

Supporting Information

Designing SAPO-18 with Energetically Favorable Tetrahedral Si Ions for MTO Reaction

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1. Experimental section

1.1 Chemicals and materials

H₃PO₄ (85.0 wt%), tetraethyl orthosilicate (TEOS), aluminum isopropoxide (Tokoy Chemical Ind. Co. Ltd. (TCI), Japan) were used as P, Si and Al sources, respectively. 4-Hydroxy-1,2,2,6,6-pentamethyl piperidin (HPP, aladdin, >98.0% (GC)), 4-hydroxy-2,2,6,6-tetramethyl piperidin (HTP, aladdin, >98.0% (GC)), 4-amino-2,2,6,6-tetramethyl piperidin (TEP, aladdin, >98.0% (GC)), were used as organic structure directing agents (OSDAs). All agents were used without further purification.

1.2 Synthesis of SAPO-18

SAPO-18 analogues were hydrothermally synthesized with different OSDAs from the initial gels with a molar ratio of 0.5 P₂O₅ : 0.5 Al₂O₃ : 1.0 OSDA : 0.3 SiO₂ : 30 H₂O. Typically, H₃PO₄ was mixed with water, then TEOS, aluminum isopropoxide, and OSDA were added into the above solution. The mixture was stirred at room temperature for 3 h. Afterward, the mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave and crystallized in an oven at 170 °C for 7 days. The autoclave was quenched by flowing tap water, and the solid product was obtained by filtration, washing, and dried in a vacuum oven at 80 °C for 12 h. The sample was then calcined at 550 °C for 6 h and the prepared SAPO-18 with different OSDAs was denoted S18-*x*, where *x* represents OSDAs of TEP, HTP and HPP.

2. Characterization methods

X-Ray Diffraction (XRD) patterns were recorded in the range of 5-50° on a Rigaku Ultima IV X-ray diffractometer using Cu-Kα ($\lambda=1.5406\text{\AA}$) with a scanning speed of 5° min⁻¹ and operated at 30 kV, 25 mA. The Scanning Electron Microscope (SEM) images were acquired on a Hitachi S-4800. Transmission electron microscopy (TEM) images were collected on an FEI G2F30 with an acceleration voltage of 200 kV. Nitrogen adsorption isotherms at 77K were obtained on a BELSORP-MAX instrument

after activating the calcined samples at 573 K. The chemical compositions of samples were measured with an inductively coupled plasma-atomic emission spectrometer (ICP-AES) equipped with a Thermo IRIS Intrepid II XSP atomic emission spectrometer. The thermogravimetric - differential thermal analyzer (TG-DTA) was carried out using Mettler-Toledo Model TGA/SDTA851e apparatus from room temperature to 1073 K at a heating rate of 10 K min⁻¹ in air atmosphere. ²⁹Si Magic-Angle-Spinning NMR (²⁹Si MAS NMR) was performed on a VARIAN VNMRS 400 WB NMR spectrometer using the single-pulse method at a frequency of 79.43 MHz, a spinning rate of 3 kHz, and a recycling delay of 60 s. The samples' acidity was characterized by temperature-programed desorption of ammonia (NH₃-TPD) spectra with increasing temperature from 353 to 1073 K was collected on micromeritics AutoChem II Chemisorption Analyzer, at a constant heating rate of 10 K min⁻¹. CHN elemental analysis was used for the atomic ratio of C and N atoms on Elementar Vario EL III.

3. MTO reaction

MTO reactions were carried out in a fixed-bed reactor. The reaction was performed at 400 °C. The weight hourly space velocity (WHSV) of methanol was 2 h⁻¹. Typically, 100 mg catalysts were loaded at the center of a quartz reactor, where the catalyst was pretreated at 500 °C for 1 h before reaction. Then methanol was pumped into the reactor to start the reaction. The products were analyzed online using a GC-7900 gas chromatograph equipped with a flame ionization detector (FID).

4. Computation

The location of the OSDAs in AEI was investigated by molecular mechanics simulation, which was implemented in the Forcite module of Materials Studio software.¹ The CVFF forcefield was used to describe the molecular structures of OSDAs. The framework structures of AEI were kept fixed during all calculations. Periodic boundary conditions and Charge equilibration method² were applied in calculations. The charge of OSDAs was compensated by the framework, according to

the TG results, the corresponding silicon atoms were inserted into the AEI framework. Initially, the location of OSDAs was manually docked in the AEI structure. The most stable location was calculated through simulated annealing. The interaction energy is equal to the total energy minus the energy of the molecular sieve framework and the energy of the template, respectively. The Dmol³ module of Materials Studio calculated the energy.

5. Results

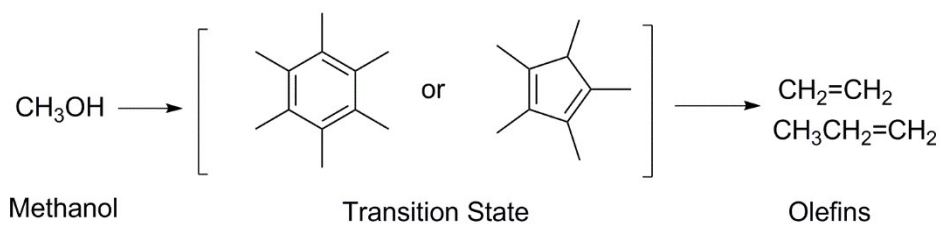


Figure S1 The molecular structures of two intermediate produced from MTO reaction.

The MTO reactions were clarified to take place through hydrocarbon pool mechanism,³⁻⁵ in which methylbenzenes or methylcyclopentenyl cations intermediates were involved.

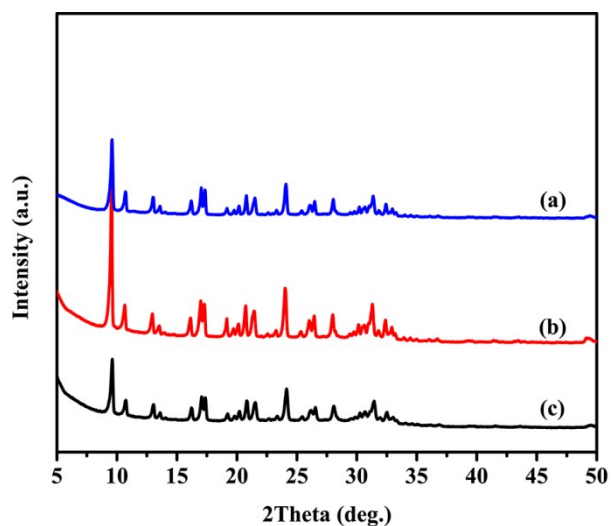


Figure S2 XRD patterns of (a) S18-HPP, (b) S18-HTP and (c) S18-TEP synthesized in this work.

The silicoaluminophosphate samples, hydrothermally synthesized with TEP, HPP and HTP as OSDA, were highly crystalline materials structurally analogous to SAPO-18 (AEI topology). No other impurity was observed.

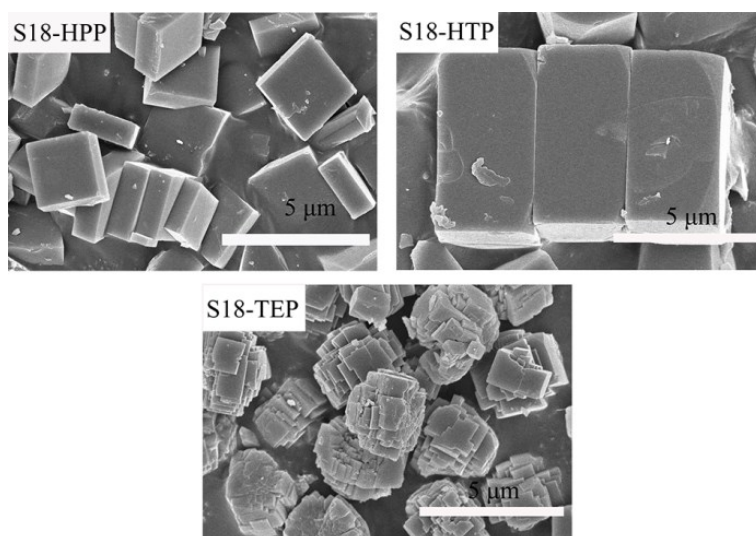


Figure S3 SEM images of S18-HPP, S18-HTP and S18-HPP.

The SEM images of sample S18-TEP, S18-TEP and S18-HTP are shown in Figure. S3. Overall, the morphology of SAPO-18 was significantly affected by the structure of OSDAs, and the OSDAs used in this work is conducive to form large SAPO-18 particles. Sample S18-HTP shows cubic-like crystals. Sample S18-TEP is very like a lot of square-platelet-like crystals growing with each other.

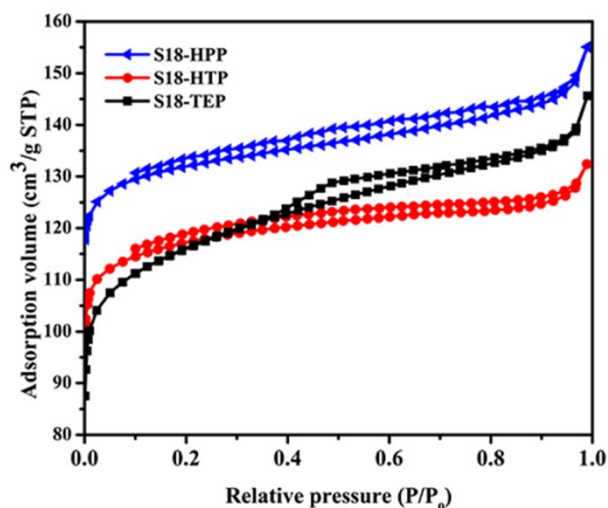


Figure S4 N₂ adsorption-desorption isotherms of sample S18-HPP, S18-HTP and S18-TEP.

The low-temperature N₂ adsorption-desorption was applied to measure the porosity of all samples. As shown in Figure S4, all samples show combination of type I and type IV isotherms, which suggested the existence of micropores and intercrystalline mesopores in all of the obtained samples.

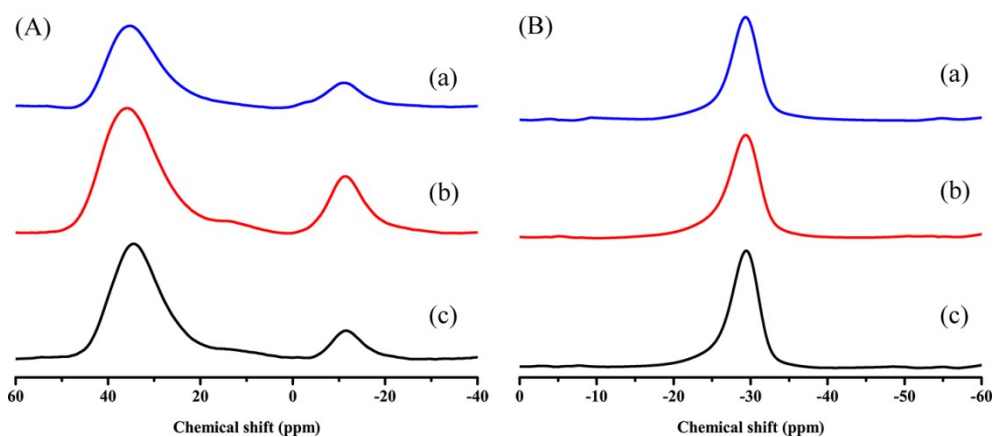


Figure S5 (A) ^{27}Al and (B) ^{31}P MAS NMR spectra of (a) S18-HPP, (b) S18-HTP and (c) S18-TEP.

The ^{27}Al and ^{31}P MAS NMR spectra of calcined sample S18-TEP, S18-HTP and S18-HPP are shown in Figure S5. As shown in Figure S5(A), a strong peak that appeared at 35 ppm arises from a tetrahedrally coordinated aluminum atom in all samples. A weak signal centered at 11 ppm can be ascribed to a penta-coordinated aluminum atom bonded with one water molecular. In the ^{31}P MAS NMR spectra (Figure S5(B)), a sharp dominating peak at -29 ppm, demonstrating all phosphorus atoms is tetrahedrally coordinated.

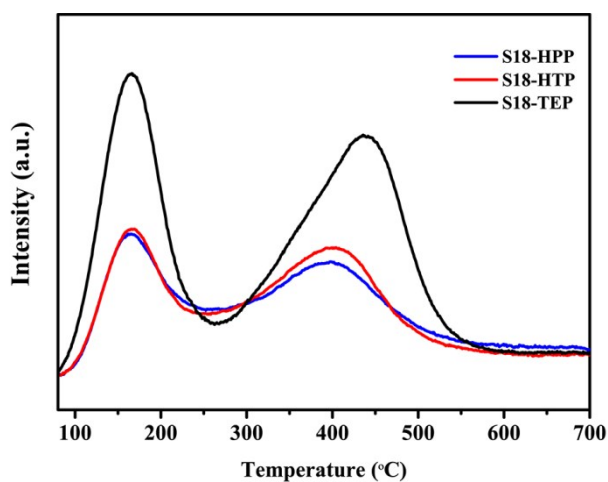


Figure S6 NH₃-TPD profiles of samples S18-HPP, S18-HTP and S18-TEP.

NH₃-TPD was used to measure the acidity of the prepared SAPO-18 with different OSDAs. As seen from the NH₃-TPD profile (Figure S6), samples S18-HPP and S18-HTP show similar distribution and concentration. Each profile shows two desorption peaks centered at about 150 ~ 200 °C and 350 ~ 450 °C, corresponding to weak acid sites and strong acid sites, respectively.

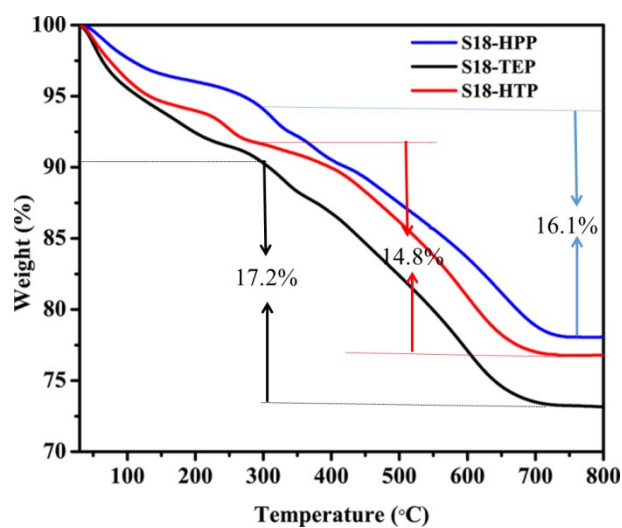
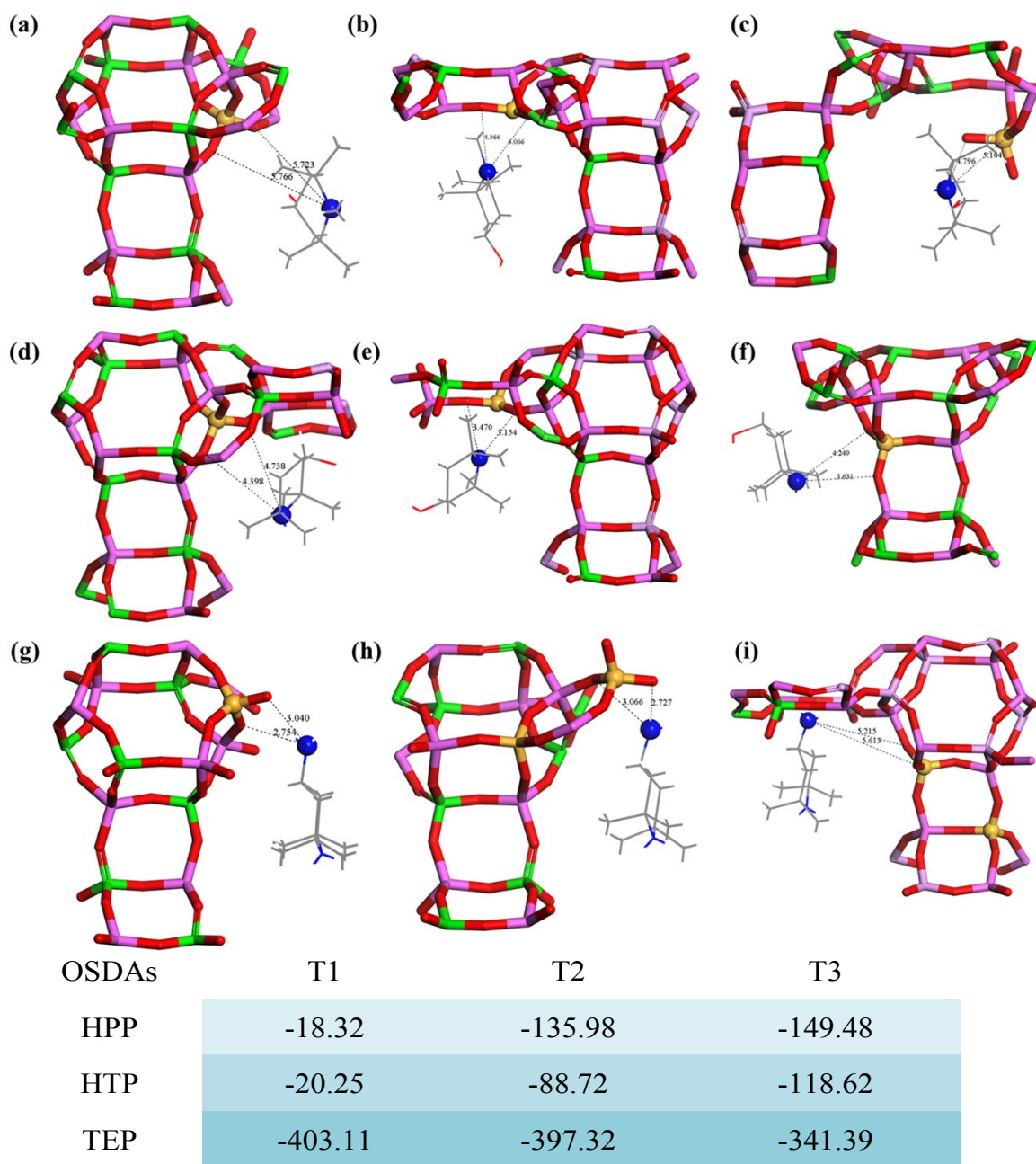


Figure S7 TG curves of as-made samples S18-HPP, S18-HTP and S18-TEP.

The OSDA content in different samples was determined by TG curves shown in Figure S7. Based on the weight losses, it is calculated that there is one OSDA per cell in all samples.



DFT calculated interaction energies in $\text{kJ}\cdot\text{mol}^{-1}$

Figure S8 The optimized structures of OSDAs located at different positions and the interaction energy of OSDA with different T sites in SAPO-18 zeolites: (a) HPP-T1, (b) HPP-T2, (c) HPP-T3, (d) HTP-T1, (e) HTP-T2, (f) HTP-T3, (g) TEP-T1, (h) TEP-T2 and (i) TEP-T3.

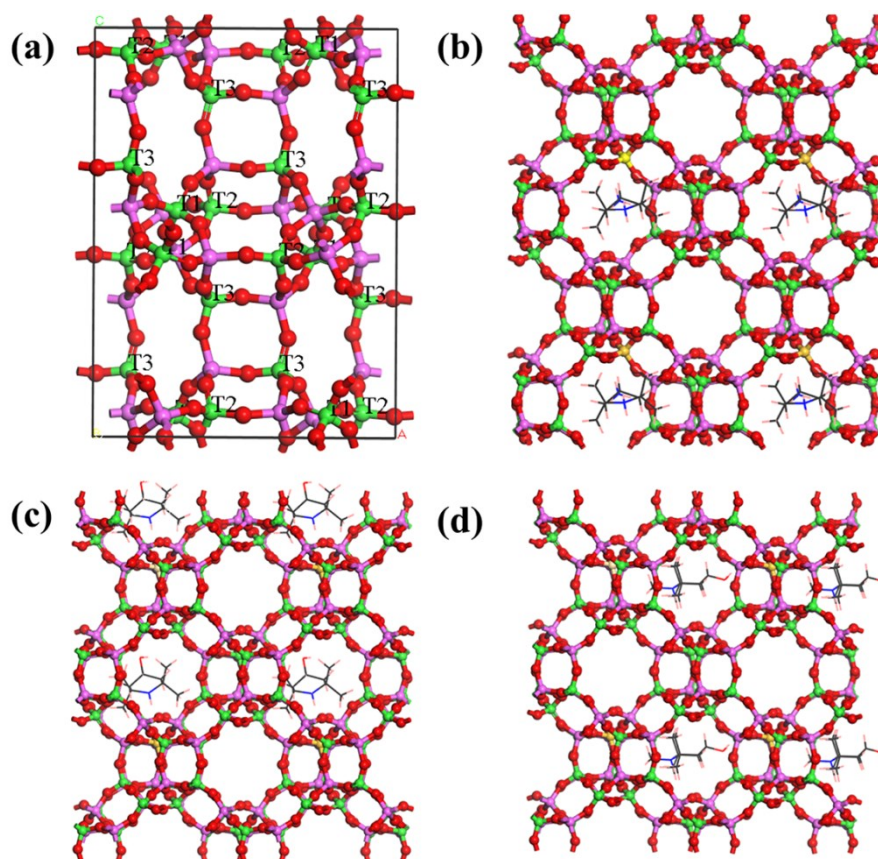


Figure S9 The positions of T1, T2, T3 in AEI framework (a), the positions of OSDAs in SAPO-18 samples, (b) S18-TEP, (c) S18-HTP and (d) S18-HPP.

There are three kinds of atom sites (T1, T2, T3) in the AEI framework (Figure S9, a). The T1 sites are the most stabilized crystallographic locations for Si ions in S18-TEP (Figure S9, b). However, using HTP and HPP as OSDAS (Figure S9, c-d), the Si ions are mainly located at T3 sites from interaction energy. The locations of OSDAs in SAPO-18 samples were shown in Figure S9. The green, violet, red, brown, black, blue, pink represent P, Al, O, Si, C, N, respectively.

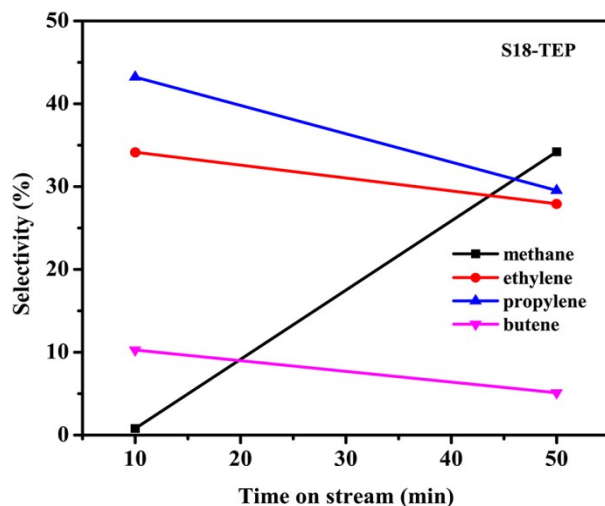


Figure S10 The selectivity of methane, C_2H_4 , C_3H_6 and C_4H_8 over sample S18-TEP.

The initial selectivity of propylene and ethylene is very high for S18-TEP, and a low selectivity of methane. However, as the reaction progresses, the selectivity of methane is rapidly improved, while at the same time, the selectivity of olefins is significantly reduced (Figure S10) .

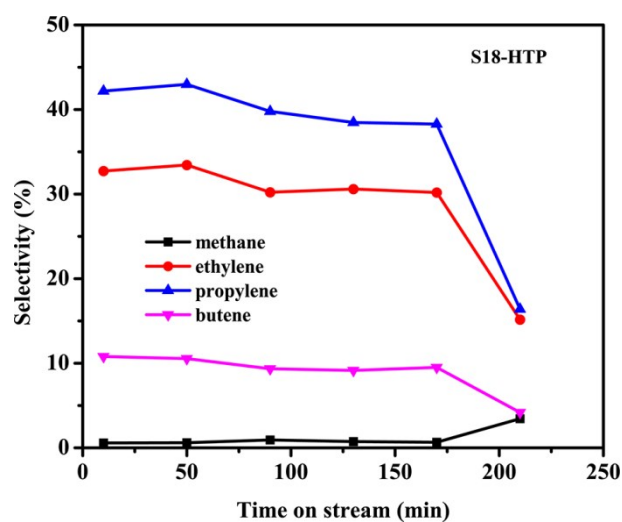


Figure S11 The selectivity of methane, C₂H₄, C₃H₆ and C₄H₈ over sample S18-HTP.

The initial selectivity of propylene is stable at about 40 %, accompanied by a low methane selectivity (Figure S11). Compared with S18-TEP, the life of S18-HTP is significantly increased, while the olefin selectivity is maintained in a relatively stable state.

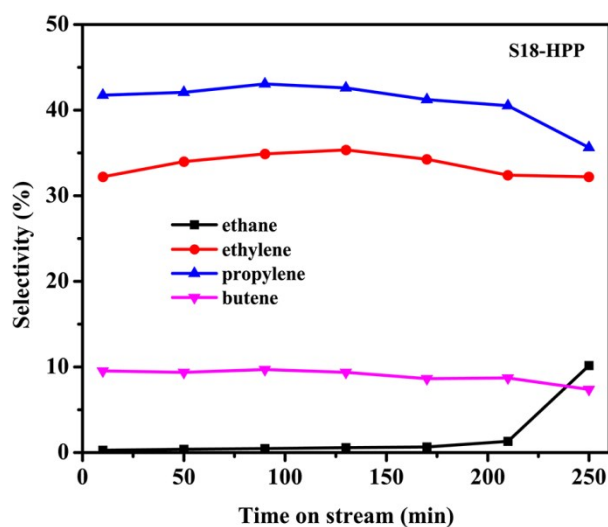


Figure S12 The selectivity of methane, C₂H₄, C₃H₆ and C₄H₈ over sample S18-HPP.

The selectivity of propylene is stable at about 40 %, accompanied by a low methane selectivity (Figure S11), and has a longer life span than S18-HTP. The acid content of sample S18-HPP is the least among the three samples in this work, and the acidity is also the weakest. The selectivity of olefin and methane is maintained at a relatively stable level.

Table S1 The physical properties of S18-HPP, S18-HTP and S18-TEP.

Sample	Surface area (m ² g ⁻¹)			Pore volume (cm ³ g ⁻¹)		
	S _{total} ^a	S _{ext} ^b	S _{micro} ^c	V _{micro} ^d	V _{meso}	V _{total} ^e
S18- HPP	466	37	429	0.19	0.05	0.24
S18- HTP	415	34	381	0.17	0.04	0.21
S18-TEP	410	78	332	0.15	0.08	0.23

^a Total surface area is calculated by the BET method.

^b External area is calculated by the *t*-plot method.

^c Micropore area = S_{total} - S_{ext}.

^d Micropore volume is calculated by the *t*-plot method.

^e Total pore volume is measured at relative pressure P/P₀=0.99.

Table S2 Chemical composition and thermal analysis of three AEI SAPO-18 materials.

Sample	Molar composition ^a	Weight loss(wt%)	
		Water	OSDA
S18-HTP	Si _{0.114} Al _{0.482} P _{0.404} O ₂	8.4	14.8
S18-TEP	Si _{0.144} Al _{0.485} P _{0.371} O ₂	9.7	17.2
S18-HPP	Si _{0.101} Al _{0.494} P _{0.405} O ₂	5.8	16.1

^a Given by ICP-AES.

Table S3 The product distribution in the MTO reaction over three SAPO-18 catalysts (TOS=10 min).

Catalyst	MeOH conv. (%)	P/E ratio	Product selectivity (%)					
			C ₁₋₄ ⁰	C ₂ ⁼	C ₃ ⁼	C ₄ ⁼	C ₅₊ ^N	Ar.
S18-HPP	99.9	1.3	7.2	32.2	41.7	9.5	9.4	0
S18-HTP	99.9	1.3	9.9	32.7	42.2	10.8	4.4	0
S18-TEP	50.0	1.3	6.3	34.2	43.2	10.3	6.0	0

Reaction conditions: catalyst, 0.1 g; WHSV = 2.0 h⁻¹; temperature, 673 K; N₂ gas flow rate, 20 mL min⁻¹. C₅₊^N: non-aromatic products with carbon numbers greater than 4; Ar.: aromatics.

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