

Supplementary Information

Synthesis of SAPO-34 nanoaggregates with the assistance of an inexpensive “three-in-one” nonsurfactant organosilane

Pengfei Wu,^{ab} Miao Yang,^a Wenna Zhang,^{ab} Shutao Xu,^a Peng Guo,^a Peng Tian,^{a,*} and Zhongmin Liu^{a,*}

^a National Engineering Laboratory for Methanol to Olefins, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.
E-mail: tianpeng@dicp.ac.cn; liuzm@dicp.ac.cn

^b *University of Chinese Academy of Sciences, Beijing 100049, P. R. China*

Sample Preparation

Orthophosphoric acid (H_3PO_4 , 85 wt%), tetraethyl orthosilicate (TEOS, 98 wt%), aluminium isopropoxide ($\text{Al}(\text{i-C}_3\text{H}_7\text{O})_3$, 99 wt%), piperazine (PIP, 99 wt%) and triethylamine (TEA, 99 wt%) were purchased from Tianjin Kemiou Chemical Reagent Company. 3-piperazinepropylmethyldimethoxysilane ($\text{N}[(\text{CH}_2)_2]_2\text{N}(\text{CH}_2)_3\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$, PZPMS, 99 wt%) were purchased from Beijing HWRK Chem Co. All chemicals were used as received without further purification.

Synthesis of SP34-M

H_3PO_4 and $\text{Al}(\text{i-C}_3\text{H}_7\text{O})_3$ were first added into deionized water and stirred for 30 min. And then, TEA, TEOS and PZPMS were added in sequence. The mixture was stirred for 14 h. The SAPO gel has a molar composition of $\text{TEA}/\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5/\text{TEOS}/\text{PZPMS}/\text{H}_2\text{O}/=4.5/1.0/1.0/0.3/x/100$. ($x=0, 0.2, 0.4, 0.6$). For SP34-M5, certain of SAPO-34 precursor was added to assist crystallization. The amount of the precursor was calculated by the following formula: $\text{Precursor amount} = 0.05 \times M_{(\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5 + \text{SiO}_2)_{\text{gel}}}$, where milled SAPO-34 and $M_{(\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5 + \text{SiO}_2)_{\text{gel}}}$ stand for the weights of the milled SAPO-34 and the dry mass of three inorganic oxides in the starting mixture, respectively.

The mixture was transferred into a stainless steel autoclave and heated at 200 °C for 24 h under rotation. The autoclave was cooled down and the solid product was recovered by filtration, washed three times with deionized water and dried at 110 °C overnight. Finally, the product was calcined at 550 °C for 4 h to remove organic species.

Synthesis of SP34-P

The synthetic procedure is the same with SP34-M except using TEOS as the only silica source and using TEA and PIP as a co-template. The SAPO gel with a molar composition of $\text{TEA}/\text{PIP}/\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5/\text{TEOS}/\text{H}_2\text{O}=4.5/0.4/1.0/1.0/0.32/100$ was prepared to control the product composition comparable to that of SP34-M5.

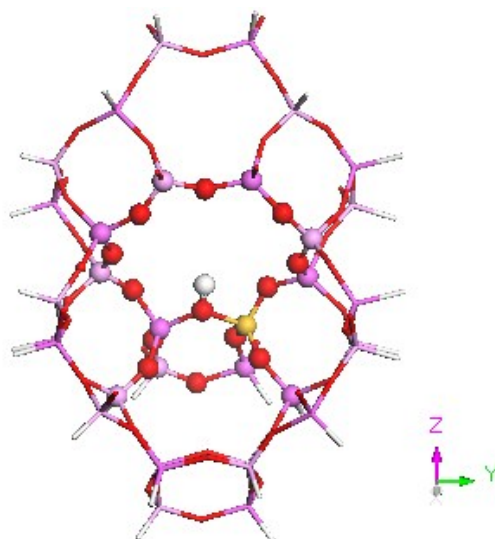
Synthesis of conventional SAPO-34 (SP34-C)

For comparison, conventional SAPO-34 with similar silica content to SP34-M5 was prepared by using the same template TEA. Pseudoboehmite, water, phosphoric acid, alkaline silica sol, and TEA were mixed in sequence with a molar composition of $\text{TEA}/\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5/\text{SiO}_2/\text{H}_2\text{O}=3.0/1.0/1.0/0.4/50$. The crystallization was conducted in a stainless steel autoclave at 200 °C for 24 h under rotation. The product was filtrated, washed thoroughly and dried in air at 110 °C. Finally, the product was calcined at 600 °C for 4 h to remove organic species.

Characterization

The powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X' Pert PRO X-ray diffractometer with Cu-K α radiation ($\lambda=1.54059$ Å), operating at 40 kV and 30 mA. The chemical composition of the samples was determined with a Philips Magix-601 X-ray fluorescence (XRF) spectrometer. The crystal morphology was observed by scanning electron microscopy (SEM) using a TM3000 (Hitachi) and field emission SEM (Hitachi SU8020). Textural properties of the calcined samples were measured by N₂ adsorption at -196 °C on a Micromeritics ASAP 2020 analyzer. The total surface area was calculated based on the BET equation. The micropore volume and micropore surface area were evaluated by using the t-plot method. The mesopore volume and mesopore surface area were evaluated from the adsorption isotherm by the Barrett–Joyner–Halenda (BJH) method. The temperature-programmed desorption of ammonia (NH₃-TPD) was carried out with Micromeritics Autochem II 2920 device. The calcined samples (200 mg) were outgassed in a He flow at 600 °C for 60 min. And then the samples were cooled down to 100 °C and subjected to a flow of NH₃/He for 60 min to saturate the sample with NH₃. Then, the samples were purged with a He flow to remove the weakly adsorbed NH₃ molecules. The measurement of the desorbed NH₃ was performed from 100 to 650 °C at a heating rate of 10 °C min⁻¹ under a He flow (20 mL min⁻¹). Thermogravimetric and differential thermal analysis (TG-DTG and DTA) were performed on a TA SDTQ600 analyzer with a temperature-programmed rate of 10 °C min⁻¹ in air. The elemental composition of the organic species in as-synthesized samples was determined with a C/H/N/O elemental analyzer (vario EL cube, Elemental Co.). ¹³C magic-angle-spinning (MAS) and ²⁹Si cross-polarization (CP) nuclear magnetic resonance (NMR) were carried out on a Bruker Avance III 600 spectrometer at 150.9 MHz for ¹³C and 119.2 MHz for ²⁹Si. ¹³C MAS NMR spectra were recorded with a 4 mm MAS probe with a spinning rate of 12 kHz. ²⁹Si CP NMR spectra were measured with a contact time of 3 ms and a recycle delay of 2 s. ²⁹Si CP NMR spectra were recorded with a 4 mm MAS probe with a spinning rate of 8 kHz. Chemical shifts were referenced to adamantane for ¹³C and 4,4-dimethyl-4-silapentane sulfonate sodium salt (DSS) for ²⁹Si.

Details of Theoretical calculation For theoretical calculations, a 74 T cluster model (Al 37 Si P 36 O 119) was extracted from the crystallographic data of CHA structure to represent the structure of H-SAPO-34 zeolite. In the theoretical calculations for the extended zeolite model, the bond length of terminal Si–H was fixed to 1.47 Å, oriented along the direction of the corresponding Si–O bond. One P atom was replaced by Si atom. And the locations of acid sites O(2) were chosen at the 8-ring window that is easy access by adsorbents and has maximum reaction space.^{1, 2}



The combined theoretical ONIOM method³⁻⁵ was applied to predict the geometries of various adsorption structures. During the structure optimizations, ω B97XD hybrid density function with 6-31G(d, p) basis sets and semi-empirical AM1 were employed for optimizing geometries of the high-level layer and low-level layer. To preserve the integrity of the zeolite structure during the structure optimizations, the 8-ring window, $(\text{SiO})_3\text{-Si-OH-Al}(\text{SiO})_3$ active center and the adsorbed species in the high-level layer were relaxed while the rest of atoms were fixed in the low-level at their crystallographic locations. To obtain high accurate energies, the single-point energies were calculated at the level of ω B97XD /6-31G(d,p). The energies reported here have been corrected for zero point vibration energies.

The interaction energy E_{inter} was calculated as: $E_{\text{inter}} = E - E_{\text{zeolite}} - E_{\text{template}}$, where E , E_{zeolite} , E_{template} refer to calculation energies of the system of the template inside SAPO-34, SAPO-34 framework and the template molecule, respectively. All density functional theory (DFT) calculations were performed with the Gaussian 09 package.⁶

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Catalytic test and qualitative analysis of coke deposits

Methanol to olefins (MTO) reaction was performed in a quartz tubular fixed-bed reactor at atmospheric pressure. 300 mg catalyst (40-60 mesh) was loaded in the quartz reactor and activated at 550 °C in a He flow of 30 mL min⁻¹ for 1 h before starting each reaction run, subsequently the temperature was adjusted to a reaction temperature of 450 °C. The methanol was fed by passing the carrier gas (28 mL min⁻¹) through a saturator containing methanol at 30 °C, which gave a weight hourly space velocity (WHSV) of 2 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. The amount of generated coke in catalysts after the MTO reactions was determined by thermal analysis on a TA SDTQ600 analyzer at a heating rate of 10 °C min⁻¹ from room temperature to 800 °C under air flow.

In order to capture the organic intermediates confined in the catalysts, the MTO reaction was operated as follow. After methanol feeding for 40 min at 350°C, the catalyst sample which had 100% methanol conversion at this stage was removed from the reactor quickly and put into liquid nitrogen to prevent the active intermediates from further reaction. The retained compounds in the catalysts were extracted by HF and analyzed by GS-MS.

The Guisnet method was used for the qualitative analysis of the coke species.¹ In a Teflon bottle, 100 mg catalyst was added into 2 mL HF solution (20 wt %). After the mixture was still standing for 1.5 h, 1 mL dichloromethane was added into the solution to extract coke species. NaOH solution (5 wt %) was added to neutralize HF. The organic phase was collected and analyzed by GC-MS testing with a HP-5 capillary column. Each compound was identified using the NIST11 database.

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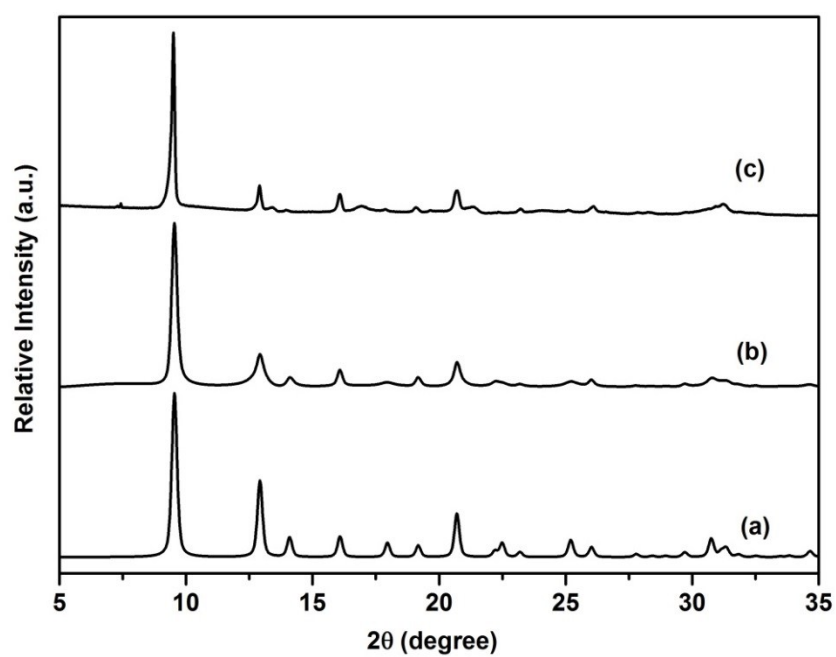


Fig. S1 DIFFaX simulations of the powder diffraction patterns of CHA/AEI intergrowths, 100% CHA (a) and 80% CHA (b). XRD patterns of calcined sample SP34-C (c).

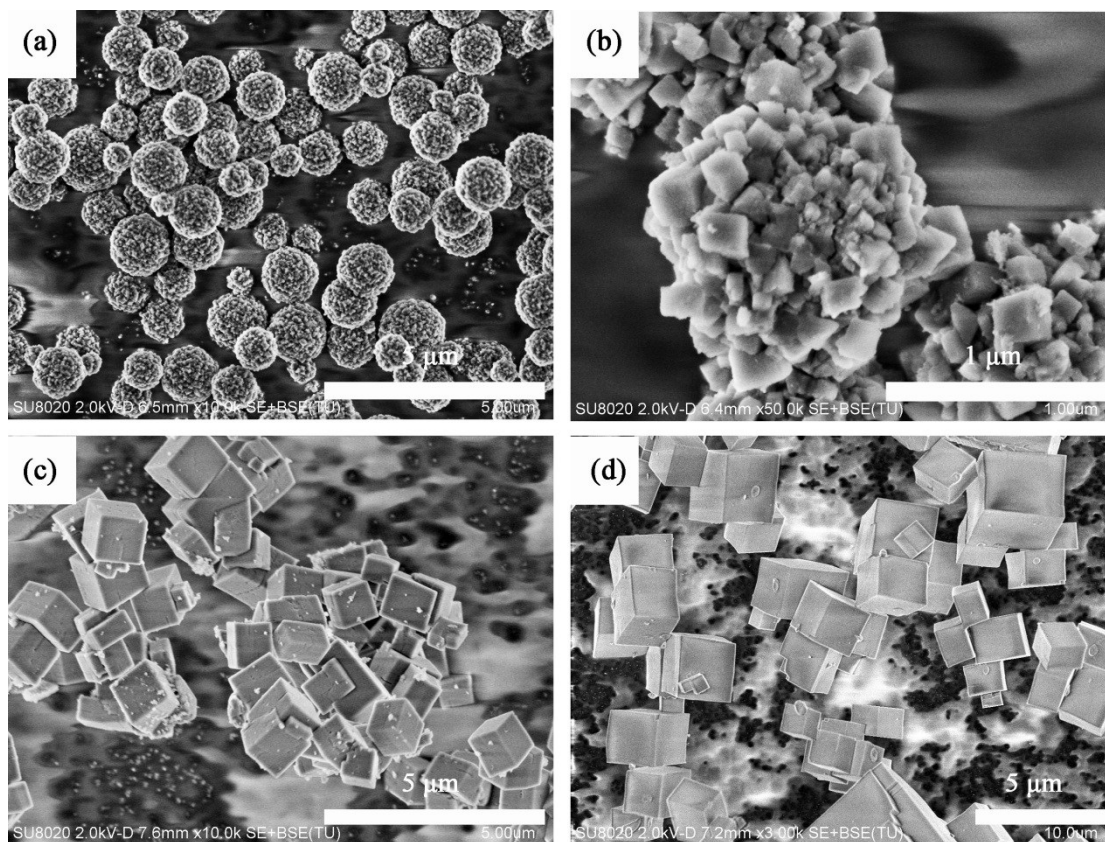


Fig. S2 SEM images of SP34-M3 (a), crushed SP34-M5 (b), SP34-P (c), and SP34-C (d).

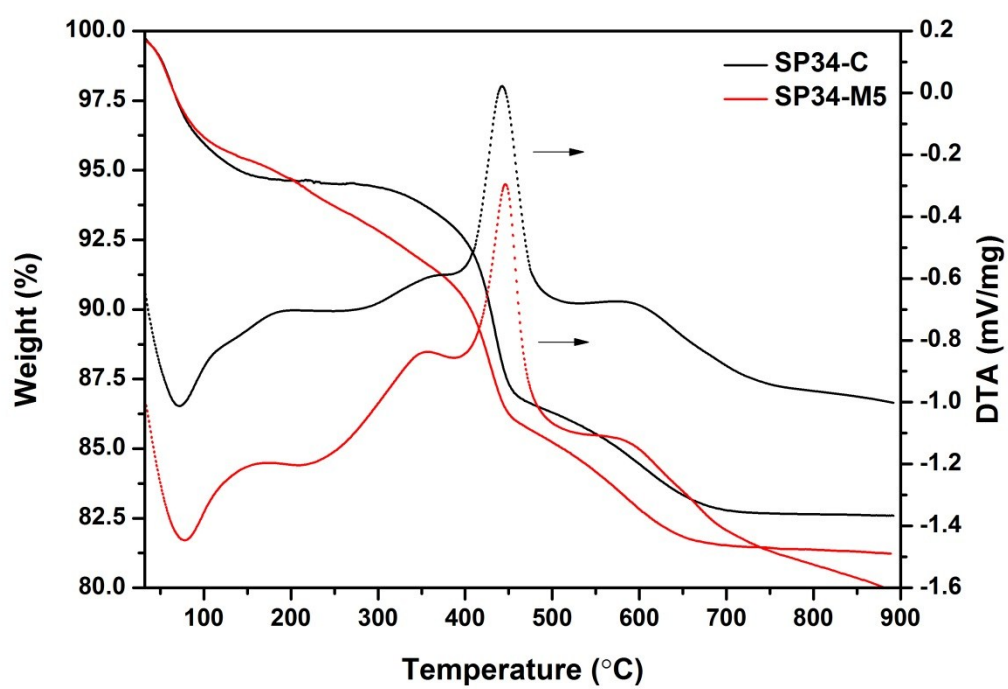


Fig. S3 TG-DTA curves of the as-synthesized SP34-M5 and SP34-C.

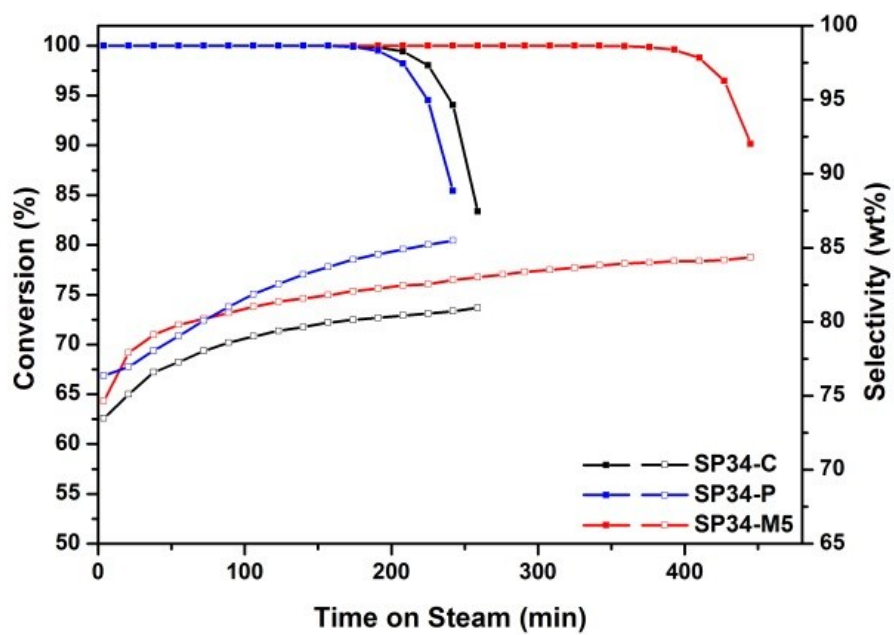


Fig. S4 Methanol conversion (solid) and ($C_2H_4+C_3H_6$) selectivity (hollow) variation with time-on-stream over samples. Experimental conditions: WHSV = 2 h^{-1} , $T = 450\text{ }^\circ\text{C}$, catalyst weight= 300 mg.

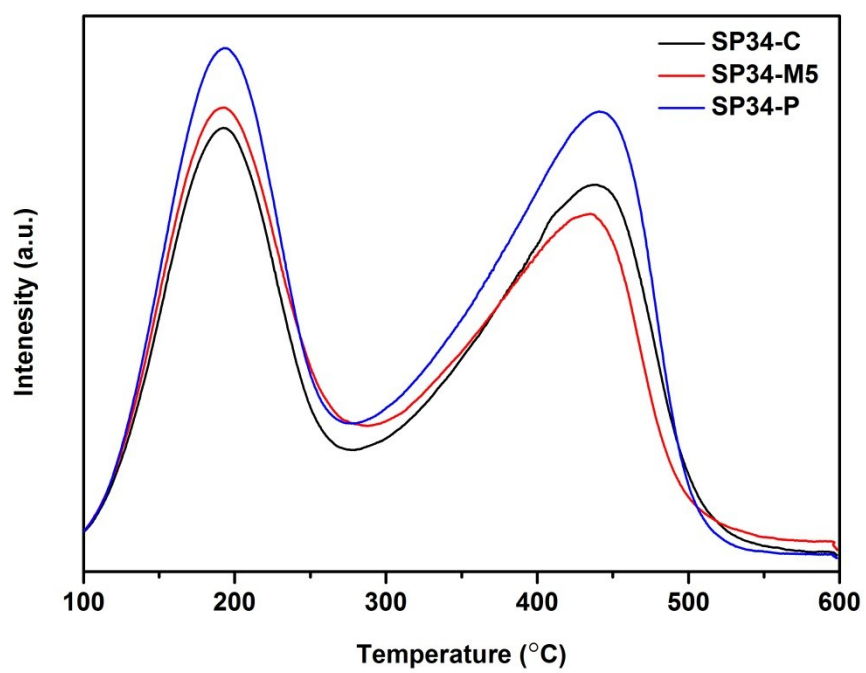


Fig. S5 NH₃-TPD profiles of samples.

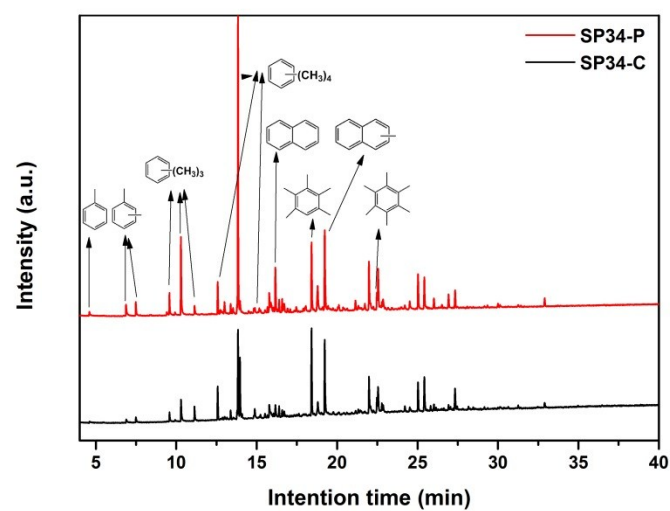


Fig.S6 GC-MS chromatograms of the hydrocarbon compounds retained in SP34-P and SP34-C after the MTO reaction. Experimental conditions: WHSV= 2 h⁻¹, T= 350 °C, reaction time= 40min, catalyst weight= 300 mg.

Table S1 Textural properties of the samples

| Sample | S_{BET}^a (m ² /g) | S_{mic}^b (m ² /g) | S_{ext}^b (m ² /g) | V_{mic}^b (cm ³ /g) | V_{meso}^c (cm ³ /g) |
|---------|---|---|---|--|---|
| SP34-M1 | 550 | 525 | 24 | 0.26 | 0.08 |
| SP34-M2 | 590 | 526 | 64 | 0.26 | 0.07 |
| SP34-M3 | 604 | 496 | 107 | 0.24 | 0.17 |
| SP34-M5 | 519 | 441 | 78 | 0.22 | 0.19 |
| SP34-P | 516 | 511 | 5 | 0.25 | 0.04 |
| SP34-C | 539 | 533 | 6 | 0.26 | 0.02 |

^a Total surface area is determined by the BET equation. ^b Micropore surface area, volume and external surface area are determined by the t-plot method. ^c Mesopore volume is determined from the adsorption isotherm by the BJH method.

Table S2 Thermogravimetric analyses and elemental analyses results of the as-synthesized samples

| Sample | Organic species weight loss ^a (%) | Molar ratio of C/N ^b | Molar ratio of TEA/PZPMS ^c |
|---------|--|---------------------------------|---------------------------------------|
| SP34-C | 12.04 | 5.99 | 1 |
| SP34-M2 | 12.96 | 5.77 | 0.89:0.11 |
| SP34-M3 | 15.26 | 5.45 | 0.73:0.27 |
| SP34-M5 | 13.49 | 5.58 | 0.79:0.21 |

^a Total organic species weight loss is determined by the TG analysis. ^b C/N ratio of as-synthesized samples is determined by the elemental analysis. ^c Calculated according to the different C/N ratio of TEA and PZPMS. The organosilane of PZPMS is considered to be hydrolyzed adequately.

Table S3 Detailed product distribution^a of samples in the MTO reaction (WHSV= 2 h⁻¹, T= 450 °C)

| Sample | CH ₄ (%) | C ₂ H ₄ (%) | C ₂ H ₆ (%) | C ₃ H ₆ (%) | C ₃ H ₈ (%) | C ₄ (%) | C ₅ (%) | C ₆ (%) | Total (%) |
|---------|---------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|--------------------|--------------------|--------------------|-----------|
| SP34-M5 | 2.15 | 50.00 | 0.36 | 33.65 | 0.44 | 8.70 | 3.59 | 1.11 | 100.00 |
| SP34-P | 1.40 | 49.85 | 0.75 | 34.71 | 1.68 | 8.39 | 2.52 | 0.70 | 100.00 |
| SP34-C | 1.88 | 43.25 | 0.60 | 37.17 | 1.85 | 10.47 | 3.61 | 1.17 | 100.00 |

^a Based on the highest selectivity of ethene and propene under >99% methanol conversion.

Table S4 Methylbenzenes distribution^a of samples in the MTO reaction (WHSV= 2 h⁻¹, T= 350 °C, reaction time= 40min)

| Sample | toluene (%) | xylene (%) | tri- (%) | tetra- (%) | penta- (%) | hexa- (%) | higher-substituted methylbenzenes ^b (%) |
|--------|----------------|---------------|-------------|---------------|---------------|--------------|---|
| SP34-P | 1.8 | 8.2 | 24.2 | 53.3 | 11.3 | 1.1 | 12.4 |
| SP34-C | 1.0 | 5.9 | 20.7 | 46.6 | 22.8 | 2.9 | 25.7 |

^a Only methylbenzenes species are calculated and normalized to 100% in order to make a better comparison. ^b The summary of the proportion of penta- and hexamethylbenzene.