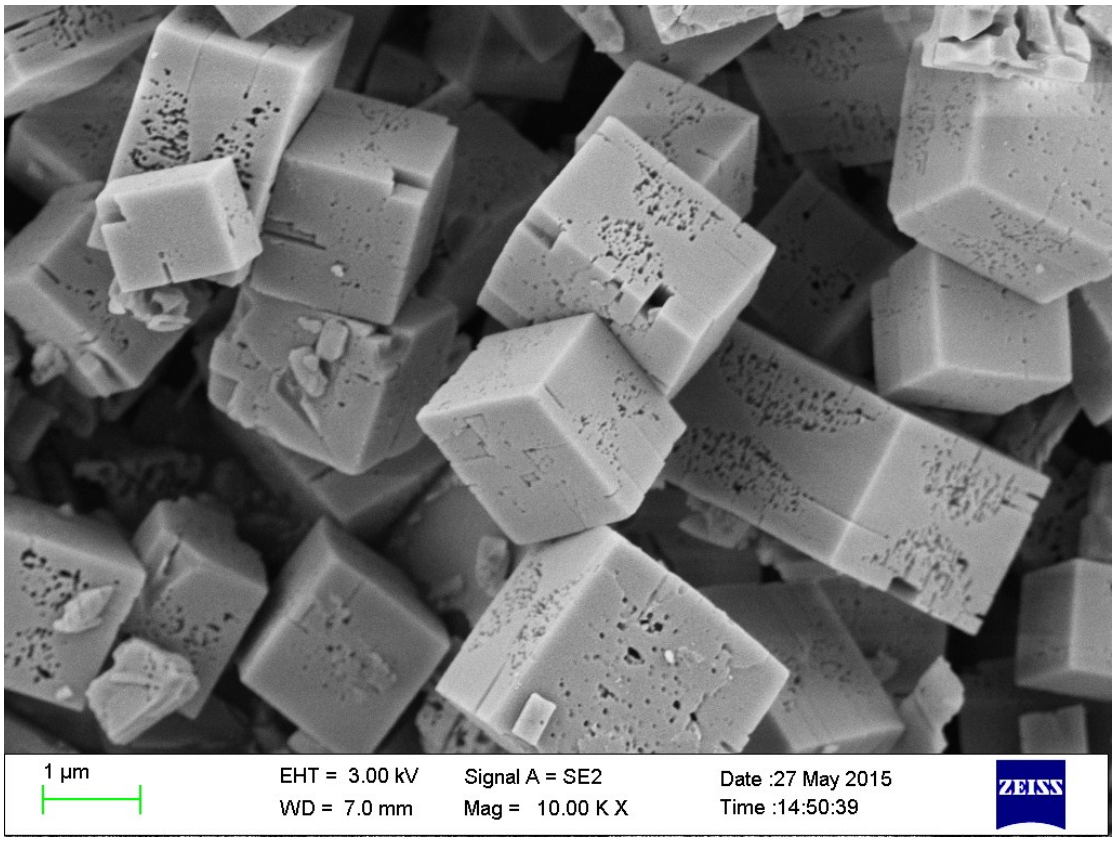

Fig. S1 SEM view of the treated SAPO-34.

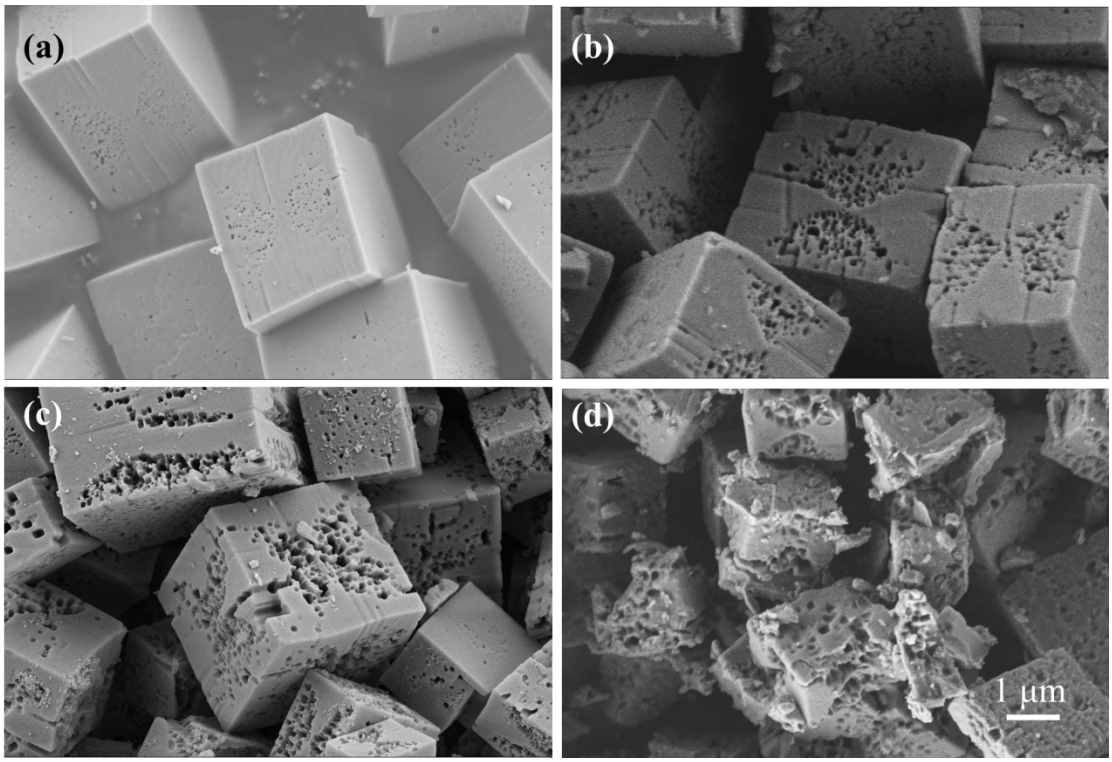

Fig. S2 SEM images of SAPO-34 treated in TEAOH with different concentration: (a) 0.05, (b) 0.10, (c) 0.15 and (d) 0.20 mol/l. (90°C, 6h, 1:20; same scale bar for all images)

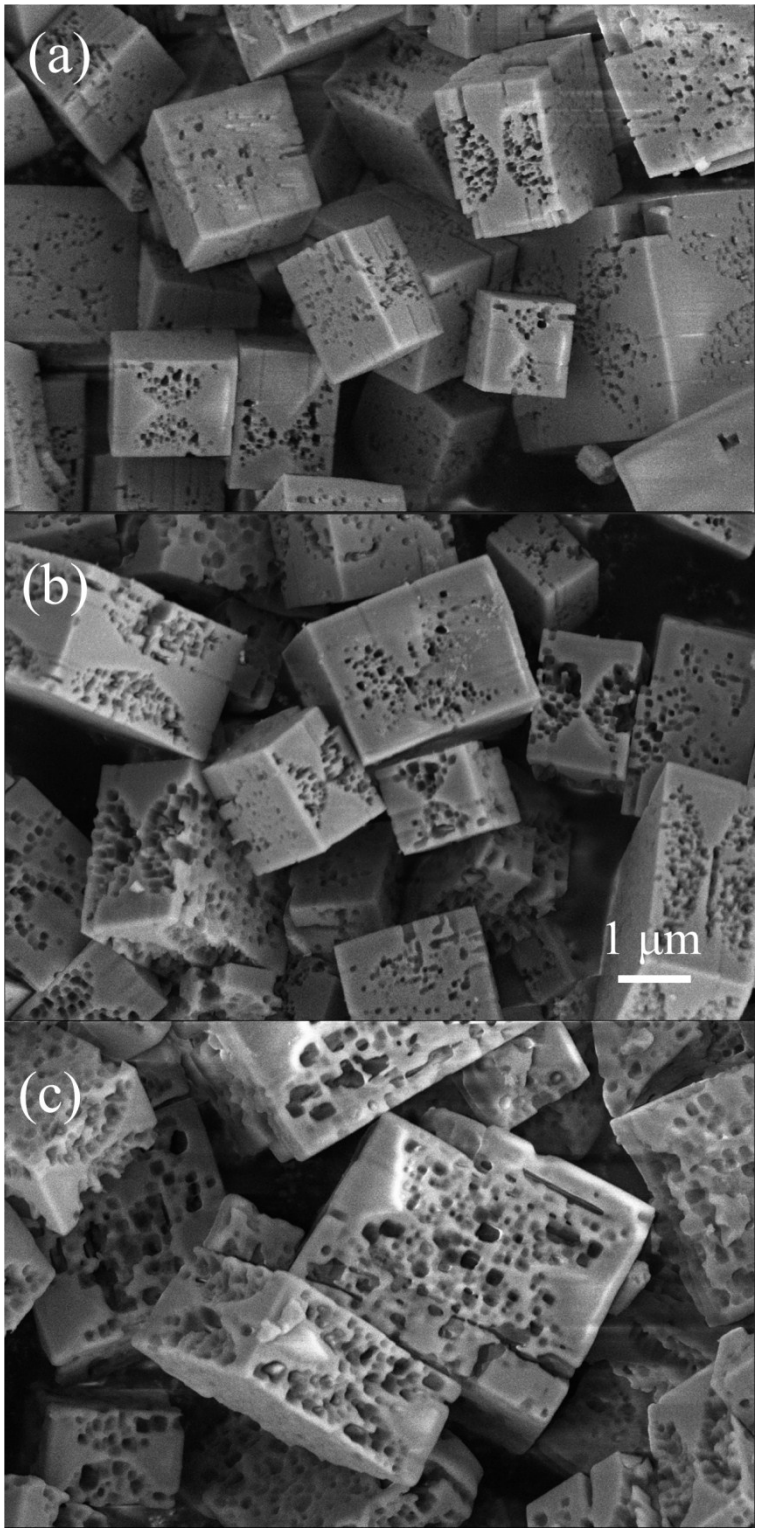

Fig. S3 SEM images of SAPO-34 treated in TEAOH with different time: (a) 3, (b) 6 and (c) 9 h. (90 oC, 0.15 mol/L, 1:20; same scale bar for all images)

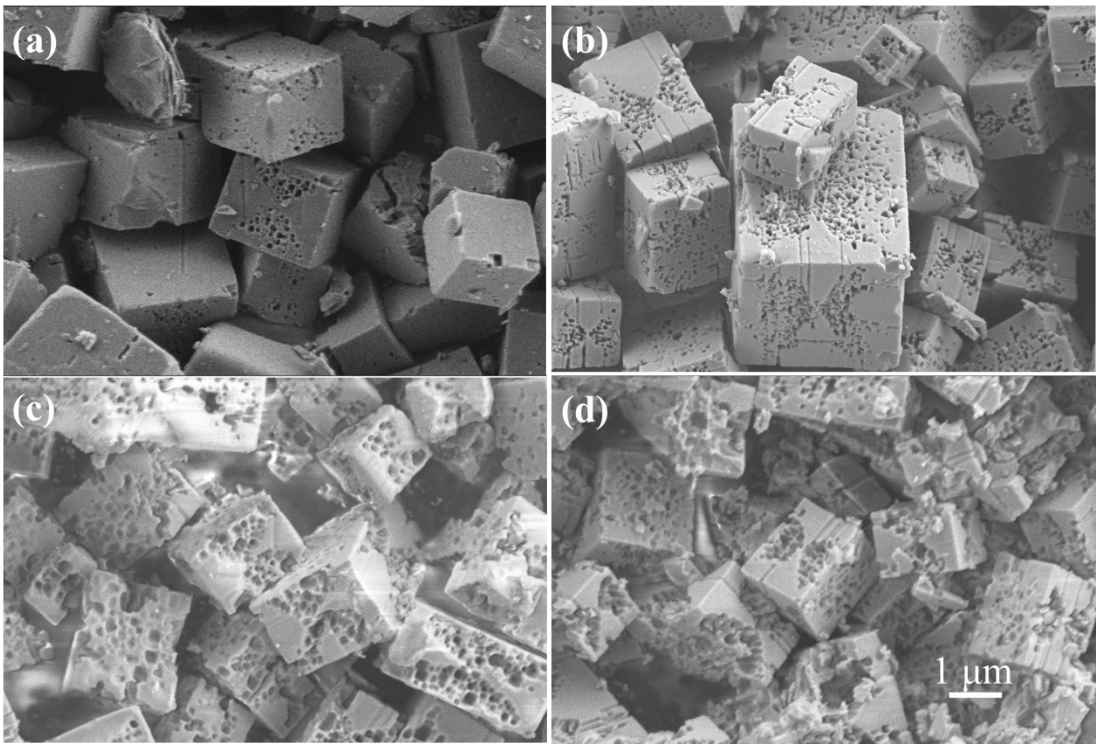

Fig. S4 SEM images of SAPO-34 treated in TEAOH with solid/liquid ratio: (a) 10, (b) 20, (c) 40 and (d) 60. (90°C, 0.15 mol/L, 6h; same scale bar for all images)

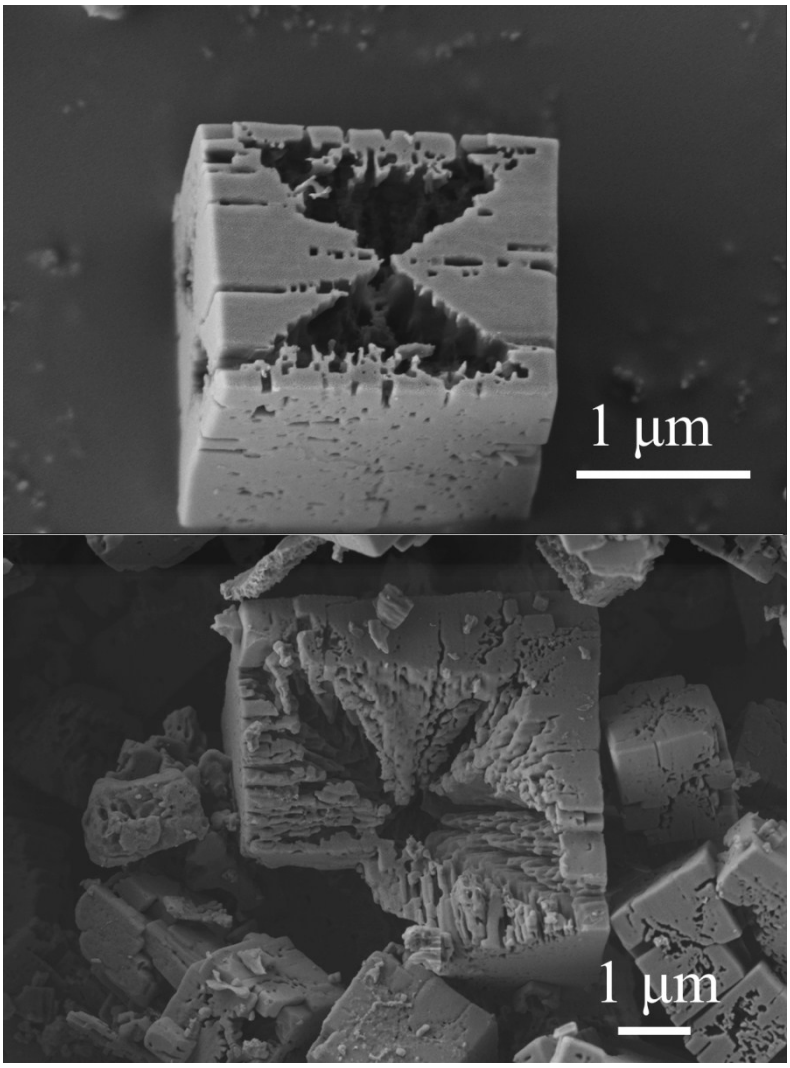

Fig. S5 SEM images of SAPO-34 etched in harsh conditions.

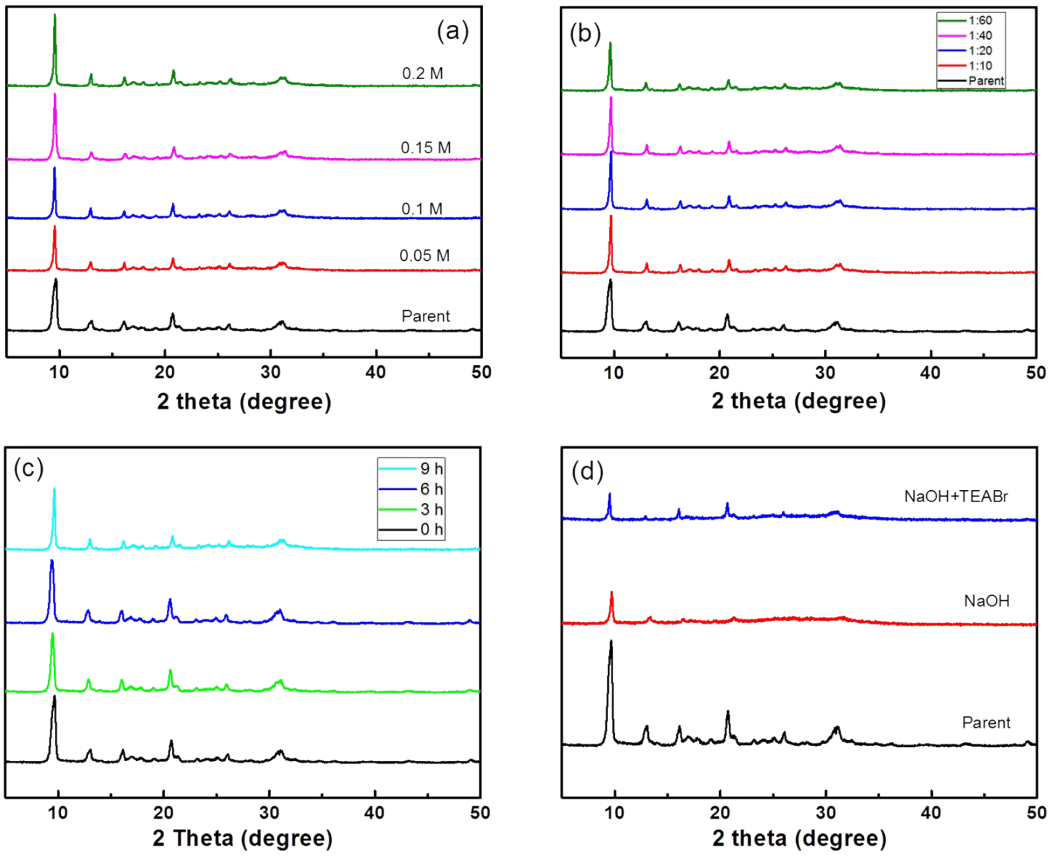

Fig. S6 XRD patterns of SAPO-34 treated with different conditions: (a) TEAOH concentration 0.05-0.20 mol/L; (b) the volume ratio of TEAOH solution to parent SAPO-34 from 10 to 60; (c) Treated time 0-9 h; (d) different alkalis.

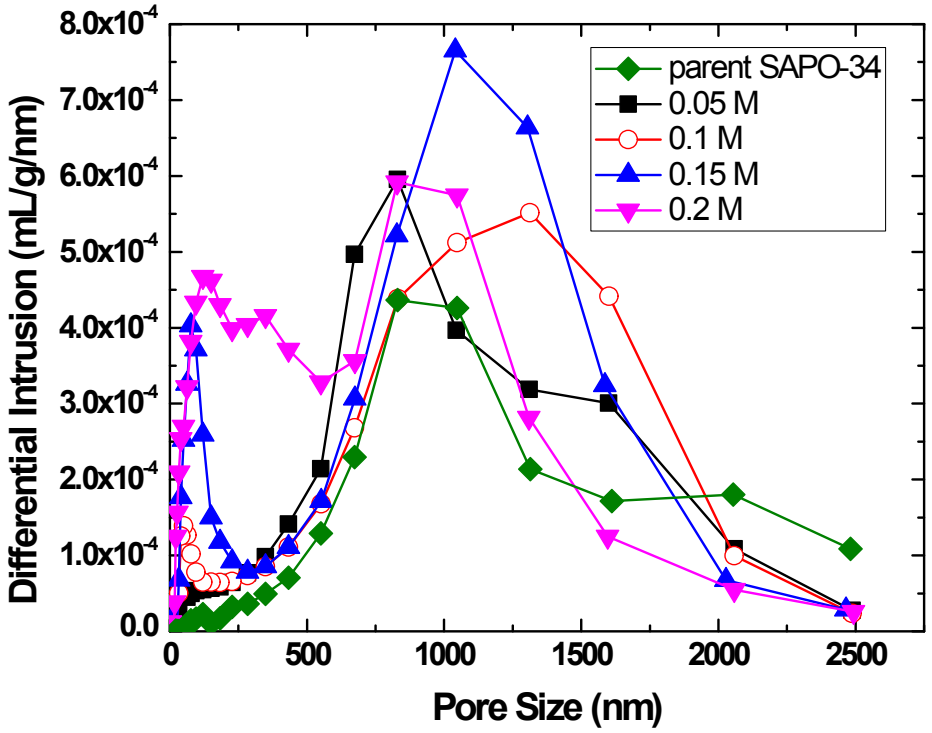

Fig. S7 Mercury intrusion porosimetry (MIP) poresize distribution for SAPO-34 samples with different TEAOH concentration.

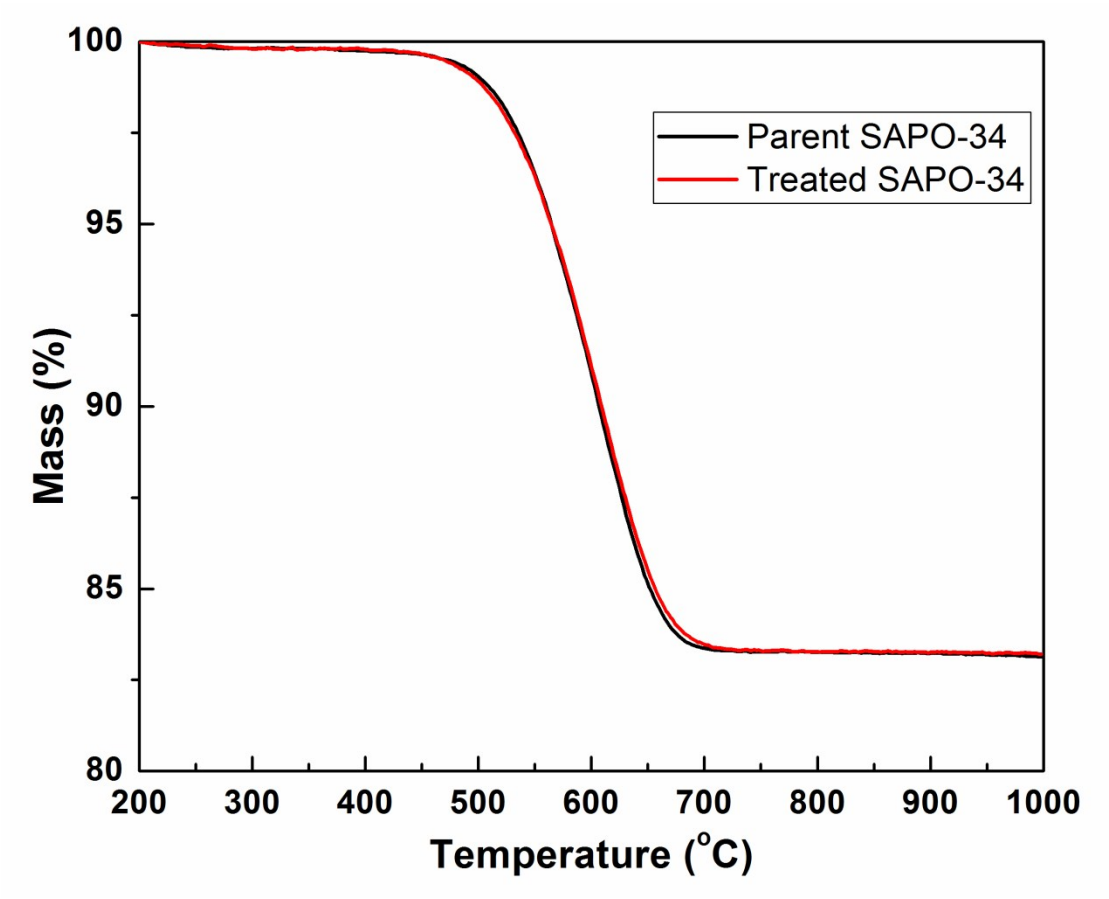

Fig. S8 Thermogravimetric analysis (TGA) results of deactivated parent and hierarchical SAPO-34 after MTO reaction.

Table S1 Composition of parent and treated SAPO-34 measured by XRF, XPS and ICP.

	XRF (%)		XPS (%)		ICP (%)
	Parent SAPO-34	Hierarchical SAPO-34	Parent SAPO-34	Hierarchical SAPO-34	TEAOH solution after etching
Al	46.2	46	39.7	47.4	46.1
Si	11.9	10.7	16.4	12.7	9.6
P	41.9	43.3	43.9	39.9	44.3

Table S2 The catalytic performance of SAPO-34 with /without hierarchical structure

Structure	Lifetime (min)	MeOH Conversion (%)	$C_2^=$ (%)	$C_3^=$ (%)	$C_2^=$+ $C_3^=$ (%)	$C_4^=$ (%)	C_2=+ C_3=+ C_4= (%)
without hierarchical structure	320	100	40.1	38.4	78.5	13.3	91.8
with hierarchical structure	640	100	39.0	40.3	79.3	14.8	94.1

Table S3 Comparison of the MTO performance with literature results

No	Synthesis method	Preparation conditions	Single-run life time (min)	Ref.
1	post-treatment	0.2 M HCl, 50 °C, 3 h	ca. 100	[1]
2	post-treatment	0.2 M oxalic acid, R.T., 6 h	ca. 130	[2]
3	multi-template	TEAOH/TPOAC, microwave heating	280	[3]
4	multi-template	TEAOH/TPOAC/C22-4-4	poor activity	[4]
5	multi-template	TPOAC as mesopore template	380	[5]
6	multi-template	TPOAC as mesopore template	500	[6]
7	growth-etching	in-situ HF etching	600	[7]
8	post-treatment	0.1 M TEAOH, 90 °C, 6h	640	This work

Reference

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