Electronic Supplementary Information (ESI)

Nanoseed-assisted Synthesis of Nanosized SAPO-34 Zeolite Using Morpholine as the Sole Template with Superior MTO Performance

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Synthesis method

Reagents. Aluminum iso-propoxide ($Al(OPr^i)_3$, 99.5 wt%, Beijing Reagents Company), Phosphoric acid (H_3PO_4, 85 wt%, Beijing Chemical Works), Colloidal silica (40 wt%, Aldrich), Tetraethyl orthosilicate (TEOS, Fuyu Reagents Company), Morpholine (MOR, C_4H_8NO, >98.5%, Fuyu Reagents Company), Tetraethylammonium hydroxide solution (TEAOH, 35 wt%, Alfa Aesar).

Synthesis of nano-sized SAPO-34 seed. The nanosized SAPO-34 seed was synthesized under conventional hydrothermal conditions from the starting gel with the molar composition of Al/P/Si/TEAOH/ H_2O=1/1.2/0.3/1/20 as reported in our previous work. Typically, the finely ground $Al(OPr^i)_3$ was firstly added into TEAOH solution and deionized water until dissolved sufficiently. Phosphoric acid was then slowly added dropwise into the resultant solution, followed by a continuous stirring for 2 h. Finally, the colloidal silica was added dropwise into the synthesis gel. The resultant mixture was further stirred for 1 h, and was then transferred into a 100 ml Teflon-lined stainless steel autoclave, followed by static crystallization in a conventional oven at 170 °C for 3 days. The obtained zeolite products were centrifuged, washed and dried, followed by calcination at 550 °C for 6 h to remove templates.

Synthesis of nano-sized SAPO-34 zeolites (SP34-S-X). The nano-sized SAPO-34 zeolites were synthesized with the molar compositions of Al/P/Si/MOR/H_2O=1/1/0.3/x/40 (x=2.5~0.6) combined with the addition of 8.0 wt% seed (based on the Al_2O_3) under hydrothermal conditions at 180 °C for 3 days. The obtained samples are named as SP34-S-X, wherein the X represents the ratio of MOR/Al. Typically, the finely ground $Al(OPr^i)_3$ was firstly added into MOR solution and stirred for 1 h. Subsequently, the phosphoric acid was slowly added dropwise into the resultant solution, followed by a continuous stirring for 2 h. The TEOS was added dropwise into the synthesis gel and stirred for 2 h. Finally, the seed was added into the solution and then stirred for 3 h continuously until the seed was dissolved completely. The synthetic gel was then transferred into a 100 mL Teflon-lined stainless steel autoclave with static crystallization at 180 °C for 36 h. The obtained zeolite products were centrifuged, washed and dried, followed by calcination at 600 °C for 6 h to remove templates.

Preparation of micron-sized SAPO-34 zeolites (SP34-N-X). The micron-sized SAPO-34 zeolites were synthesized with the molar compositions of Al/P/Si/MOR/H_2O=1/1/0.3/x/40 (x=2.5~0.6) with the same synthesis procedure of nano-sized SAPO-34 zeolites without adding the seed. The obtained

samples are named as SP34-N-X, wherein the X represents the ratio of MOR/Al.

Characterizations

X-ray diffraction patterns were recorded on powder X-ray diffraction on a Rigaku D-Max 2550 diffractometer using Cu Kα radiation (λ = 1.5418 Å). TEM images and SEM images were taken on a Tecnai F20 electron microscope operating at an acceleration voltage of 200 kV and 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 of samples were analyzed by inductively coupled plasma (ICP) using Perkin-Elmer Optima 3300 DV ICP instrument. The acidity of samples was characterized by temperature-programmed desorption of ammonia (NH_3-TPD) experiments using a Micromeritics AutoChem II 2920 automated chemisorption analysis unit. 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. ^{29}Si NMR spectra were performed on a Bruker AVANCE III 400 WB spectrometer. 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).

MTO Catalytic Tests

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 500 °C in a N_2 flow of 30 ml min^{-1} for 1 h before starting each reaction run and then the temperature was adjusted to reaction temperature of 450 °C. The methanol was fed by passing the carrier gas (15 mL/min) through a saturator containing methanol at 49 °C, which gave a WHSV of 4.0 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. To analysize the coke species in the deactivated SAPO-34 catalysts, the deactivated catalysts were etched by HF solution for 24 h, 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).

Figures and Tables

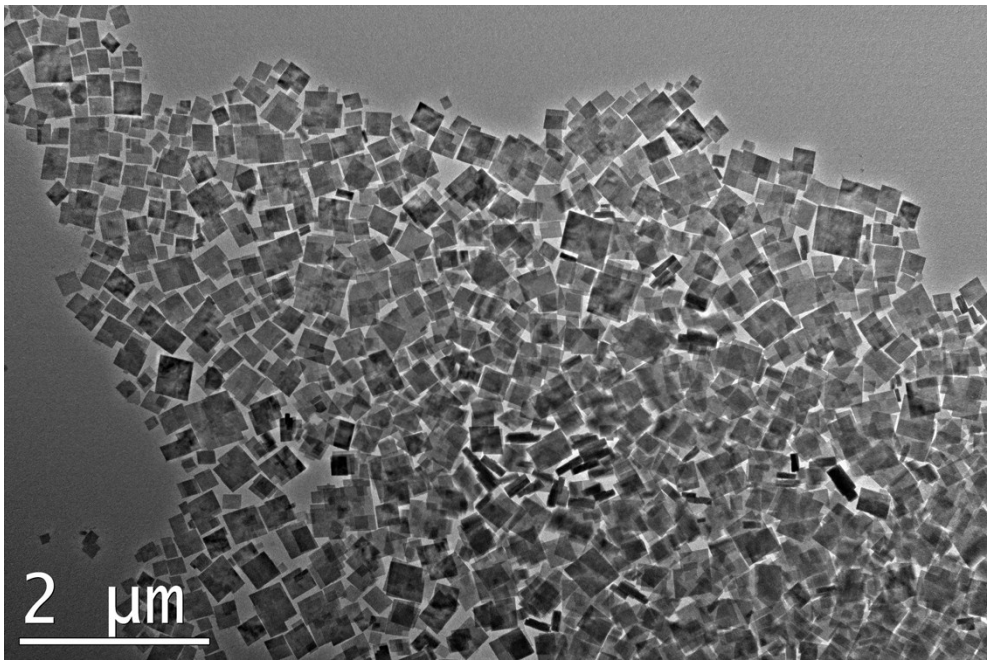

Figure S1 TEM images of nanosheet-like SAPO-34 seeds synthesized using TEAOH as template.

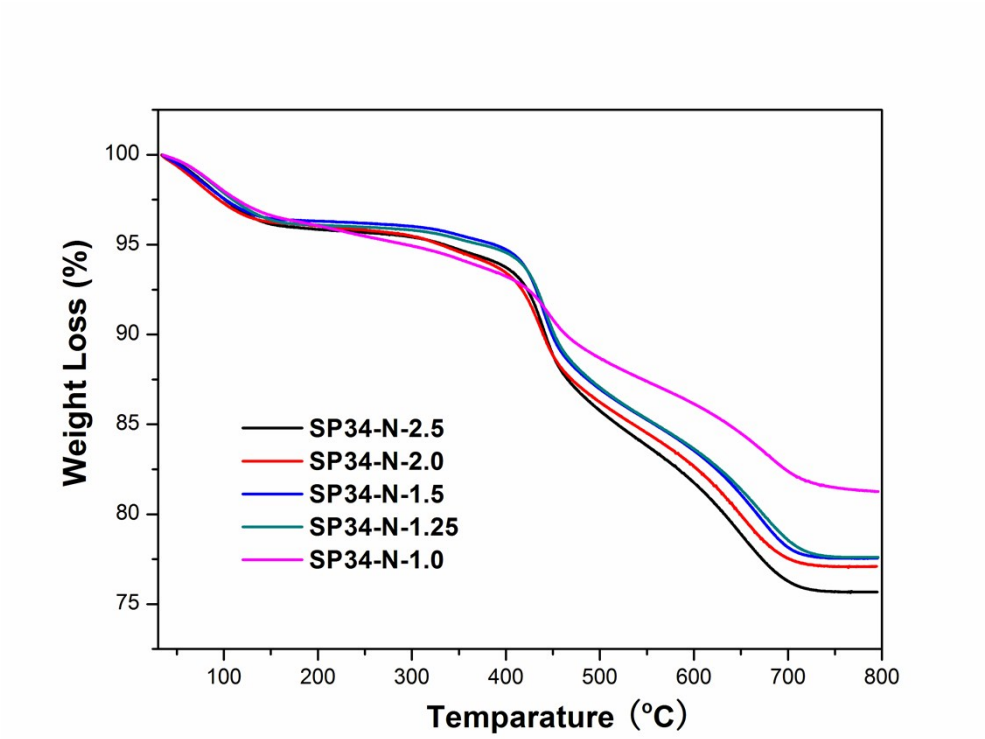

Figure S2 TG curves of micron-sized SAPO-34 samples.

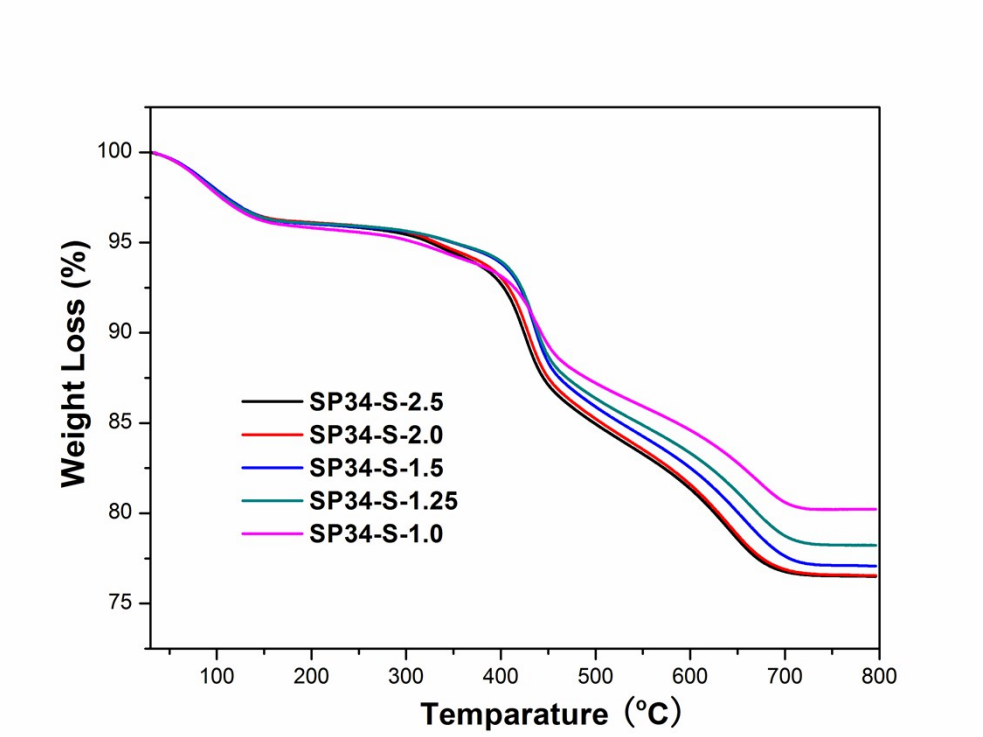

Figure S3 TG curves of nano-sized SAPO-34 samples synthesized using nanoseed-assisted method.

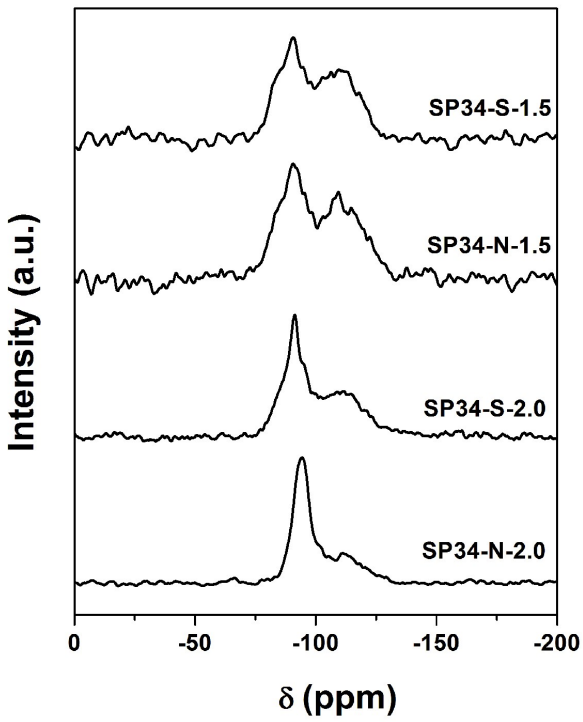

Figure S4 ^{29}Si MAS NMR spectra of micron-sized SAPO-34 samples SP34-N-2.0 and SP34-N-1.5, and nano-sized SAPO-34 samples SP34-S-2.0 and SP34-S-1.5.

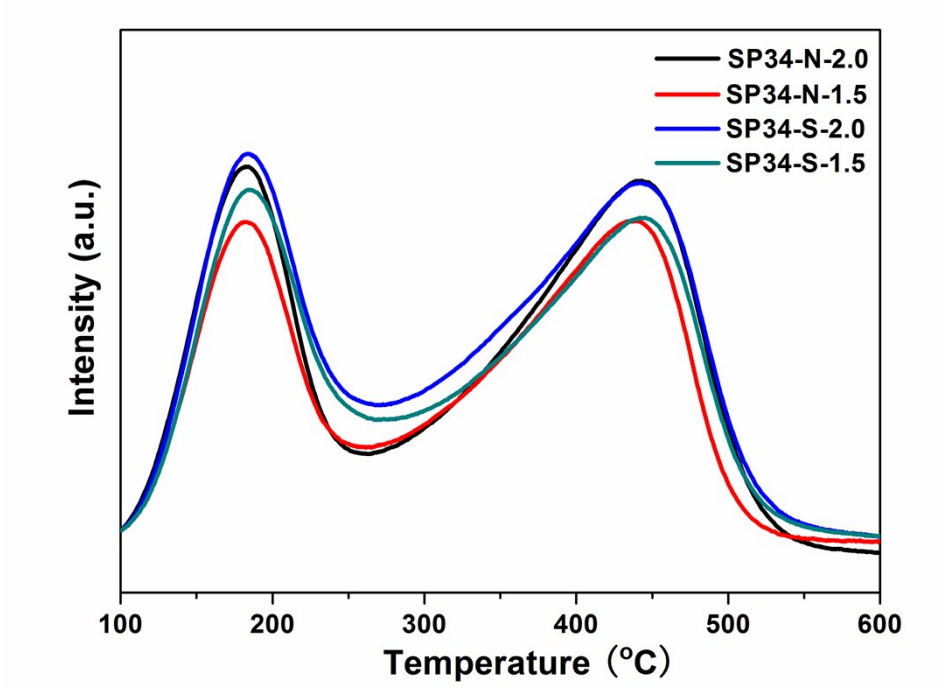

Figure S5 NH_3-TPD profiles of micron-sized SAPO-34 samples SP34-N-2.0 and SP34-N-1.5, and nano-sized SAPO-34 samples SP34-S-2.0 and SP34-S-1.5.

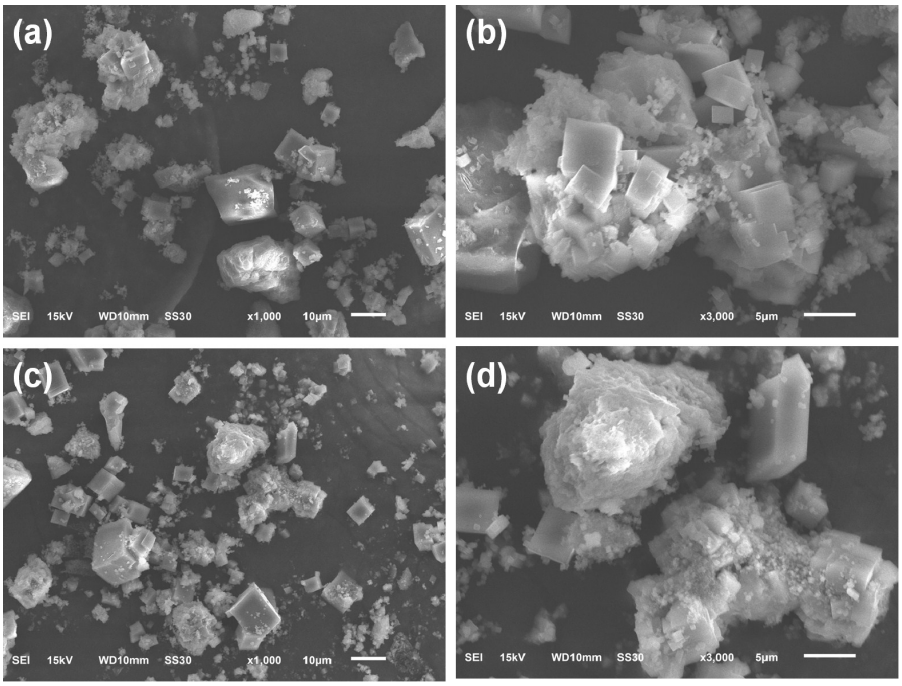

Figure S6 SEM images of samples SP34-MS-2.0 (a, b) and SP34-MS-1.5 (c, d) using micron-sized SAPO-34 crystals as the seed (MS means addition of the micron-sized seed, and 2.0 and 1.5 represent the ratios of MOR/Al).

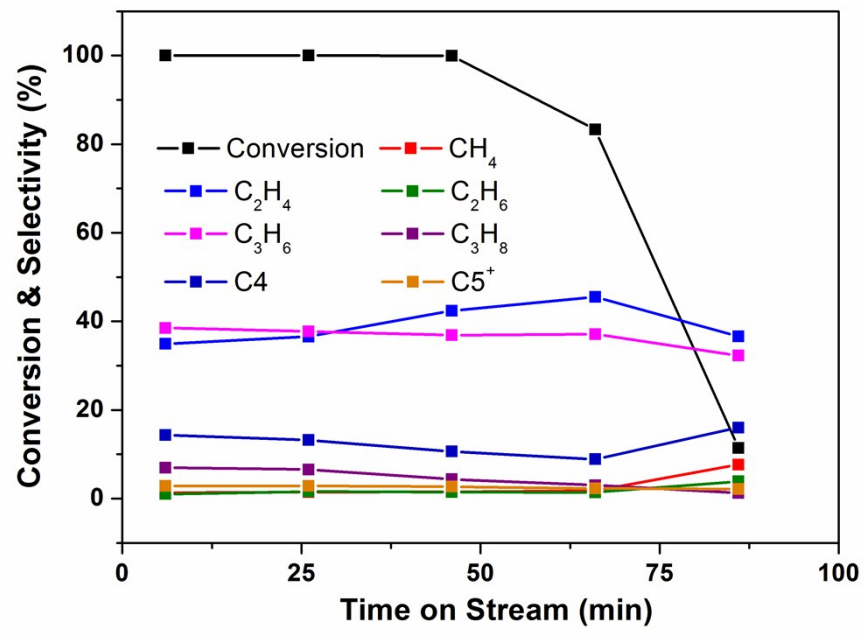

Figure S7 Catalytic lifetime and products selectivity of micron-sized SAPO-34 catalyst SP34-N-2.0. Experimental conditions: WHSV = 4 h^{-1}, T = 450 ° C.

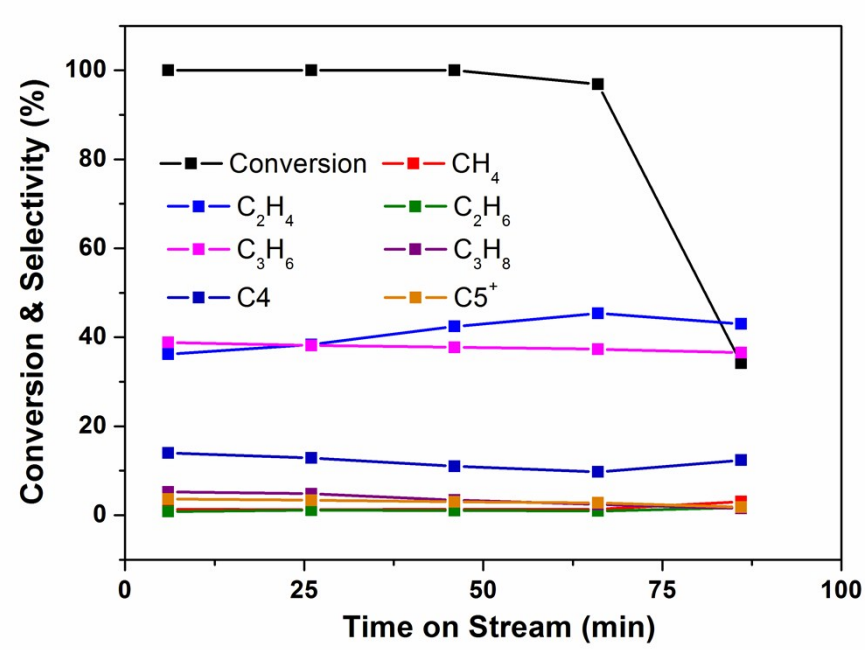

Figure S8 Catalytic lifetime and products selectivity of micron-sized SAPO-34 catalyst SP34-N-1.5. Experimental conditions: WHSV = 4 h^{-1}, T = 450 ° C.

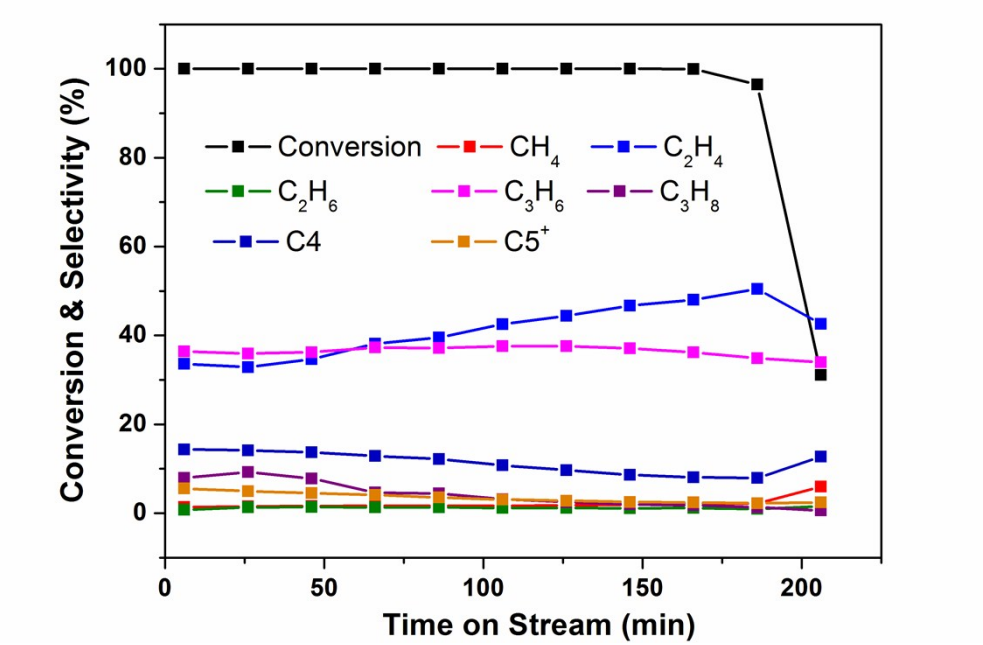

Figure S9 Catalytic lifetime and products selectivity of nano-sized SAPO-34 catalyst SP34-S-2.0. Experimental conditions: WHSV = 4 h^{-1}, T = 450 ^{o}C.

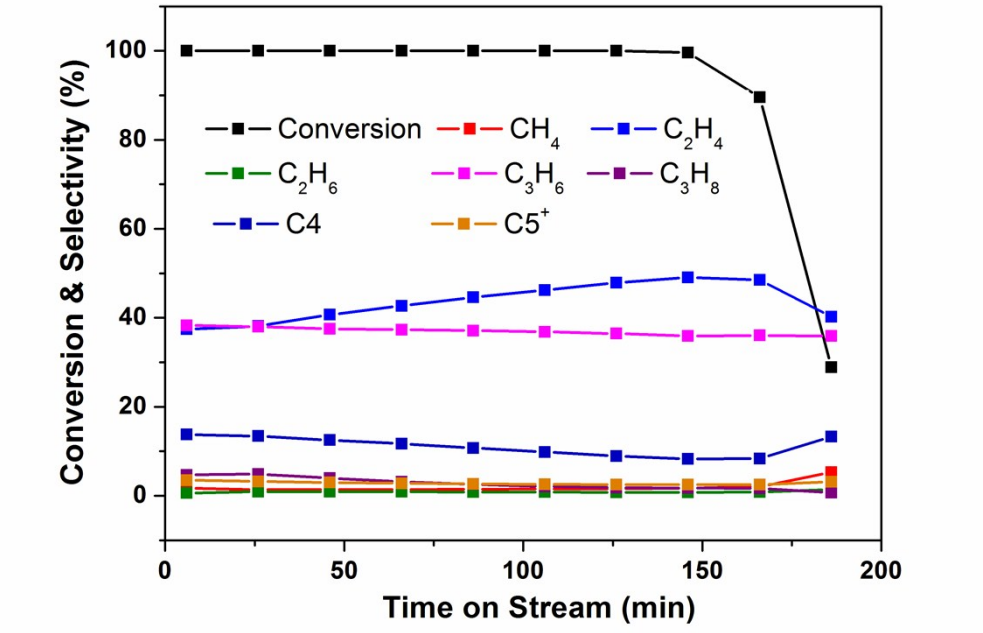

Figure S10 Catalytic lifetime and products selectivity of nano-sized SAPO-34 catalyst SP34-S-1.5. Experimental conditions: WHSV = 4 h^{-1}, T = 450 ^{o}C.

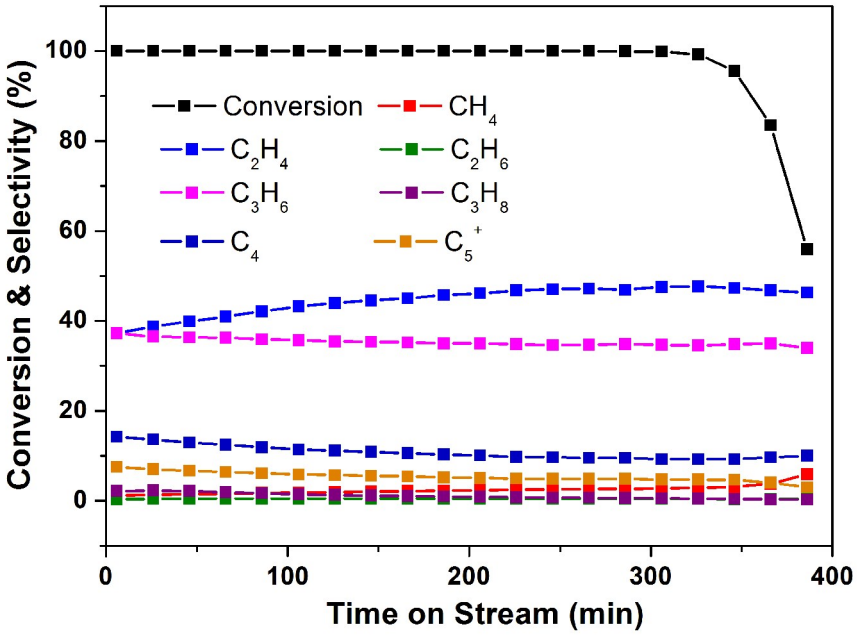

Figure S11 Catalytic lifetime and products selectivity of nanosheet-like SAPO-34 seed catalyst using TEAOH as template. Experimental conditions: WHSV = 4 h^{-1}, T = 450 ºC.

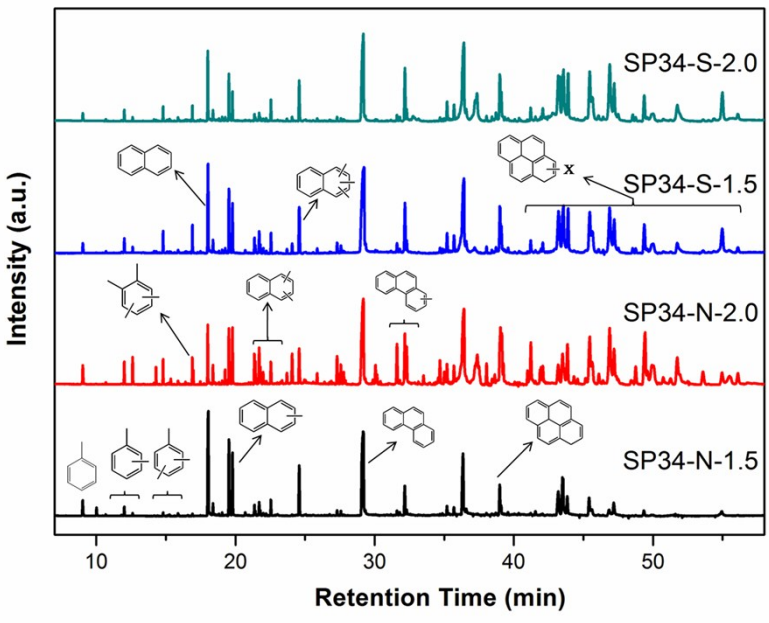

Figure S12 GC-MS chromatograms of occluded organic species retained in deactivated SAPO-34 catalysts SP34-S-2.0, SP34-S-1.5, SP34-N-2.0 and SP34-N-1.5. The structures annotated onto the chromatograms are peak identifications in comparison with the mass spectra to those in the NIST database.

Table S1 MTO catalytic results of SP34-N-2.0, SP34-N-1.5, SP34-S-2.0 and SP34-S-1.5 catalysts.

Catalysts	TOS (min)	Selectivity（%）								
		CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4	C_5	$C6^+$	$C_2^=+C_3^=$
SP34-N-2.0	46*	1.5	42.4	1.5	36.9	4.4	10.6	2.3	0.4	79.3
SP34-N-1.5	46*	1.3	42.0	1.1	37.7	3.4	11.0	2.5	0.5	79.7
SP34-S-2.0	166*	2.2	48.1	1.2	36.2	1.8	8.1	2.0	0.4	84.3
SP34-S-1.5	126*	1.6	47.9	0.8	36.5	1.8	8.9	2.1	0.4	84.4
Nanosheets -like Seed	286*	2.6	47.0	0.4	34.9	0.6	9.5	2.6	4.9	81.9

Reaction conditions: WHSV = 4 h^{-1}, T = 450 ° C.

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

Table S2 The rates of coke formation in methanol conversion over of SP34-N-2.0, SP34-N-1.5, SP34-S-2.0 and SP34-S-1.5 catalysts.

Catalysts	Coke (mg/g Cat.) [(a)]	TOS (min) [(b)]	R_{coke} (mg/min) [(c)]	P_{coke} (g/g MeOH) [(d)]
SP34-N-2.0	169.9	46	1.12	0.055
SP34-N-1.5	157.5	46	1.03	0.051
SP34-S-2.0	211.6	166	0.38	0.019
SP34-S-1.5	198.5	126	0.47	0.024

(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).