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Cost-Effective Synthesis of Hierarchical SAPO-34 Zeolites with Abundant Intracrystalline Mesopores and Excellent MTO Performance

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A. Materials and methods

The reagents used in this work include aluminum iso-propoxide ($Al(OPr^i)_3$ (99.5 wt%, Beijing Reagents Company), phosphoric acid (H_3PO_4, 85 wt%, Beijing Chemical Works), morpholine (MOR, C_4H_9NO, >98.5%, Tianjin Guangfu fine chemical research institute), tetraethylorthosilicate (TEOS) (Beijing Chemical Works), PDADMAC (poly-diallyldimethylammonium chloride, $(C_8H_{16}NCl)_n$ Aladdin, MW ≤10w, 20 wt% in water)

Synthesis of hierarchical SAPO-34 catalysts (S_{H1}, S_{H2} and S_{H3}): The hierarchical SAPO-34 catalysts (S_{H1}, S_{H2} and S_{H3}) were synthesized under hydrothermal conditions from the starting gel with the optimized molar composition of $1.0Al_2O_3$: $1.0P_2O_5$: 3.0MOR: $0.6SiO_2$: $80H_2O$: xPDADMAC ($x = 1.0\times10^{-4}$, 1.5×10^{-4} and 2.0×10^{-4}) at 180 °C by using the morpholine (MOR) as the microporous template and the PDADMAC as mesoporous template. Typically, a certain amount of PDADMAC was firstly mixed with MOR solution and deionized water at room temperature. Then the finely ground $Al(OPr^i)_3$ (100 mesh) was added into the mixture under vigorous stirring for 2 h. Subsequently, the phosphoric acid solution was added dropwise to the resultant solution, followed by a continuous stirring for 2 h. Finally, TEOS was added slowly. The reaction mixture was further stirred for 1 h and then was transferred into a 100mL Teflon-lined stainless steel autoclave. The crystallization was conducted in a conventional oven at 180 ^oC for 3 days under the static condition. The as-synthesized solid products were centrifuged, washed with water and ethanol for several times, and then dried at 80 °C in the oven overnight, followed by calcination at 550 °C for 8 h.

Conventional microporous SAPO-34 catalysts (S_M and S_{M1}): The conventional microporous SAPO-34 catalyst (S_M) was synthesized from the starting gel with the molar composition of $1.0Al_2O_3$: $1.0P_2O_5$: 3.0MOR: $0.6SiO_2$: $80H_2O$ under hydrothermal condition at 180 °C for 3 days. The microporous SAPO-34 catalyst (S_{M1}) was synthesized from the starting gel with lower silicon content and the molar composition is $1.0Al_2O_3$: $1.0P_2O_5$: 3.0MOR: $0.4SiO_2$: $80H_2O$. The synthetic process was similar with that of hierarchical SAPO-34 catalysts except for without adding the surfactants.

B. Characterizations

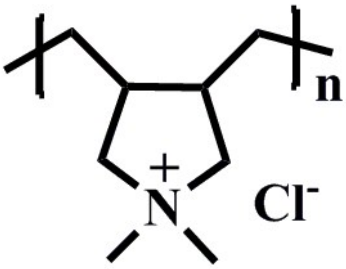
The crystallinity and phase purity of the samples were characterized by power X-ray diffraction (XRD) on a Rigaku D-Max 2550 diffractometer using Cu Kα radiation (λ = 1.5418 Å). The crystal size and morphology were recorded with a scanning electron microscopy (SEM) using a JSM-6510F (JEOL) electron microscope. Transmission electron microscopy (TEM) images were measured by a Tecnai F20 electron microscope. The selected area electron diffraction patterns were measured on a JEM-2100F electron microscope. Chemical compositions were analyzed by an X-ray fluorescence (XRF) spectrometer (PANalytical, AXIOS). CHN elemental analyses were analyzed by a CHN elemental analyzer (vario MICRO). Thermogravimetric (TG) analysis was performed on a TA company TGA Q500 unit in air at a heating rate of 10 K min^{-1} from room temperature to 800 °C in air. 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 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. 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 frequency in this field strength was 79.5 MHz for ^{29}Si. Chemical shifts were referenced to 2, 2-dimethyl-2-ilapentane-5-sulfonate sodium salt (DSS) for ^{29}Si. Liquid ^{13}C NMR measurements were carried out on a nuclear magnetic resonance spectrometer (Avance III).

C. Catalytic tests

The MTO reaction was carried out using a quartz reactor fixed-bed reactor at atmospheric pressure. 0.3 g calcined SAPO-34 crystals was loaded into quartz reactor (6 mm inner diameter) after being ground into powder (40~60 mesh). The catalyst was activated at 773 K in a nitrogen flow of 30 mL/min for 1 h before starting each reaction run, and then the temperature was adjusted to reaction temperature of 673 K. Methanol was fed by passing the carrier gas (15 mL/min) through a saturator containing methanol at 40 °C, which gave a weight hourly space velocity (WHSV) of 2.0 h^{-1}. In addition, the methanol was fed by passing the carrier gas (20 mL/min) through a saturator containing methanol at 60 °C, which gave a WHSV of 23.0 h^{-1}. The reaction products were analyzed using an online gas chromatograph (Agilent GC 7890N), equipped with a flame ionization detector (FID) and Plot-Q column (Agilent J&W GC Columns, HP-PLOT/Q 19091-Q04, 30 m×320 μm×10 μm). The conversion and selectivity were calculated on CH_2 basis and dimethyl ether (DME) was considered as reactant in the calculation.

The amount of generated coke in SAPO-34 catalysts after the MTO reactions was determined by thermal analysis (TG) on a Perkin-Elmer TGA7 at a heating rate of 10 K 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 until the zeolites dissolved completely, and then extracted by CH_2Cl_2. 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 figures and tables



Scheme S1. Chemical structure formula of poly-diallyldimethylammonium chloride (PDADMAC).

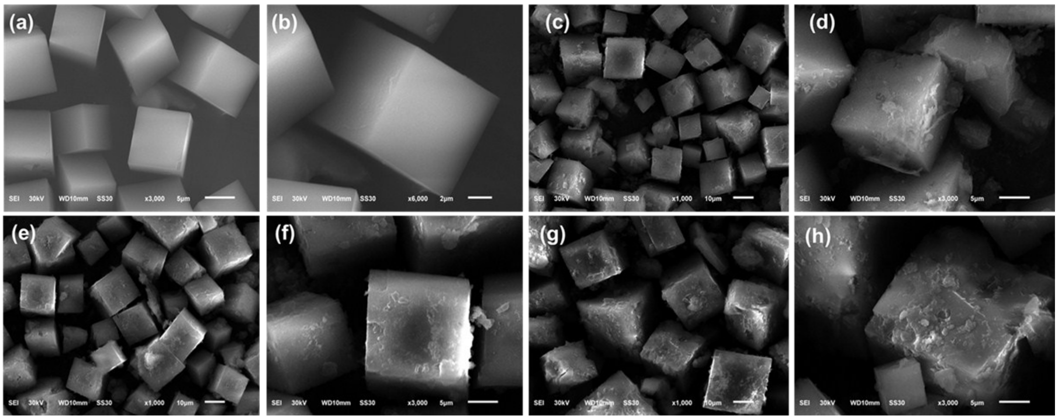


Figure S1. SEM images of conventional microporous SAPO-34 sample (a, b) and hierarchical SAPO-34 samples S_{H1} (c, d), S_{H2} (e, f) and S_{H3} (g, h).

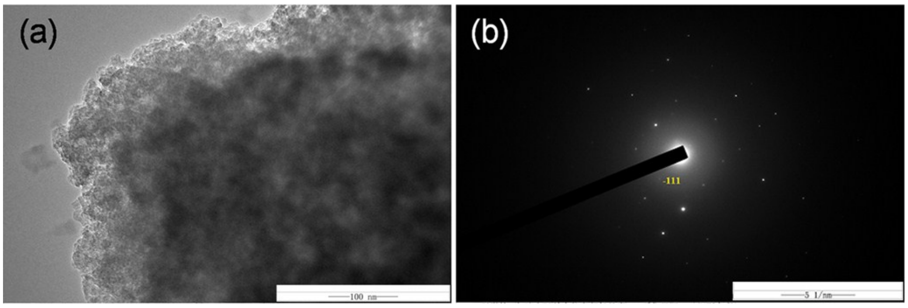


Figure S2. TEM image of hierarchical SAPO-34 sample S_{H3} (a) and corresponding selected area electron diffraction pattern (b).

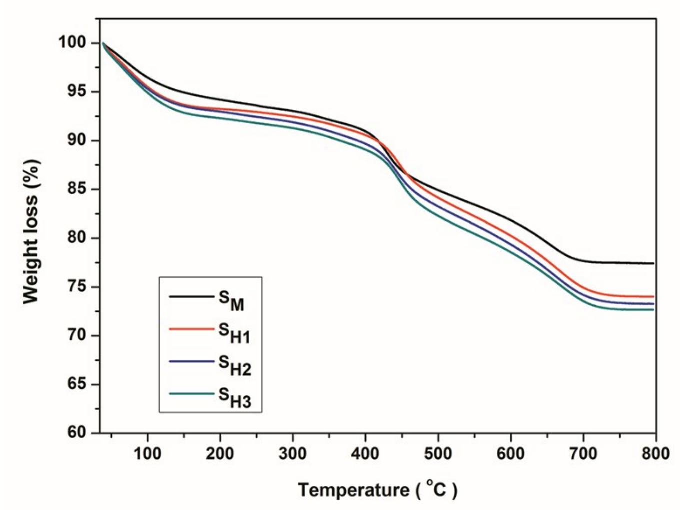


Figure S3. TG curves of conventional microporous SAPO-34 (S_M) and hierarchical SAPO-34 ($S_{H1,}$ S_{H2} and S_{H3}) catalysts.

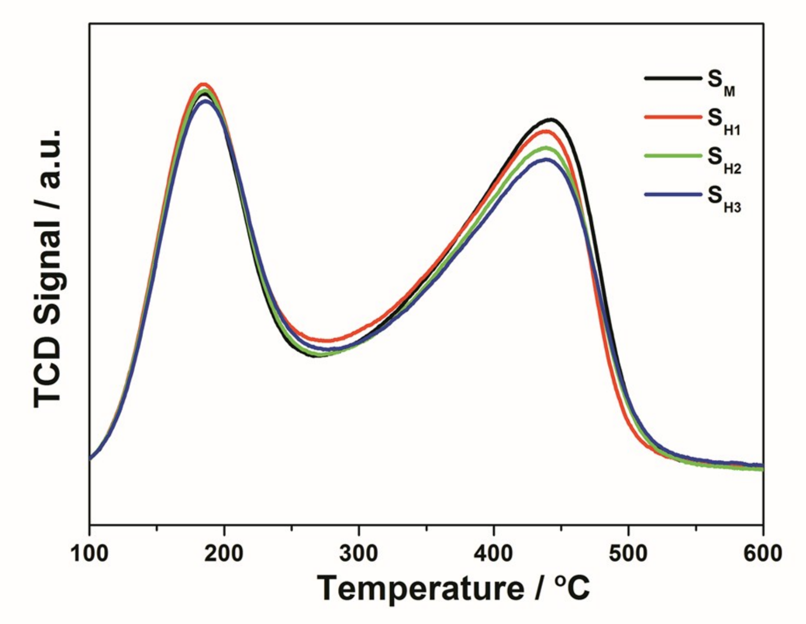


Figure S4. NH_3-TPD profiles of conventional microporous SAPO-34 (S_M) and hierarchical SAPO-34 ($S_{H1,}$ S_{H2} and S_{H3}) catalysts.

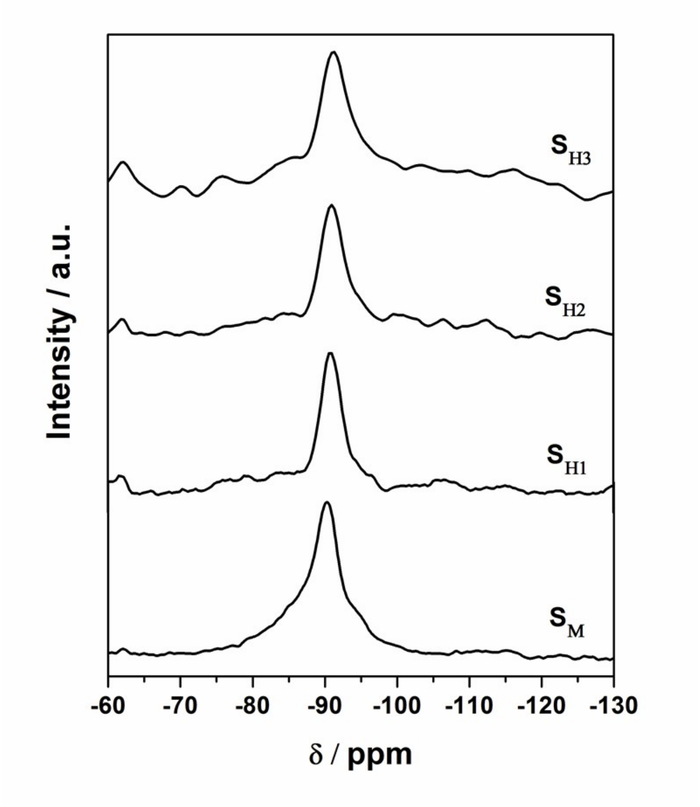


Figure S5. ^{29}Si MAS NMR spectra of conventional microporous SAPO-34 (S_M) and hierarchical SAPO-34 (S_{H1}, S_{H2} and S_{H3}) catalysts.

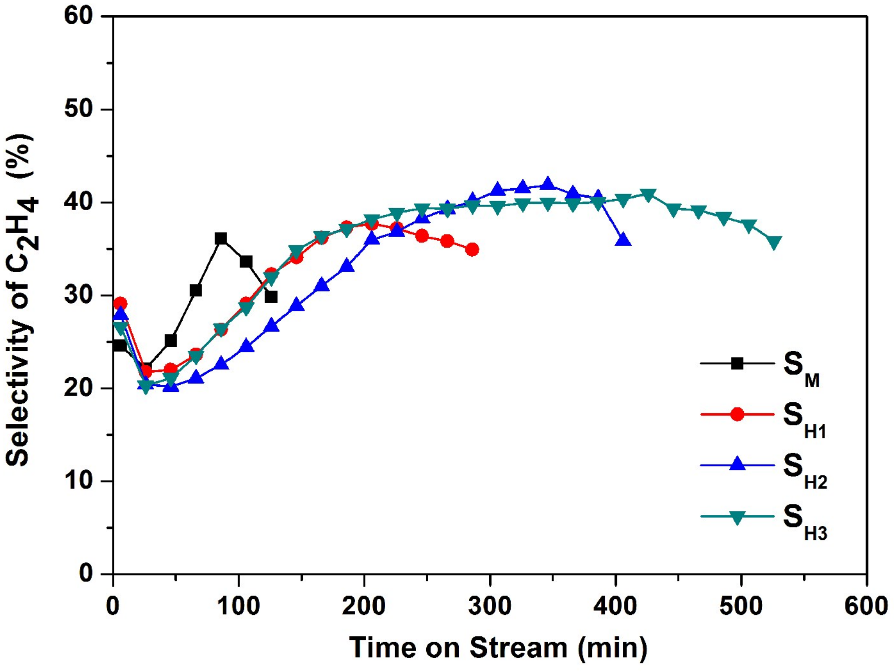


Figure S6. Selectivity of ethylene over conventional microporous SAPO-34 (S_M) and hierarchical SAPO-34 (S_{H1}, S_{H2} and S_{H3}) catalysts. Experimental conditions: WHSV=2 h^{-1}, T=673 K, catalyst weight =300 mg.

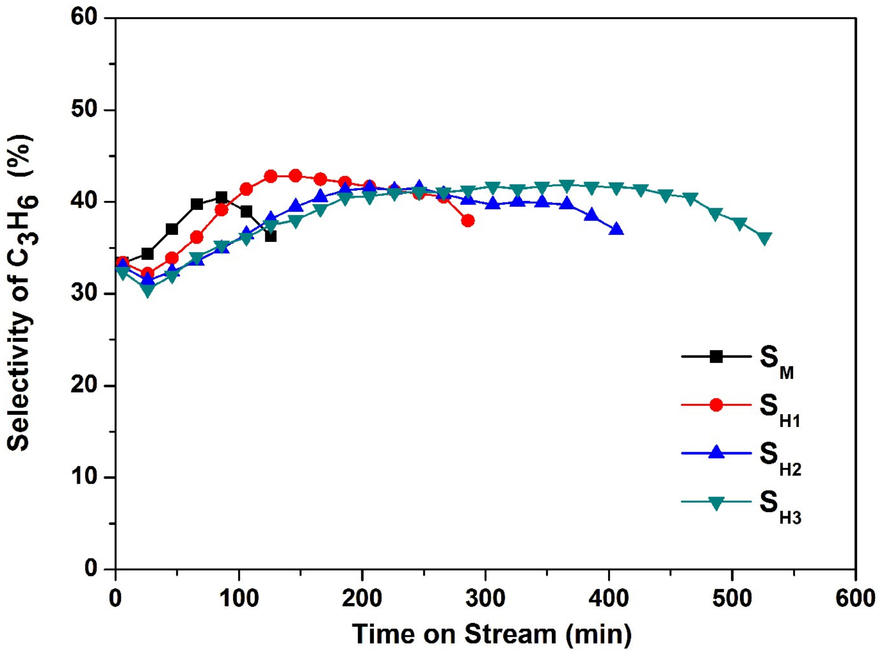


Figure S7. Selectivity of propylene over conventional microporous SAPO-34 (S_M) and hierarchical SAPO-34 ($S_{H1,}$ S_{H2} and S_{H3}) catalysts. Experimental conditions: WHSV=2 h^{-1}, T=673 K, catalyst weight =300 mg.

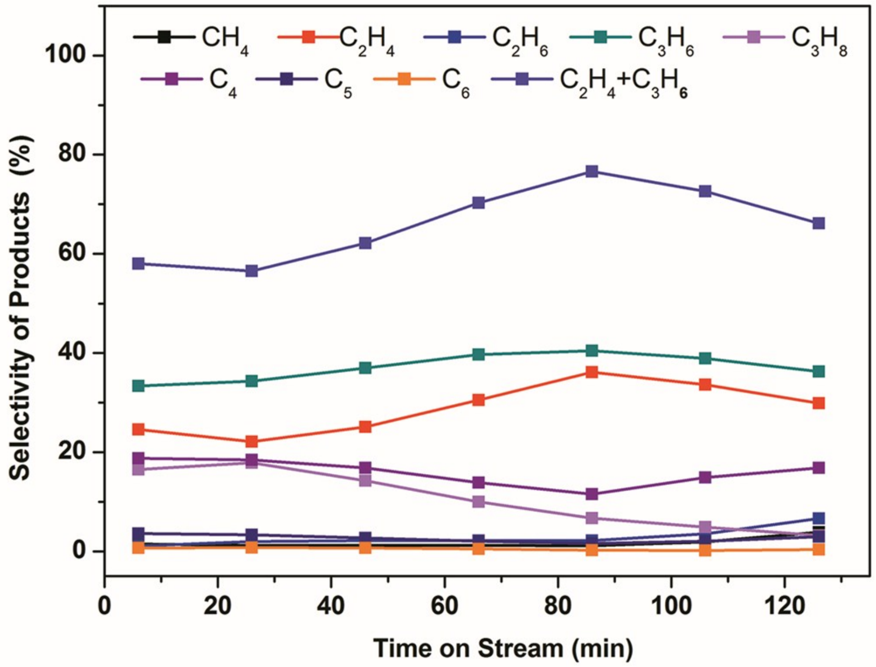


Figure S8. Products distribution of conventional microporous SAPO-34 catalysts (S_M) in MTO reaction. Experimental conditions: WHSV = 2 h^{-1}, T = 673 K, catalyst weight = 300 mg.

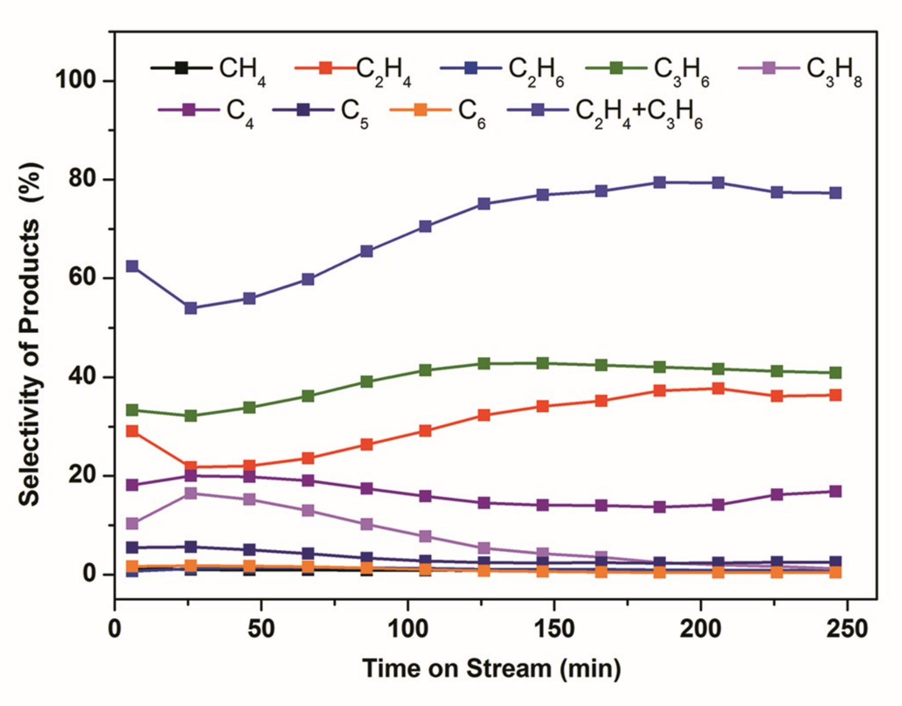


Figure S9. Products distribution of hierarchical SAPO-34 catalysts (S_{H1}) in MTO reaction. Experimental conditions: WHSV = 2 h^{-1}, T = 673 K, catalyst weight = 300 mg.

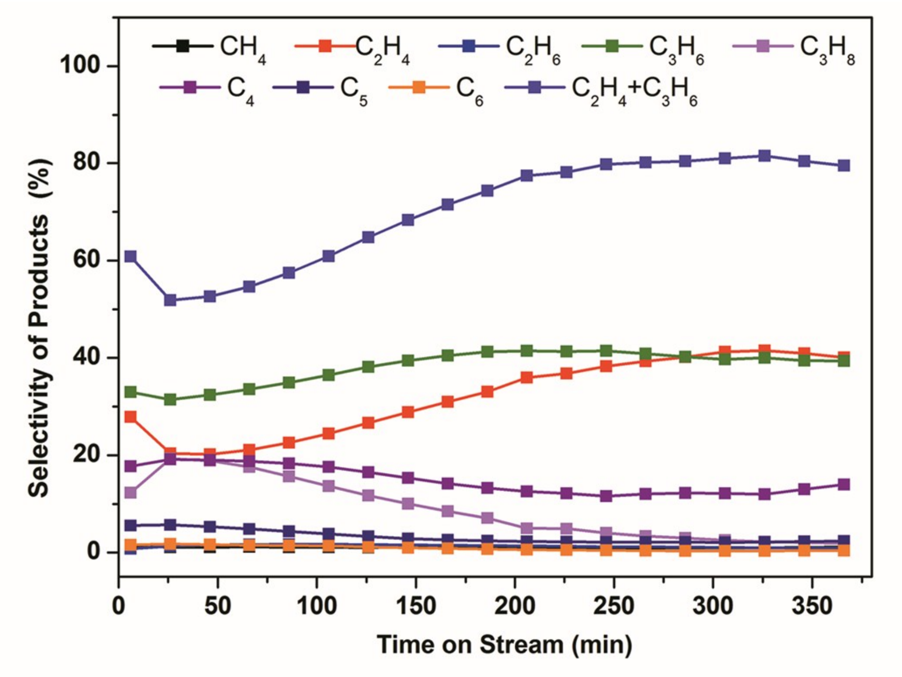


Figure S10. Products distribution of hierarchical SAPO-34 catalysts (S_{H2}) in MTO reaction. Experimental conditions: WHSV = 2 h^{-1}, T = 673 K, catalyst weight = 300 mg.

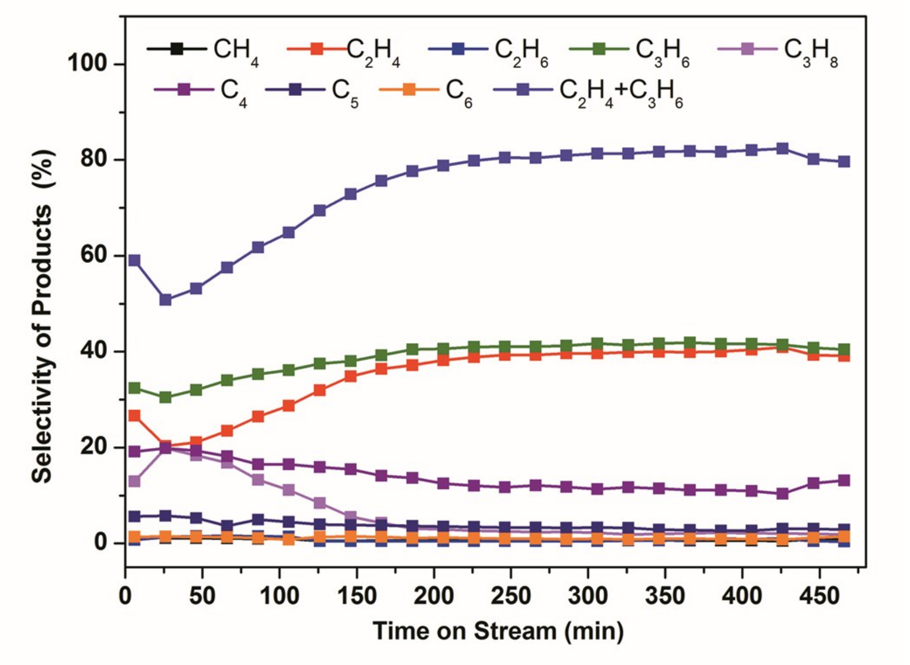


Figure S11. Products distribution of hierarchical SAPO-34 catalysts (S_{H3}) in MTO reaction. Experimental conditions: WHSV = 2 h^{-1}, T = 673 K, catalyst weight = 300 mg.

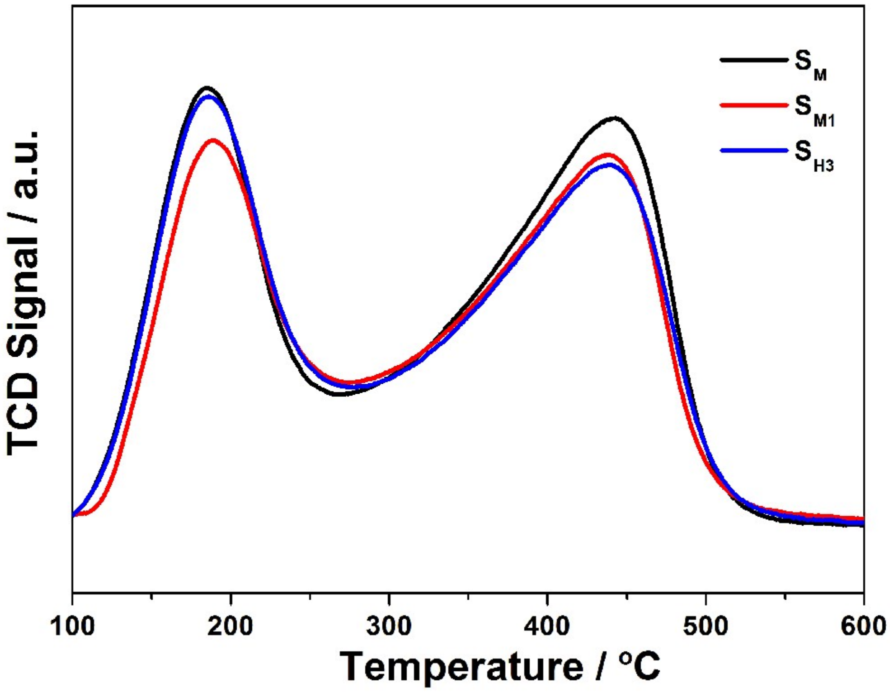


Figure S12. NH$_3$-TPD profiles of conventional microporous S_M and S_{M1} as well as hierarchical S_{H3} catalysts.

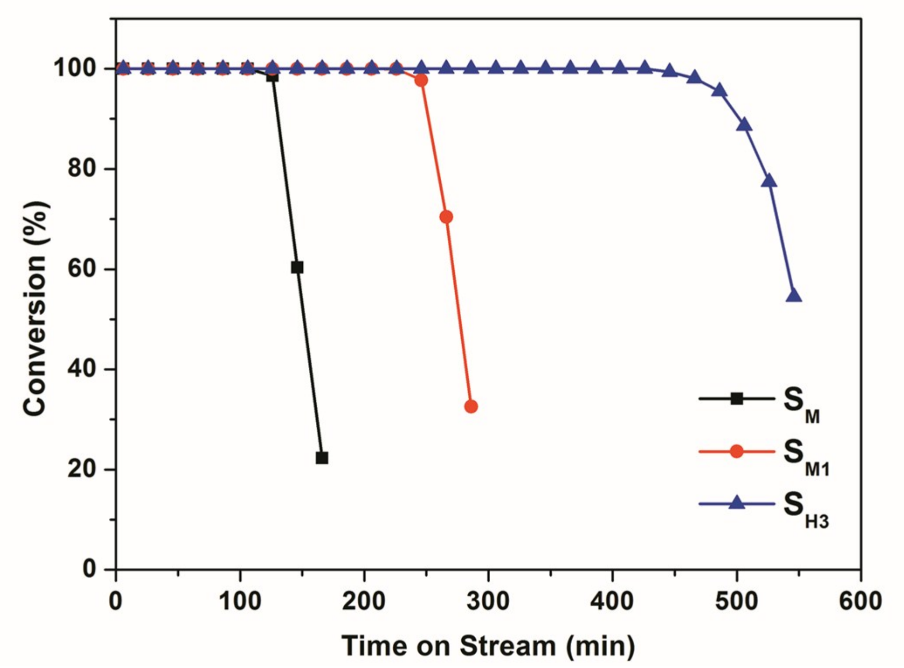


Figure S13. Lifetime of conventional microporous S_M and S_{M1} as well as hierarchical S_{H3} catalysts. Experimental conditions: WHSV = 2 h^{-1}, T = 673 K, catalyst weight = 300 mg.

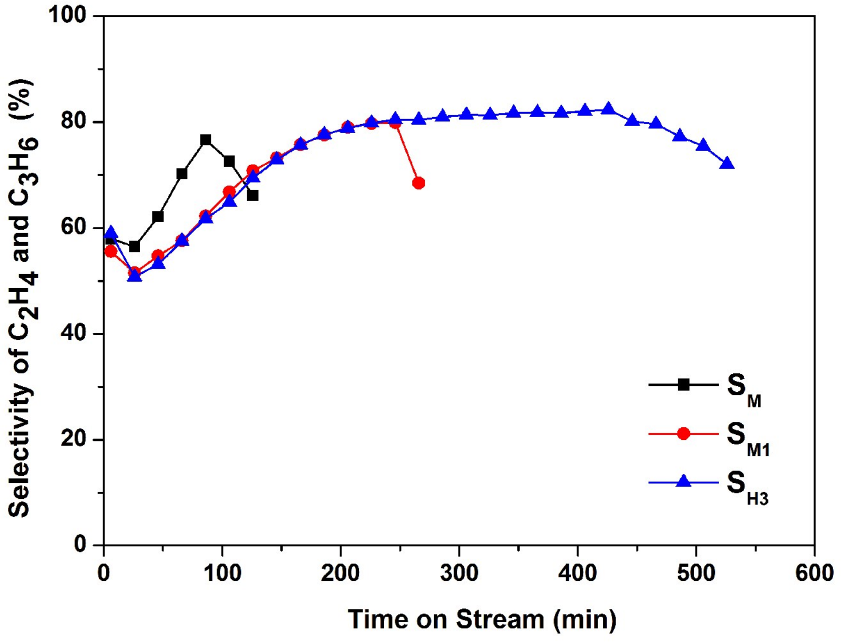


Figure S14. Selectivity of ethylene and propylene of conventional microporous S_M and S_{M1} as well as hierarchical S_{H3} catalysts. Experimental conditions: WHSV = 2 h^{-1}, T = 673 K, catalyst weight = 300 mg.

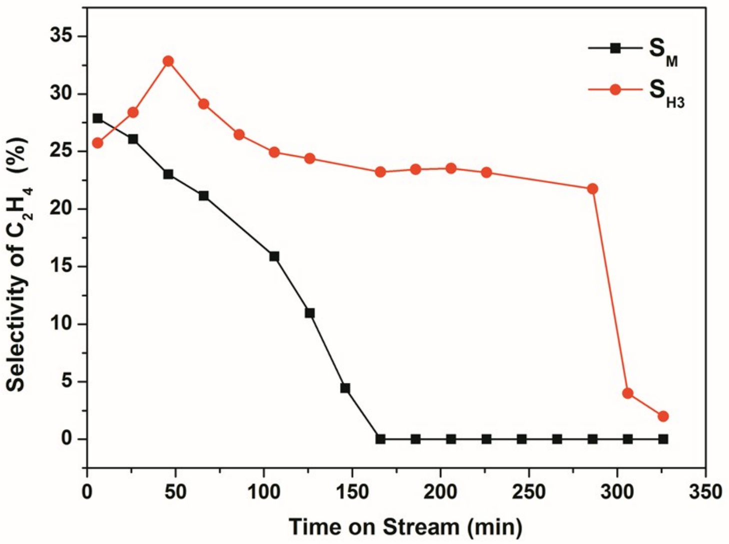


Figure S15. Selectivity of ethylene over conventional microporous SAPO-34 (S_M) and hierarchical SAPO-34 (S_{H3}). Experimental conditions: WHSV=23 h^{-1}, T=673 K, catalyst weight =300 mg.

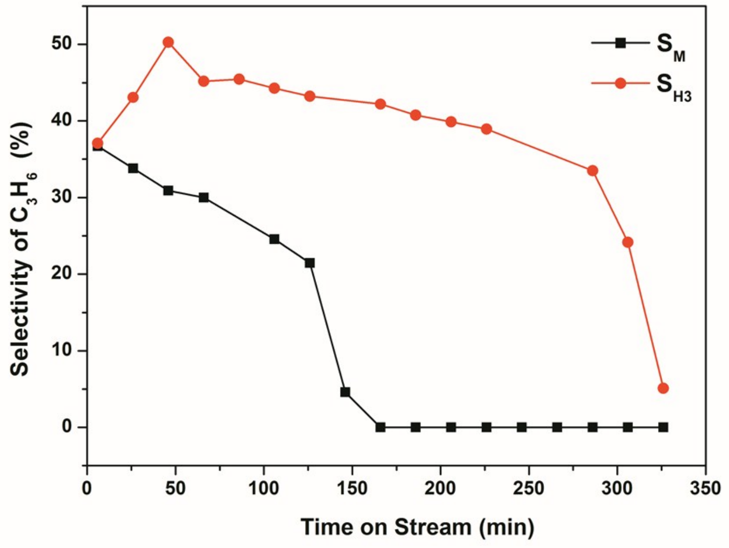


Figure S16. Selectivity of propylene over conventional microporous SAPO-34 (S_M) and hierarchical SAPO-34 (S_{H3}). Experimental conditions: WHSV=23 h^{-1}, T=673 K, catalyst weight =300 mg.

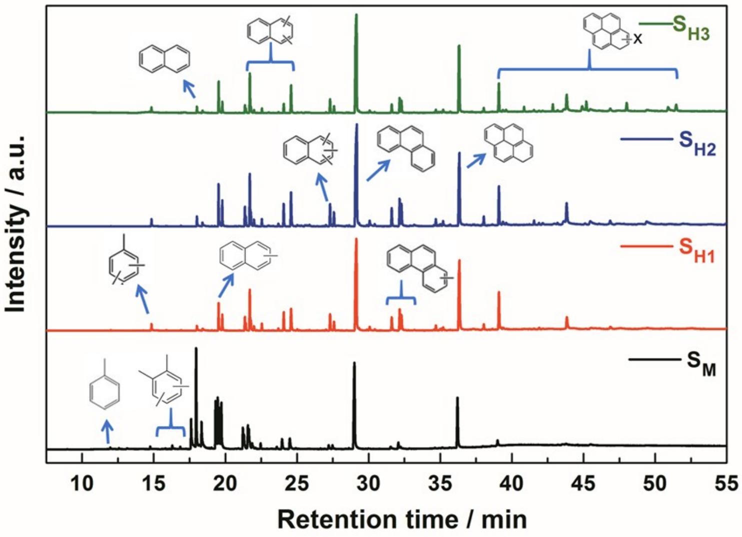


Figure S17. GC-MS of occluded organic species retained in the SAPO-34 catalysts after methanol conversion at 673K. The structures annotated onto the chromatograms are peak identifications in comparison with the mass spectra of those in the NIST database.

Table S1. MTO catalytic results of conventional microporous SAPO-34 (S_M) and hierarchical SAPO-34 ($S_{H1,}$ S_{H2} and S_{H3}) catalysts.

Catalysts	TOS	Selectivity (%)							
	(min)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4	C_5^+	$C_2^=+C_3^=$
S_M	86*	1.2	30.5	2.2	39.7	10.0	13.9	2.5	70.2
S_{H1}	206*	0.8	37.7	0.9	41.7	2.2	14.0	2.7	79.4
S_{H2}	326*	0.6	40.5	1.0	40.9	2.2	12.0	2.8	81.4
S_{H3}	426*	0.5	40.9	0.9	41.6	2.1	10.4	3.6	82.5

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

* Lifetime: the reaction duration with the 100% conversion of methanol.

Table S2. The rates of coke formation in methanol conversion over conventional microporous SAPO-34 (S_M) and hierarchical SAPO-34 ($S_{H1,}$ S_{H2} and S_{H3}) catalysts.

Catalysts	S_M	S_{H1}	S_{H2}	S_{H3}
Coke (%, g/g Cat.)$^{(a)}$	14.01	17.43	20.88	21.42
TOS(min)$^{(b)}$	86	206	326	426
R_{coke} (mg/min)$^{(c)}$	0.489	0.254	0.192	0.151
P_{coke} (g/gMeOH)$^{(d)}$	0.048	0.026	0.019	0.015

(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).