

## Supporting Information

### Capture and identification of coke precursors to elucidate the deactivation route of methanol to olefins process over H-SAPO-34

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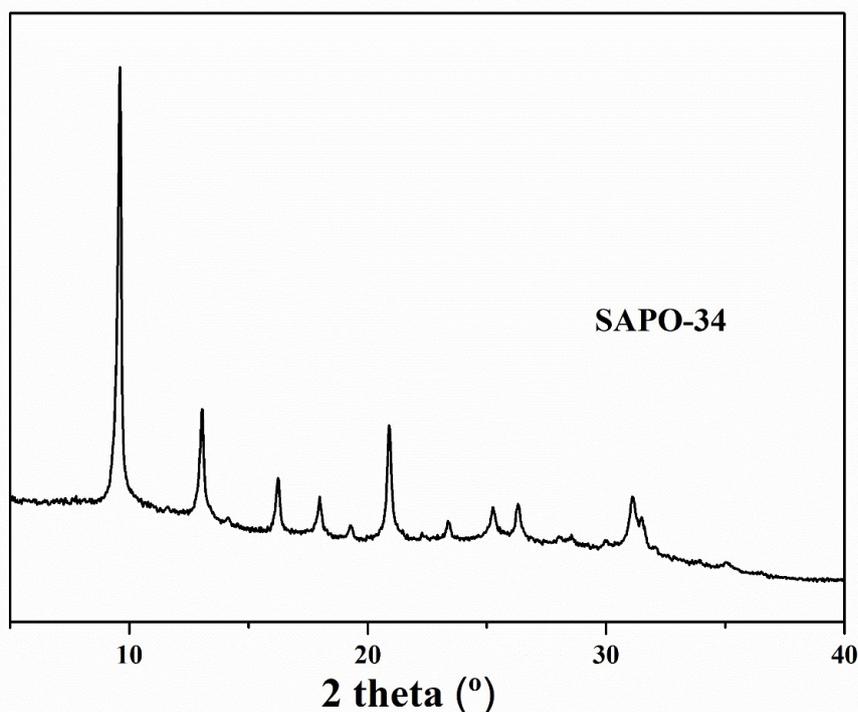
# 1. Catalyst Characterizations

## 1.1 Material Synthesis

H-SAPO-34 ( $n_{Si}/(n_{Si}+n_{Al}+n_P)=0.06$ ) was synthesized following the procedure described in the literature.<sup>1</sup> SAPO-34 was synthesized by a hydrothermal method with diethylamine (DEA) as a template.

## 1.2 Powder X-ray Diffraction (XRD)

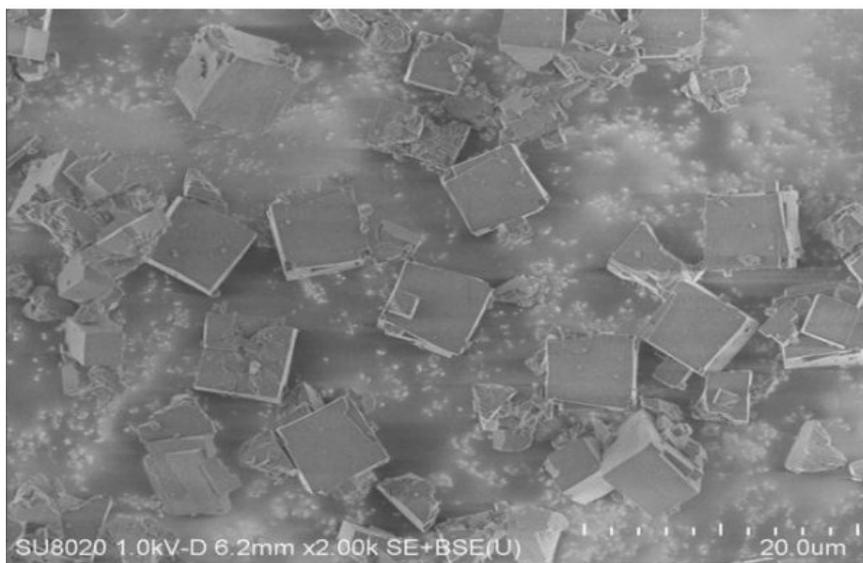
Powder X-ray diffraction (XRD) pattern of H-SAPO-34 was recorded on a PANalytical X'Pert PRO X-ray diffractometer equipped with Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm) from 5 and 40° with a scan speed of  $2\theta = 5.0$  °/min at 40 kV and 40 mA. The powder XRD pattern of SAPO-34 catalyst with high crystallinity was presented in Figure S1.



**Fig. S1** XRD patterns of H-SAPO-34 catalysts.

## 1.3 Scanning Electron Microscopy (SEM)

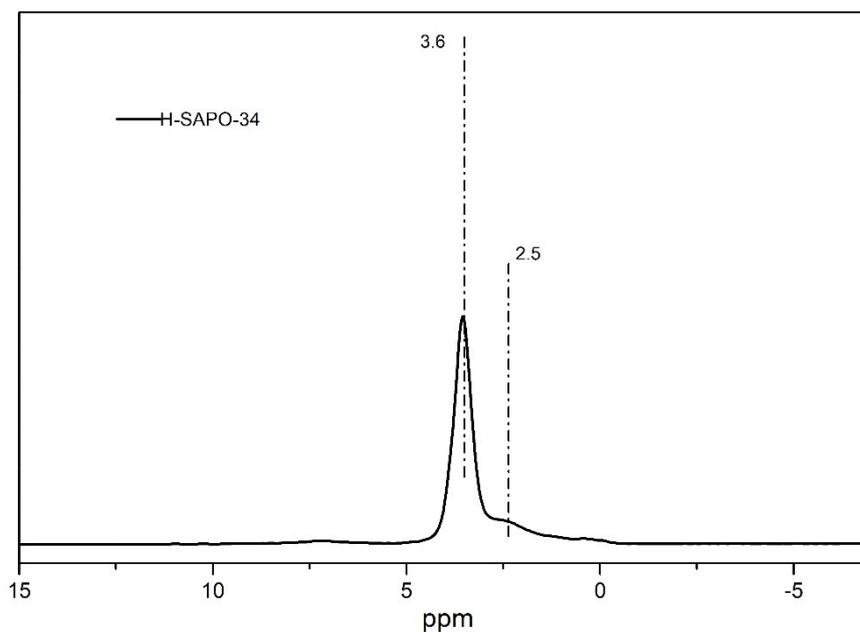
A HITACHI SU8020 Scanning Electron Microscope was employed to investigate the crystal size and morphology of H-SAPO-34 catalyst.



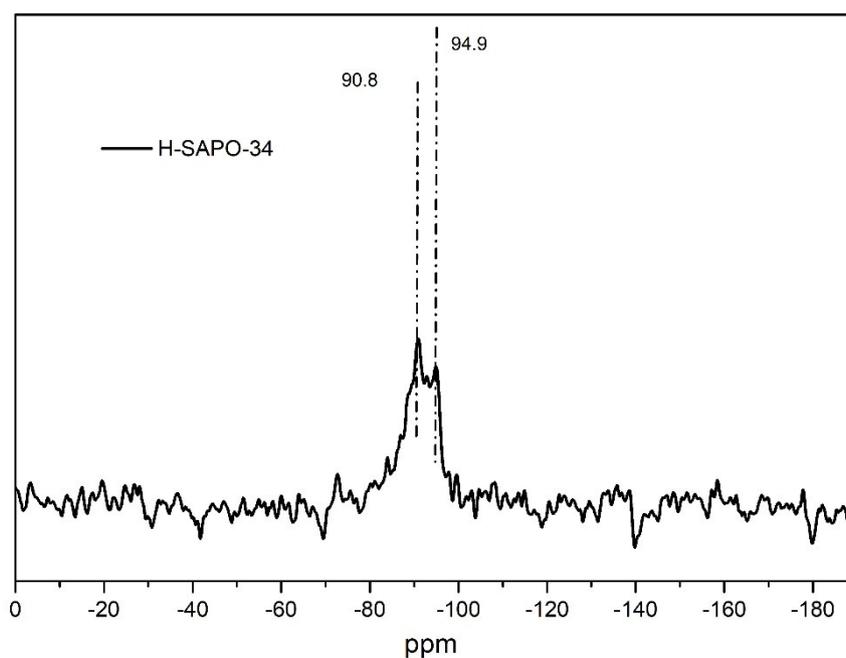
**Fig. S2** SEM images of H-SAPO-34 molecular sieves

#### **1.4 $^1\text{H}$ and $^{29}\text{Si}$ MAS NMR spectra**

$^1\text{H}$  NMR and  $^{29}\text{Si}$  NMR experiments were performed on a Bruker Avance III 600 spectrometer equipped with 14.1T wide-bore magnet. The resonance frequencies in this field strength were 119.2 MHz and 600.13 MHz for  $^{29}\text{Si}$ ,  $^1\text{H}$  respectively. The  $^{29}\text{Si}$  MAS NMR spectrum was recorded with a high power proton decoupling sequence with a spinning rate of 8 kHz. Chemical shifts of  $^{29}\text{Si}$  NMR spectrum was referenced to kaolinite at -91.5 ppm. Prior to  $^1\text{H}$  MAS NMR experiments, catalysts were pretreated at 693 K for 15 h under vacuum to completely remove adsorbed water and impurities in pore space. The  $^1\text{H}$  MAS NMR spectrum was recorded with onepulse sequence with a spinning rate of 12 kHz, and chemical shifts were referenced to adamantane at 1.74 ppm.



**Fig. S3**  $^1\text{H}$  MAS NMR spectra of H-SAPO-34-(Si/Si+Al+P=0.06 in molar ratio).



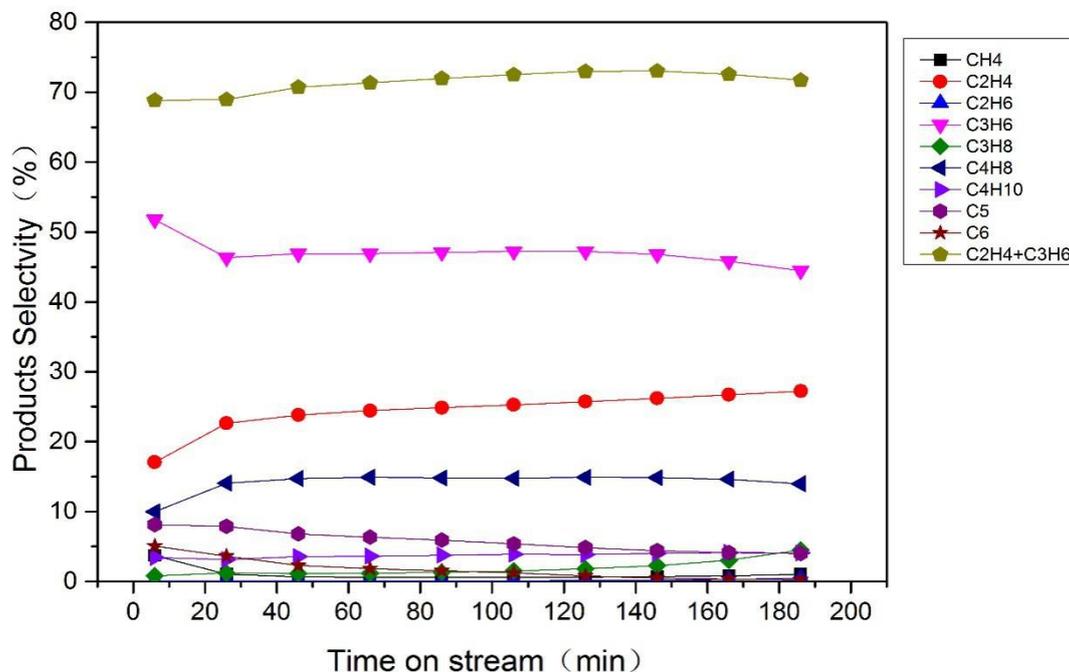
**Fig. S4**  $^{29}\text{Si}$  MAS NMR spectra of H-SAPO-34 (Si/Si+Al+P=0.06 in molar ratio).

## 2. Experimental and Theoretical section

### 2.1 Product Distribution of Methanol to Olefins Conversion

Methanol conversion was performed in a fixed-bed quartz tubular reactor at atmospheric pressure. A catalyst sample of 33.3 mg (40-60 mesh) was loaded into the reactor and the reactions was carried out at 350 °C. Methanol was fed by passing helium through a saturation evaporator with a WHSV of 6.0 h<sup>-1</sup>. The reaction products were analyzed by an on-line gas

chromatograph (Agilent GC 7890A) equipped with an HP-PLOT Q capillary column and a FID detector. The conversion and selectivity were calculated on a CH<sub>2</sub> basis. Dimethyl ether (DME) was considered as a reactant in the calculation.



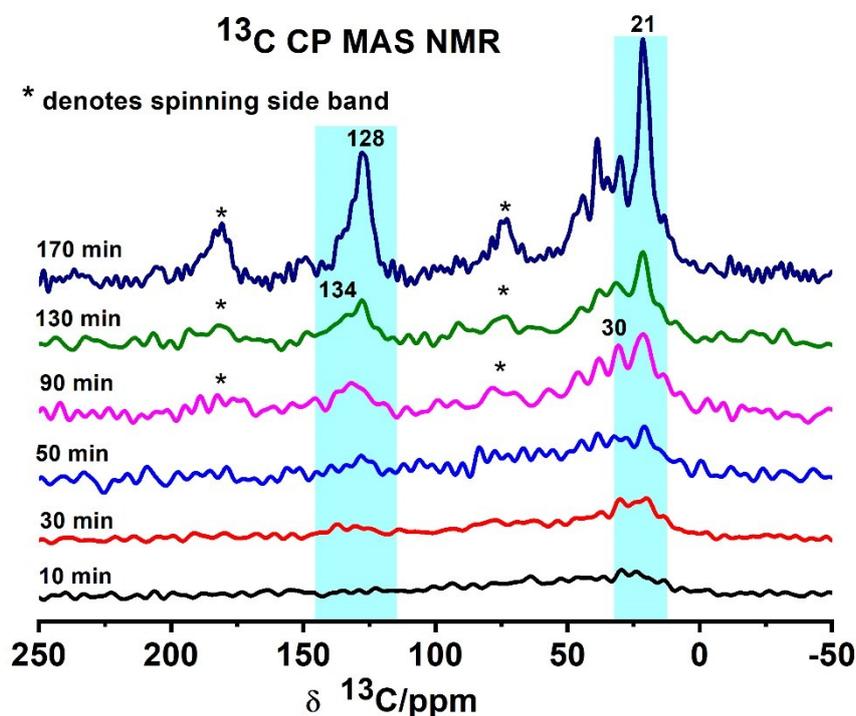
**Fig. S5** The gas phase products distribution of MTO reaction with time on stream over H-SAPO-34 at 350 °C, WHSV=6 h<sup>-1</sup>.

## 2.2 <sup>1</sup>H-<sup>13</sup>C CP MAS NMR experiment

Solid-state NMR spectra were recorded on a Bruker Avance III 600 MHz spectrometer equipped with a 14.1 T wide-bore magnet. <sup>13</sup>C MAS NMR spectra were collected at 150.9 MHz with a 3.2 mm HXY probe using a <sup>1</sup>H→<sup>13</sup>C cross polarization (CP) pulse sequence with a spinning speed of 8 kHz. The chemical shifts were referenced to adamantane with the up field methine peak at 29.5 ppm. The <sup>13</sup>C CP/MAS NMR spectra were acquired with a contact time of 3 ms and relaxation delay of 2 s.

Two distinct regions of aliphatic carbon (10-30 ppm) and aromatic carbon (120-137 ppm) were observed. Signals at 19-21 ppm accompanied by signals at 128 and 134 ppm confirm the formation of polymethyl-substituted benzenes. The occurrence of signals at 125-137 ppm reveal the formation of polycyclic aromatics combined with the analysis and identification of these retained organics by GC-MS. Moreover, the intensity of naphthalene derivatives and

polycyclic aromatics increase with time on-stream and these evolving trends virtually coincide with the results obtained from GC-MS.



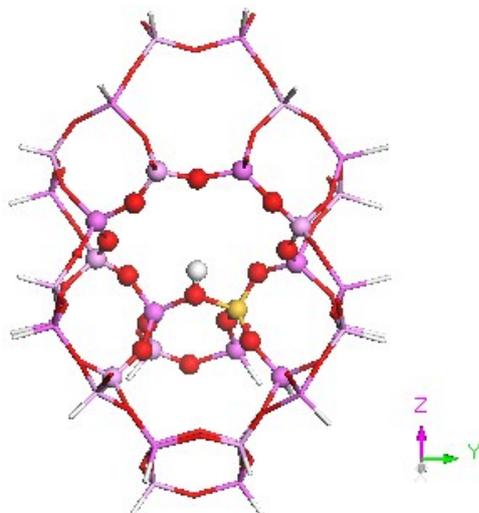
**Fig. S6**  $^{13}\text{C}$  MAS NMR spectra of retained organic species in H-SAPO-34 with time on stream over H-SAPO-34 after methanol conversion at 350 °C and WHSV of 6 h<sup>-1</sup>.

### 2.3 TG analysis

The total amount coke was analyzed by thermogravimetric analysis (TGA). 10mg of the spent catalyst was heated with 10 °C/min heating rate to 800 °C and was held isothermal for 1 h.

### 2.4 Theoretical calculation for the conversion of coke precursor

For theoretical calculations, a 74 T cluster model ( $\text{Al}_{37}\text{SiP}_{36}\text{O}_{119}$ ) represents the structure of H-SAPO-34 zeolite, which were extracted from the crystallographic data from the structure of CHA. In the theoretical calculations for the extended zeolite model, one P atom was then replaced by Si atom (see **Fig. S7**). 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<sup>2,3</sup>.



**Fig. S7** Representations of H-SAPO-34 framework structures by 74T cluster models.

The combined theoretical ONIOM method<sup>4-6</sup> was applied to predict the geometries of various adsorption structures and transition states (TS). During the structure optimizations,  $\omega$ 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. The  $\omega$ B97XD method is the hybrid meta DFT developed by Chai and Head-Gordon, where implicitly accounts for empirical dispersion and can describe long-range dispersion interactions well with respect to the traditional DFT methods<sup>7</sup>. To preserve the integrity of the zeolite structure during the structure optimizations, the 8-ring window,  $(\text{SiO})_3\text{-Si-OH-Al-(SiO)}_3$  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  $\omega$ B97XD /6-31G(d,p). The frequency calculations were performed at the same level as geometry optimizations to check whether the saddle points exhibit the proper number of imaginary frequencies. Only a single imaginary frequency was observed for the transition state. The energies reported here have been corrected for zero-point vibration energies. All density functional theory (DFT) calculations were performed with the Gaussian 09 package<sup>8</sup>. The intrinsic free energies ( $\Delta G^\ddagger$ ) are obtained from the  $\omega$ B97XD/6-31G(d, p) total electronic energies and the thermal correction from the  $\omega$ B97XD/6-31G(d,p):AM1 frequency calculations at 623 K. The reaction rate constants were obtained through transition state theory (TST) as implemented in the TAMkin program<sup>9</sup>, which was developed by Van Speybroeck's group.

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