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Electronic Supplementary Information (ESI)

Seeding induced nano-sized hierarchical SAPO-34 zeolites: cost-effective synthesis and superior MTO performance

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1. Experiment Section

1.1 Reagents. The reagents used were aluminum iso-propoxide ($Al(OPr^i)_3$, 99.5 wt%, Beijing Reagents Company), pseudoboehmite (Al_2O_3, 62.5 wt%, Vista), phosphoric acid (H_3PO_4, 85 wt%, Beijing Chemical Works), tetraethylammonium hydroxide solution (TEAOH, 35 wt%, Alfa Aesar), triethylamine (TEA, 99%, Fuyu company), colloidal silica (40 wt%, Aldrich), fumed silica (Changling Refining Company).

1.2 Synthesis of nanosheet-like SAPO-34 zeolite seeds. The nanosheet-like SAPO-34 zeolite seeds were synthesized under conventional hydrothermal conditions from the starting gel with the molar composition of $1.0Al_2O_3$: $1.2P_2O_5$: 2.0TEAOH: $0.6SiO_2$: $40H_2O$ as reported in our previous work. Typically, the finely ground $Al(OPr^i)_3$ was firstly mixed with TEAOH solution and deionized water at room temperature until dissolved completely. Phosphoric acid was then added dropwise to the resultant solution, followed by a continuous stirring for 2 h. Finally, colloidal silica was added slowly. The reaction mixture was further stirred for 1 h, and was then transferred into a 100 ml Teflon-lined stainless steel autoclave. The crystallization was conducted in a conventional oven at 170 °C for 3 days under static conditions. 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 6 h.

1.3 Preparation of nano-sized hierarchical SAPO-34 zeolites (S_{H1}, S_{H2}, and S_{H3}). The nano-sized hierarchical SAPO-34 zeolites were synthesized with the molar composition of $1.0Al_2O_3$: $1.0P_2O_5$: 4.7TEA: $xSiO_2$: $70H_2O$: 8.0 wt% Seeds (x=0.4, 0.6 and 0.8) under hydrothermal conditions at 200 °C for 36 h, and the resulting products were named as S_{H1}, S_{H2}, and S_{H3}. Typically, the initial gel was prepared by mixing the deionized water with phosphoric acid together with pseudoboehmite, followed by a continuous stirring for 2 h. Then triethylamine was added into the above mixture. After a continuous stirring for 1 h, fumed silica was added into the resultant solution slowly, and then stirred for 2 h continuously. Finally, the seeds were added into the solution and then stirred for 2 h continuously until the seed dissolved completely. The synthetic gel was then transferred into a 100 mL Teflon-lined stainless steel autoclave. The crystallization was conducted in a conventional oven at 200 °C for 36 h under static conditions. 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 600 °C for 8 h.

1.4 Preparation of micron-sized microporous SAPO-34 zeolites (S_M). The micron-sized microporous SAPO-34 zeolites were synthesized with the molar composition of $1.0Al_2O_3$: $1.0P_2O_5$: 4.7TEA: $0.8SiO_2$: $70H_2O$ under hydrothermal conditions at 200 °C for 36 h. The synthesis procedure is the same with that of nano-sized hierarchical SAPO-34 zeolites except not adding the seeds.

2. Characterizations

The crystallinity and phase purity of the samples were characterized by powder X-ray diffraction on a Rigaku D-Max 2550 diffractometer using Cu Kα radiation (λ = 1.5418 Å). The crystal size and morphology were measured by transmission electron microscopy (TEM) using a Tecnai F20 and JEM-2200FS electron microscope operating at an acceleration voltage of 200 kV and scanning electron microscopy (SEM) using a JSM-6510 (JEOL) electron microscope. Thermogravimetric (TG) analysis was performed on a TA company TGA Q500 unit in air at a heating rate of 10 °C min^{-1} from room temperature to 800 °C in air. Chemical compositions were determined with an X-ray fluorescence (XRF) spectrometer (PANalytical, AXIOS). 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. 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 macropore size distributions of SAPO-34 catalysts were measured by the Autopore IV 9510 mercury porosimeter (Micromeritics, USA). ^{29}Si NMR and ^{27}Al 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 79.5 MHz and 104.1 MHz and the spinning rate of the samples at the magic angle was 4 kHz and 7 kHz, respectively. The organic species retained in the nano-sized SAPO-34 catalysts after methanol conversion were analyzed by GC-MS (Thermo Fisher Trace ISQ, equipped with TG-5MS column, 60 m × 320 µm × 25 µm).

3. Catalytic Tests and Carbon Deposit Analyses.

Methanol conversion was performed in a quartz tubular fixed-bed reactor at atmospheric pressure. The catalyst (300 mg, 40-60 mesh) loaded in the quartz reactor (6 mm inner diameter) was activated at 773 K in a N_2 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. The methanol was fed by passing the carrier gas (15 mL/min) through a saturator containing methanol at 40 °C, which gave a WHSV of 2.0 h^{-1}. The reaction products were analyzed using an on-line gas chromatograph (Agilent GC 7890N), equipped with a flame ionization detector (FID) and Plot-Q column (Agilent J&W GC Columns, HP-PLOT/Q 19091P-Q04, 30 m × 320 μm × 20 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 TGA Q500 at a heating rate of 10 °C min^{-1} from room temperature to 800 °C under air flow.

4. Supplementary Figures and Tables

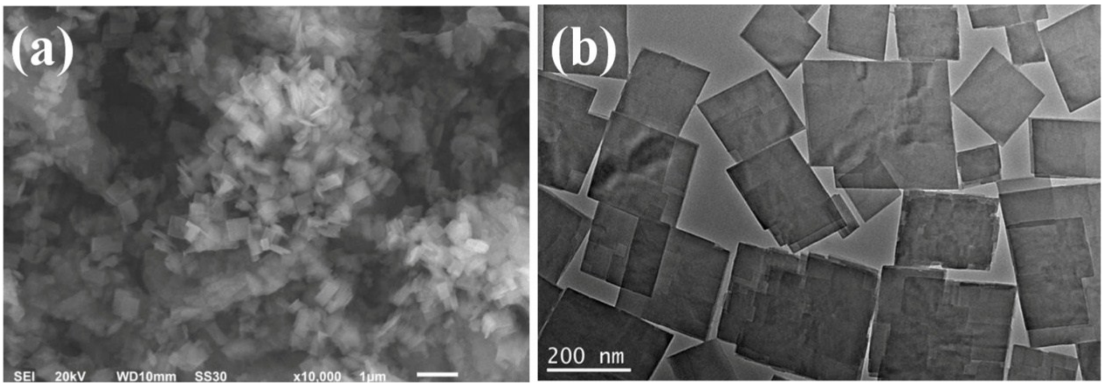

Figure S1 SEM (a) and TEM (b) images of nanosheet-like seeds using TEAOH as template.

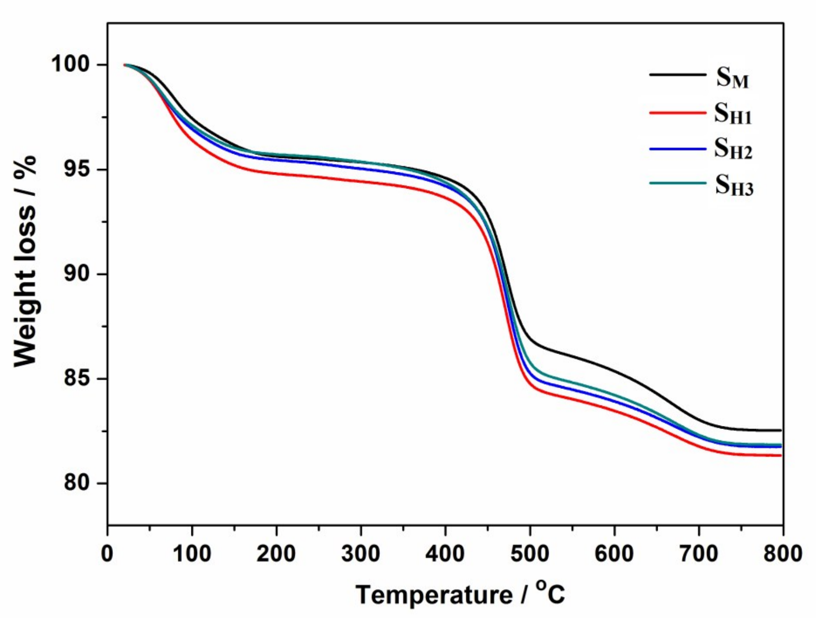

Figure S2 The TG curves of micron-sized microporous (S_M) and nano-sized hierarchical SAPO-34 (S_{H1}, S_{H2}, and S_{H3}) samples.

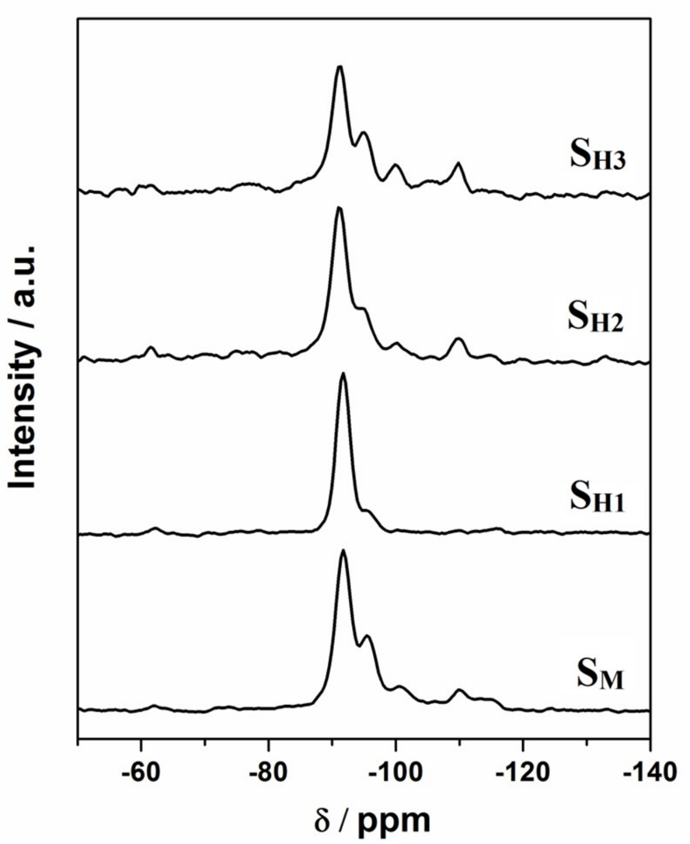

Figure S3 ^{29}Si MAS NMR spectra micron-sized microporous (S$_{M}$) and nano-sized hierarchical SAPO-34 (S$_{H1}$, S$_{H2}$, and S$_{H3}$) samples.

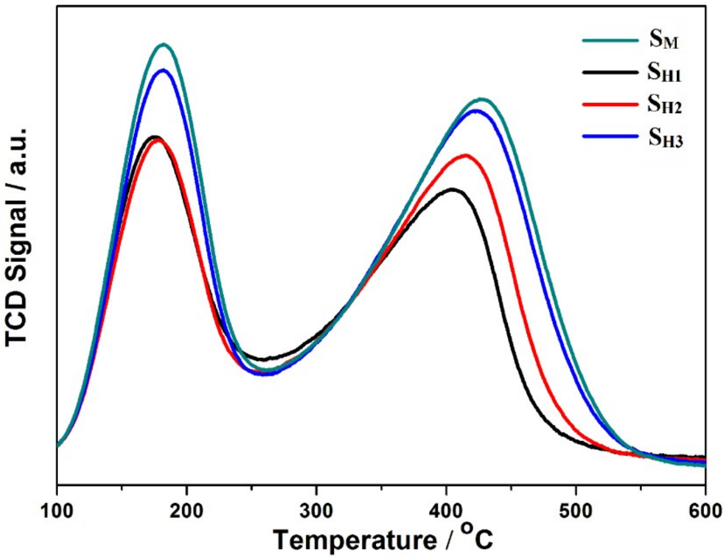

Figure S4 NH$_3$-TPD profiles of micron-sized microporous (S$_{M}$) and nano-sized hierarchical SAPO-34 (S$_{H1}$, S$_{H2}$, and S$_{H3}$) samples.

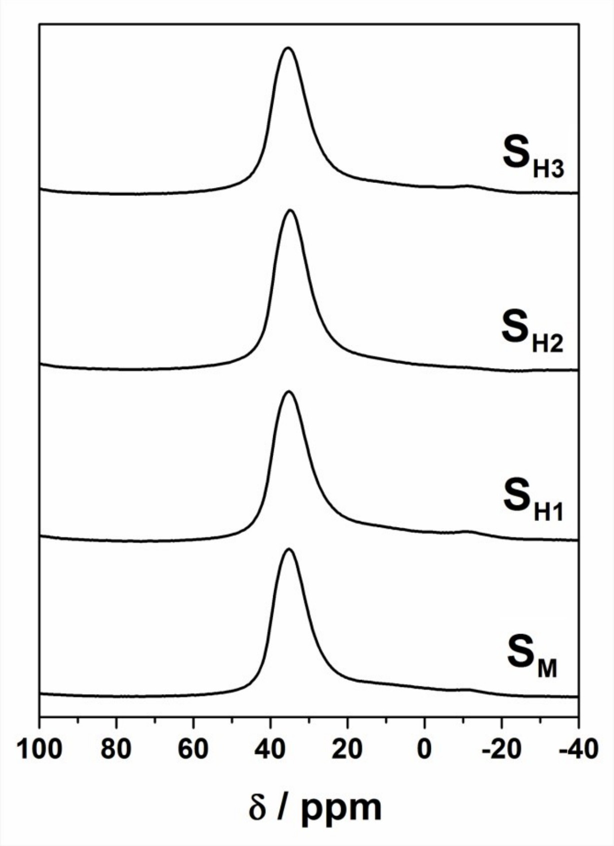

Figure S5 ^{27}Al MAS NMR spectra of micron-sized microporous (S_M) and nano-sized hierarchical SAPO-34 (S_{H1}, S_{H2}, and S_{H3}) samples.

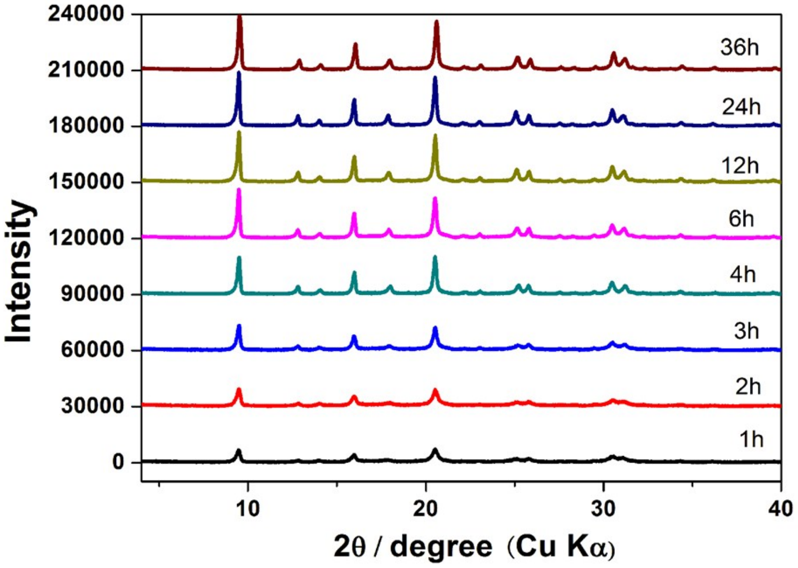

Figure S6 XRD patterns of nano-sized hierarchical SAPO-34 samples S_{H1} synthesized with different crystallization times

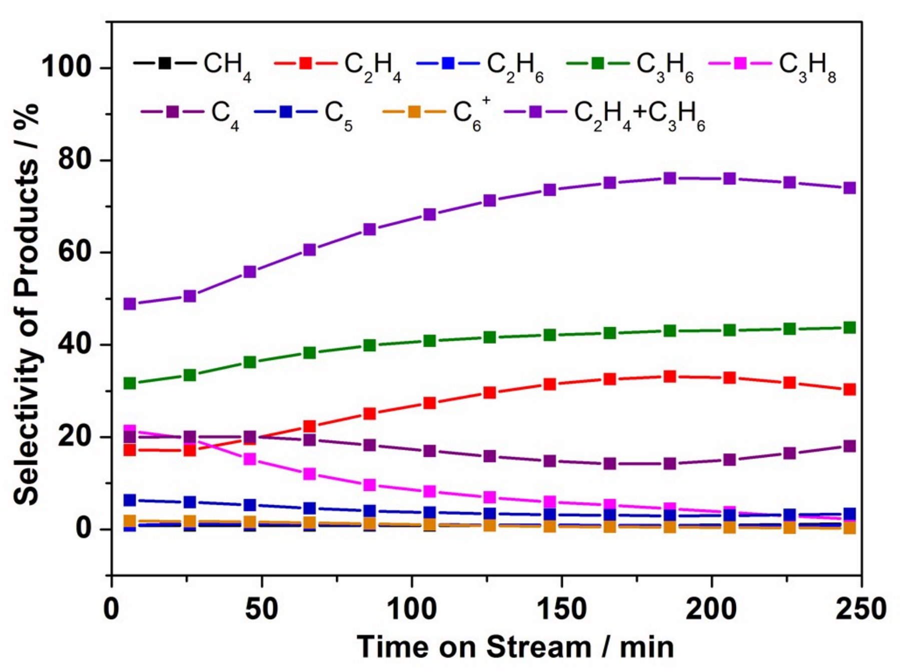

Figure S7 Products distribution of micron-sized microporous SAPO-34 catalyst (S_M). Experimental conditions: WHSV = 2 h^{-1}, T = 673 K, catalyst weight = 300 mg.

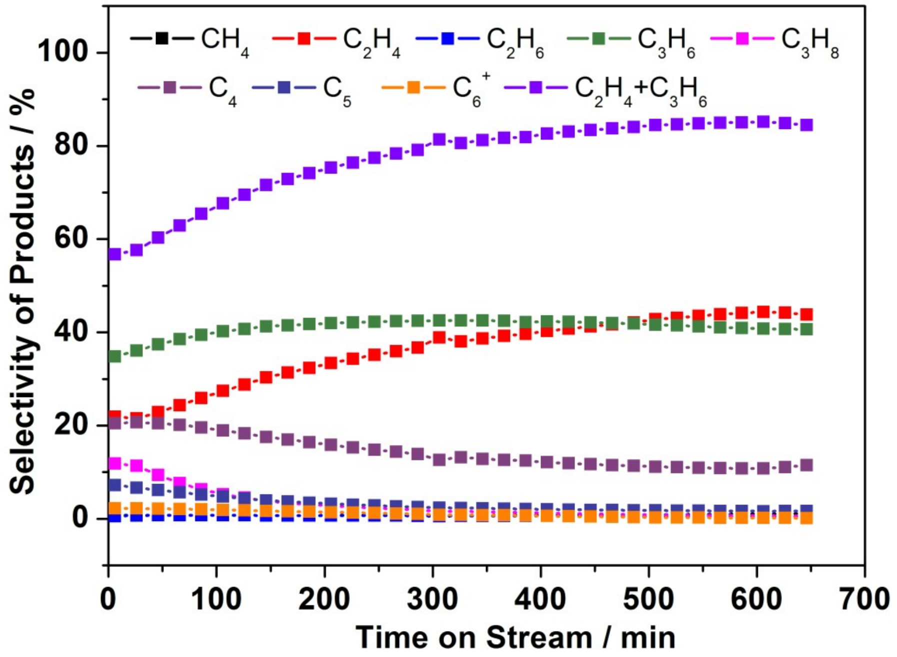

Figure S8 Products distribution of nano-sized hierarchical SAPO-34 catalyst (S_{H1}). Experimental conditions: WHSV = 2 h^{-1}, T = 673 K, catalyst weight = 300 mg.

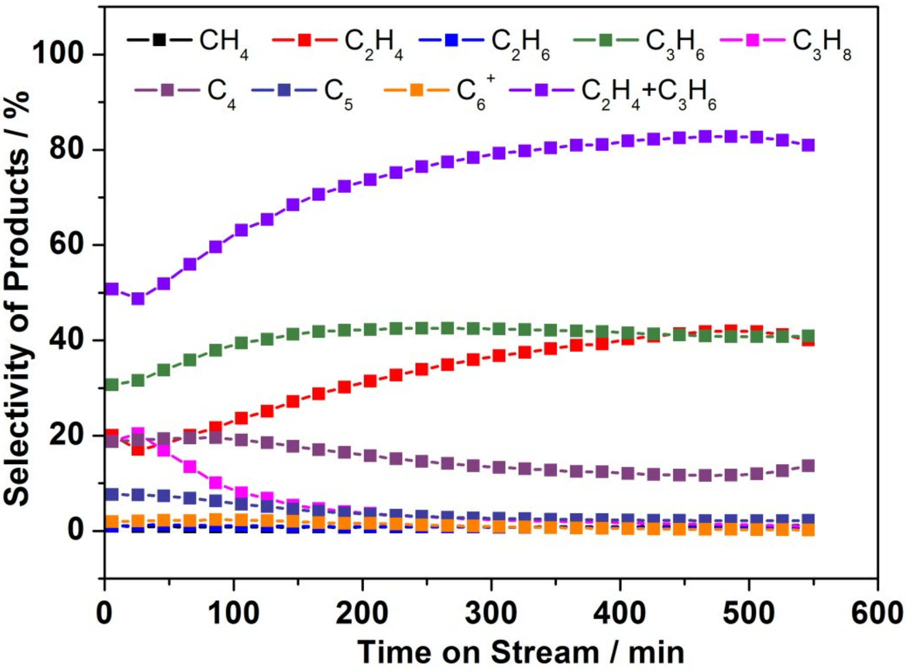

Figure S9 Products distribution of nano-sized hierarchical SAPO-34 catalyst (S_{H2}). Experimental conditions: WHSV = 2 h^{-1}, T = 673 K, catalyst weight = 300 mg.

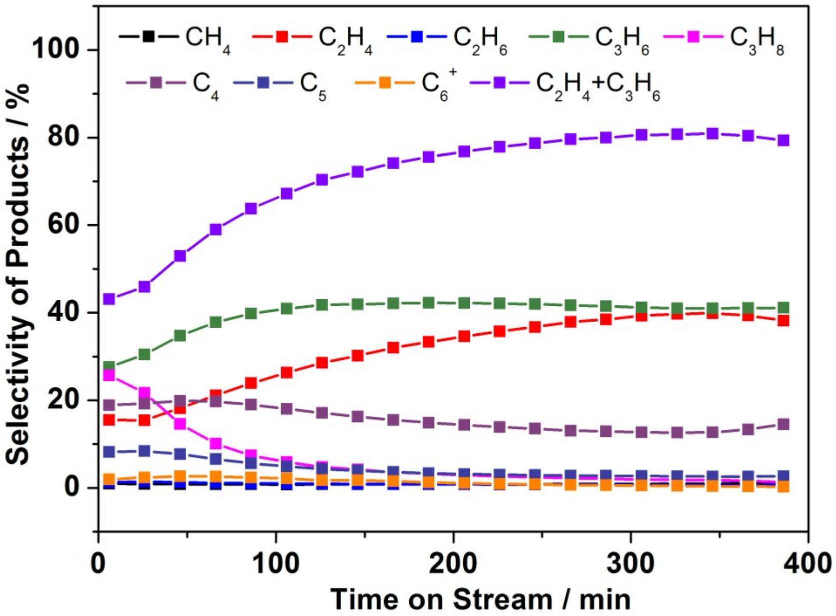

Figure S10 Products distribution of nano-sized hierarchical SAPO-34 catalyst (S_{H3}). Experimental conditions: WHSV = 2 h^{-1}, T = 673 K, catalyst weight = 300 mg.

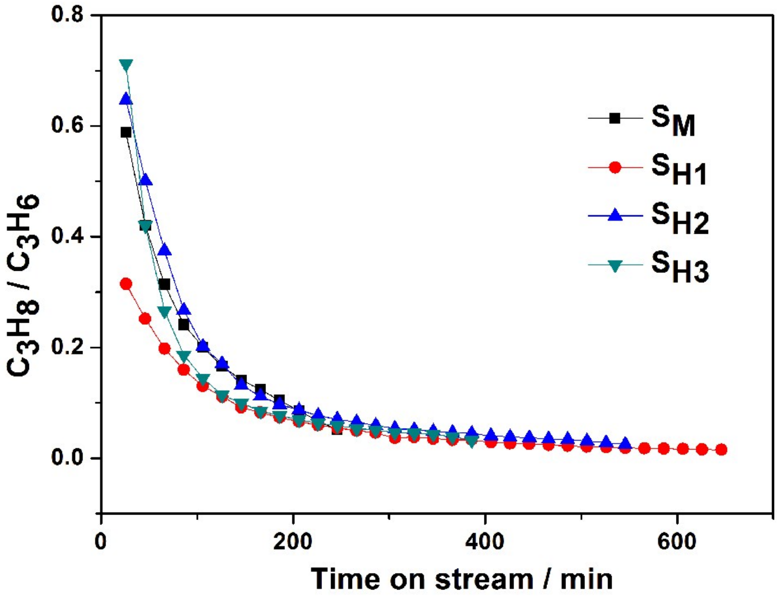

Figure S11 Hydrogen transfer index (HTI, C_3H_8/C_3H_6) value of methanol conversion over micron-sized microporous (S_M) and nano-sized hierarchical SAPO-34 (S_{H1}, S_{H2}, and S_{H3}) catalysts. Experimental conditions: WHSV = 2 h^{-1}, T = 673 K, catalyst weight = 300 mg.

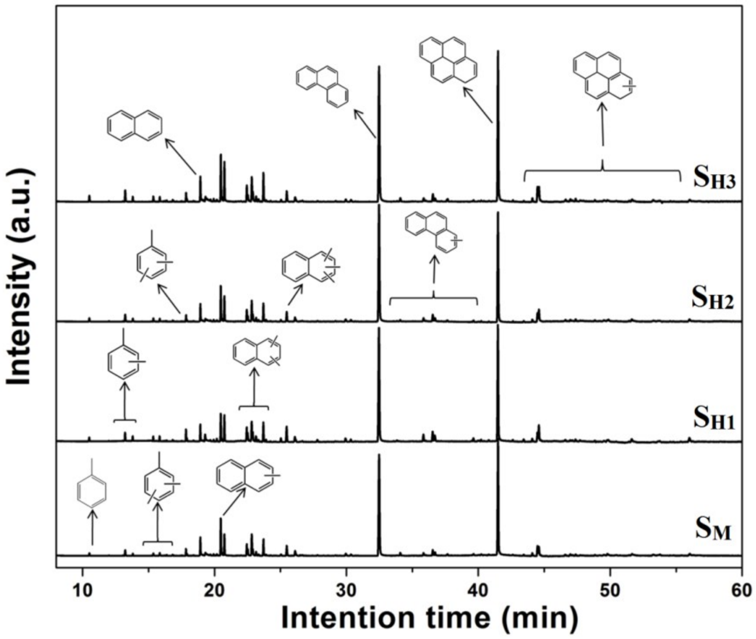

Figure S12 GC-MS chromatograms of occluded organic species retained in micron-sized microporous (S_M) and nano-sized hierarchical SAPO-34 (S_{H1}, S_{H2}, and S_{H3}) catalysts after methanol conversion at 673 K. The structures annotated onto the chromatograms are peak identifications in comparison with the mass spectra to those in the NIST database.

Table S1 The molar composition and relative crystallinity of nano-sized hierarchical SAPO-34 samples S_{H1} synthesized with different crystallization times.

Crystallization time (h)	Molar composition[a]	Intensity of peaks[b]			Relative crystallinity (%)[c]
		9.5°	16.0°	20.5°	
1	$Si_{0.18}Al_{0.47}P_{0.35}O_2$	6890	4380	7320	26
2	$Si_{0.17}Al_{0.49}P_{0.34}O_2$	9390	5580	9190	34
3	$Si_{0.13}Al_{0.49}P_{0.38}O_2$	13490	7880	12250	48
4	$Si_{0.12}Al_{0.48}P_{0.40}O_2$	20000	11880	20190	74
6	$Si_{0.10}Al_{0.47}P_{0.43}O_2$	26310	13490	21635	87
12	$Si_{0.10}Al_{0.47}P_{0.43}O_2$	26910	13680	25230	94
24	$Si_{0.10}Al_{0.49}P_{0.41}O_2$	28810	14425	26215	99
36	$Si_{0.10}Al_{0.48}P_{0.42}O_2$	29433	14705	26212	100
Seeds	$Si_{0.13}Al_{0.48}P_{0.39}O_2$	—	—	—	—

[a] Measured by X-ray fluorescence (XRF) spectrometer; [b] based on the XRD patterns of samples in Figure S6. [c] The relative crystallinity is calculated based on the intensity of the three strongest peaks ($2\theta=9.5^{\circ}$, 16.0°, and 20.5°) in the XRD patterns.

Table S2 MTO results on micron-sized microporous (S_M) and nano-sized hierarchical SAPO-34 (S_{H1}, S_{H2}, and S_{H3}) catalysts.

Catalysts	TOS (min)	Selectivity（%）							
		CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4	C_5^+	$C_2^=+C_3^=$
S_M	146*	0.8	31.5	0.9	42.1	6.0	14.8	3.9	73.6
S_{H1}	586*	1.0	43.9	0.5	41.1	0.7	10.9	1.9	85.0
S_{H2}	466*	1.0	41.4	0.7	41.1	1.5	11.7	2.6	82.5
S_{H3}	306*	0.9	39.3	0.7	41.2	1.9	12.7	3.3	80.5
Seed	606*	1.7	41.7	0.3	38.1	0.4	11.5	6.3	79.8

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

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

Table S3 The variation of coke formation in methanol conversion over micron-sized microporous (S_M) and nano-sized 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)	16.11	17.51	17.74	16.81
TOS (min) (b)	246	726	586	446
R_{coke} (mg/min) (c)	0.20	0.07	0.09	0.11
P_{coke} (g/g MeOH) (d)	0.02	0.007	0.009	0.011

(a) Coke weight percent at about 60% methanol conversion;

(b) Time-on-stream (TOS) at about 60% methanol conversion;

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

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