Electronic Supplementary Information

Insights into the growth of small-sized SAPO-34 crystals synthesized by vapor-phase transport method

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1. Synthesis of SAPO-34 samples

1.1 Synthesis of TM-SAPO-34 (H)

2.5 g aluminum isopropoxide (AIP) was mixed with 2.58 g tetraethylammonium hydroxide (TEAOH, 35 wt%) solution, followed by dilution with 3 g deionized water and stirring for 4 h. Then 0.765 g tetraethyl orthosilicate (TEOS, 98%) was added into the gel and stirred for another 4 h. Subsequently, a dilute phosphoric acid solution prepared by dissolving 1.41 g orthophosphoric acid (85 wt%) in 2.8 g deionized water was added dropwise into the above gel. The composition of crude materials was as follows: Al_2O_3: SiO_2: P_2O_5: TEAOH: H_2O=1: 0.6: 1: 1: 70. The finally obtained gel was stirred at room temperature overnight and then dried at 80 °C over an oil bath with continuous stirring, allowing evaporation of water. The as-prepared dry gel was transferred to a 10 mL Teflon cup, placed in a Teflon-lined autoclave (100 mL) with 7.5 g water and 2.5 g morpholine (MOR) at the bottom of the autoclave. The crystallization of the dry gel was carried out at 200 °C for 72 h. The products were washed, air-dried and finally calcined at 550 °C for 6 h to remove the organic templates.

The synthesized sample is denoted as TM-SAPO-34 (H), wherein T, M stand for TEAOH and MOR, respectively. Besides, H stands for Heat, which is the pareparation method of dry gel.

1.2 Synthesis of TM-SAPO-34 (US+H)

The composition of hydrogel was Al_2O_3: SiO_2: P_2O_5: TEAOH: H_2O=1: 0.6: 1: 1: 70, the same with that of TM-SAPO-34 (H). Before being dried into a dry gel, the hydrogel was irradiated with ultrasound at a frequency of 37 kHz for 15 min. The sonication temperature was controlled by using a water bath at temperature of 45 °C. Then the ultrasonically treated hydrogel was dried by heating and stirring at 80 °C. The obtained dry gel was treated by a vapor generated from 7.5 g water and 2.5 g morpholine (MOR). The products were washed, air-dried and finally calcined at 550 °C for 6 h to remove the organic templates.

The synthesized sample is denoted as TM-SAPO-34 (US+H), wherein T, M stand for TEAOH and MOR, respectively. Besides, H and US stand for Heat and Ultrasonic treatment, respectively.

1.3 Synthesis of T-SAPO-34 (H)

The composition of hydrogel was Al_2O_3: SiO_2: P_2O_5: TEAOH: H_2O=1: 0.6: 1: 1: 70. Then the hydrogel was dried by heating and stirring at 80 °C. The obtained dry gel was treated by a vapor generated from 7.5 g water. The products were washed, air-dried and finally calcined at 550 °C for 6 h to remove the organic templates.

The synthesized sample is denoted as T-SAPO-34 (H), wherein T stands for TEAOH and H stands for Heat.

1.4 Synthesis of M-SAPO-34 (H)

The composition of hydrogel was Al_2O_3: SiO_2: P_2O_5: H_2O=1: 0.6: 1: 70. Then the hydrogel was dried by heating and stirring at 80 ^oC. The obtained dry gel was treated by a vapor generated from 7.5 g water and 2.5 g morpholine (MOR). The products were washed, air-dried and finally calcined at 550 ^oC for 6 h to remove the organic templates.

The synthesized sample is denoted as M-SAPO-34 (H), wherein M stands for MOR and H stands for Heat.

1.5 Synthesis of TM-SAPO-34 (E)

The composition of hydrogel is Al_2O_3: SiO_2: P_2O_5: TEAOH: H_2O=1: 0.6: 1: 1: 70. Then the hydrogel was diluted with 30 g ethanol, followed by being dispersed in a dish for solvent evaporation under reduced pressure. It took 5 ‒ 8 h to evaporate the solvent at room temperature in the drafty closet. The obtained dry gel was treated by a vapor generated from 7.5 g water and 2.5 g morpholine (MOR). The products were washed, air-dried and finally calcined at 550 ^oC for 6 h to remove the organic templates.

The synthesized sample is denoted as TM-SAPO-34 (E), wherein T, M stand for TEAOH and MOR, respectively. Besides, E stands for ethanol or evaporation.

1.6 Synthesis of Tb1M-SAPO-34 (H)

2.5 g aluminum isopropoxide (AIP) and 1.29 g tetraethylammonium bromide (TEABr) were mixed in 4.51 g water and stirred for 2 h. Then 0.918 g tetraethyl orthosilicate (TEOS, 98%) was added into the gel and stirred for another 4 h. Subsequently, a dilute phosphoric acid solution prepared by dissolving 1.41 g orthophosphoric acid in 3 g deionized water was added dropwise into the above gel. The compositions of hydrogel is Al_2O_3: SiO_2: P_2O_5: TEABr: H_2O=1: 0.6: 1: 1: 70. Then the hydrogel was dried by heating and stirring at 80 ^oC. The obtained dry gel was treated by a vapor generated from 7.5 g water and 2.5 g morpholine (MOR). The products were washed, air-dried and finally calcined at 550 ^oC for 6 h to remove the organic templates.

The synthesized sample is denoted as Tb1M-SAPO-34 (H), wherein Tb and M stand for TEABr and MOR, respectively. The number 1 stands for the mole ratio of TEABr to Al_2O_3. H stands for Heat.

1.7 Synthesis of Tb2M-SAPO-34 (H)

The composition of hydrogel is Al_2O_3: SiO_2: P_2O_5: TEABr: H_2O=1: 0.6: 1: 2: 70, and the other procedure is the same with that of Tb1M-SAPO-34 (H).

The synthesized samples are denoted as Tb2M-SAPO-34 (H), wherein Tb and M stand for TEABr and MOR, respectively. The number 2 stands for the mole ratio of TEABr to Al_2O_3. H stands for Heat.

2. Characterizations

X-ray diffraction (XRD) patterns were recorded with a Rigaku D/Max2550V diffractometer, with CuKa Radiation at 40 kV and 100 mA. The XRD patterns were collected in the range of 5–50^o in $2\theta/\theta$ scanning mode with a 0.02^o step and a scanning speed of 12 degrees per min. Nitrogen adsorption–desorption isotherms were measured on an ASAP 2020 (Micromeritics, USA) analyzer at -196 ^oC after the samples were degassed under vacuum for several hours at 250 ^oC. The specific surface area was calculated by the BET (Brunauer–Emmett–Teller) method based on the adsorption data at P/P_0 of 0.05–0.2. The micropore volume was calculated using *t*-plots at a P/P_0 of 0.1–0.4 (de Boer). The pore size distribution was calculated from the adsorption branch using the BJH (Barrett–Joyner–Halenda) method, and the total pore volume was obtained from the adsorption at P/P_0 = 0.99. Scanning electron microscopy (SEM) images were recorded on a Nova NanoSEM 450 at an acceleration voltage of 5 kV. The Fourier transform infrared spectra (Nicolet 6700 FTIR) of the sample were recorded in the range of 400~4000 cm^{-1} with a resolution of 2 cm^{-1}. The solid samples were pressed into KBr pellets. Solid-state ^{27}Al, ^{31}P and ^{29}Si MAS NMR spectra were conducted at room temperature in a Bruker AVANCE-400 spectrometer, operated at 12 kHz for ^{27}Al signals and 10 kHz for ^{29}Si and ^{31}P signals. ^{27}Al chemical shift of 0.0 ppm were obtained with reference to A 1.0 M solution of aluminum nitrate as an external standard. ^{31}P chemical shift of 0.0 ppm were obtained with reference to 85% H_3PO_4 as an external standard. ^{29}Si chemical shifts of 0.0 ppm were obtained with reference to tetramethylsilane (TMS) as an external standard. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris 1 TGA instrument at a heating rate of 10 ^{o}C min^{-1} in an air flow. Temperature programmed desorption of ammonia (NH_3-TPD) was performed on an apparatus TP-5080 (Tianjin Xianquan Technology Development Co., Ltd.). The sample (70 mg) was heated up to 500 ^{o}C using He (30 mL min^{-1}) to remove adsorbed components and then cooled down to 50 ^{o}C. Pure NH_3 was injected until adsorption saturation was reached. Subsequently, the system was flushed with He at a flow rate of 30 mL min^{-1} for 1 hour. The temperature was ramped up to 600 ^{o}C at a rate of 10 ^{o}C min^{-1}. A thermal conductivity detector (TCD) was used to measure the desorption profile of NH_3.

3. Catalytic testing

MTO reaction was carried out with a fixed-bed reactor at atmospheric pressure. 0.15 g of catalyst (40-60 mesh) was loaded into the quartz reactor (7 mm inner diameter). The sample was activated in a nitrogen flow at 500 ºC for 1 h, and then the temperature was reduced to a reaction temperature 450 ºC. The methanol was fed by passing the carrier gas (30 mL/min) through a saturator containing methanol at 20 °C. The weight hourly space velocity (WHSV) was 2.35 h^{-1}. The reaction products were analyzed using on online gas chromatograph (Ruimin GC-2060), equipped with a flame ionization detector (FID) and HP-PLOT Q capilliary column. The conversion and selectivity were calculated on CH_2 basis. Dimethyl ether (DME) was considered as reactant in the calculation.

Table S1 Parameters controlled in the synthesis of SAPO-34

Sample	SDA[a] in vapor	SDA in dry gel	Ultrasonic treatment	Drying method
T-SAPO-34 (H)	7.5 g H_2O	$TEAOH/Al_2O_3=1$	/	Heat, 80 ^{o}C
M-SAPO-34 (H)	2.5g MOR+7.5 g H_2O	$TEAOH/Al_2O_3=0$	/	Heat, 80 ^{o}C
TM-SAPO-34 (H)	2.5g MOR+7.5 g H_2O	$TEAOH/Al_2O_3=1$	/	Heat, 80 ^{o}C
TM-SAPO-34 (US+H)	2.5g MOR+7.5 g H_2O	$TEAOH/Al_2O_3=1$	45 ^{o}C, 15 min	Heat, 80 ^{o}C
TM-SAPO-34 (E)	2.5g MOR+7.5 g H_2O	$TEAOH/Al_2O_3=1$	/	Ethanol, RT
Tb1M-SAPO-34 (H)	2.5g MOR+7.5 g H_2O	$TEABr/Al_2O_3=1$	/	Heat, 80 ^{o}C
Tb2M-SAPO-34 (H)	2.5g MOR+7.5 g H_2O	$TEABr/Al_2O_3=2$	/	Heat, 80 ^{o}C

[a] SDA is short for structure-directing agent

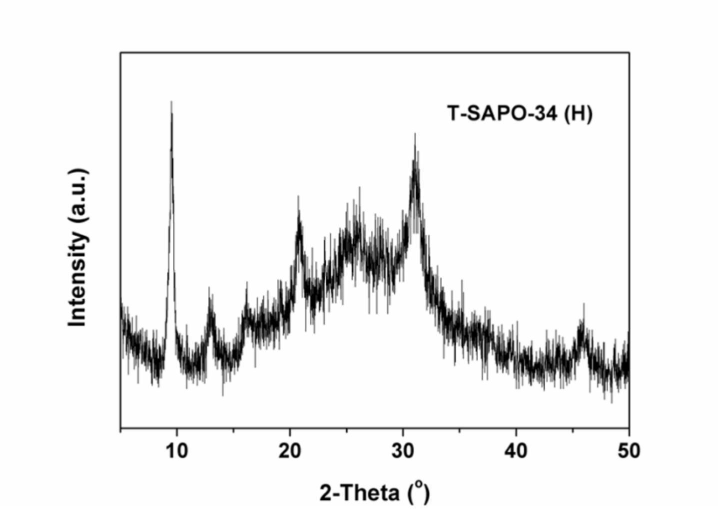

Fig. S1 XRD pattern of T-SAPO-34 (H) synthesized by steam-assisted conversion of dry gel with TEAOH/Al_2O_3=1.

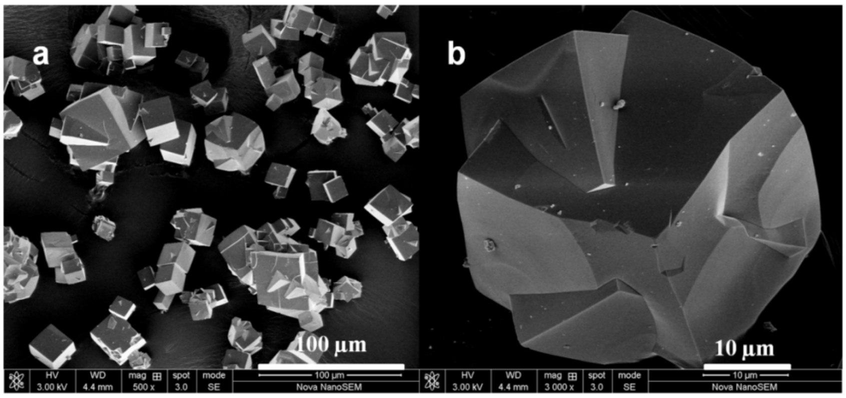

Fig. S2 SEM images of M-SAPO-34 (H).

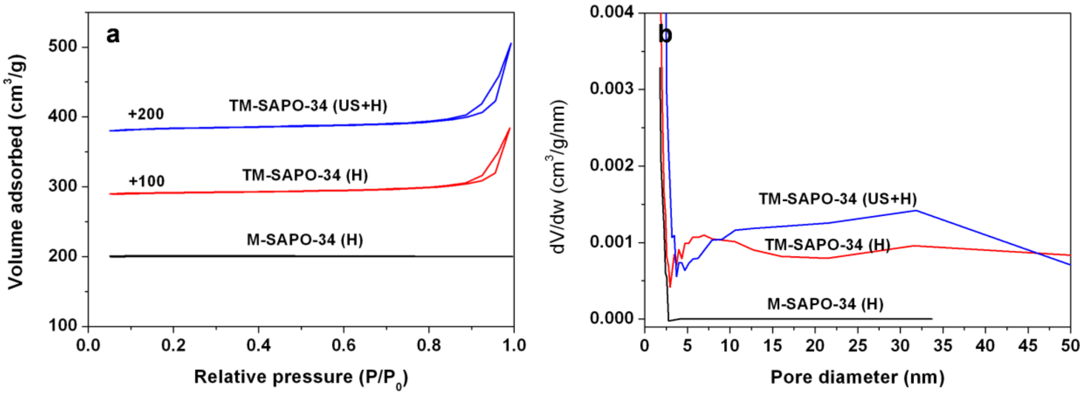

Fig. S3 (a) N_2 adsorption-desorption isotherms and (b) the corresponding pore size distributions of M-SAPO-34(H), TM-SAPO-34(H) and TM-SAPO-34 (US+H).

Table S2 Textural properties obtained by nitrogen physisorption experiments

Sample	S_{BET} (m^2g^{-1})	${}^aV_{micro}$ (cm^3g^{-1})	V_{total} (cm^3g^{-1})	${}^bV_{meso}$ (cm^3g^{-1})
M-SAPO-34 (H)	599	0.30	0.31	0.01
TM-SAPO-34 (H)	575	0.28	0.44	0.16
TM-SAPO-34 (US+H)	566	0.26	0.47	0.21

[a]Calculated from the t-plot method. [b] $V_{meso} = V_{ads,P/P0=0.99} - V_{micro}$.

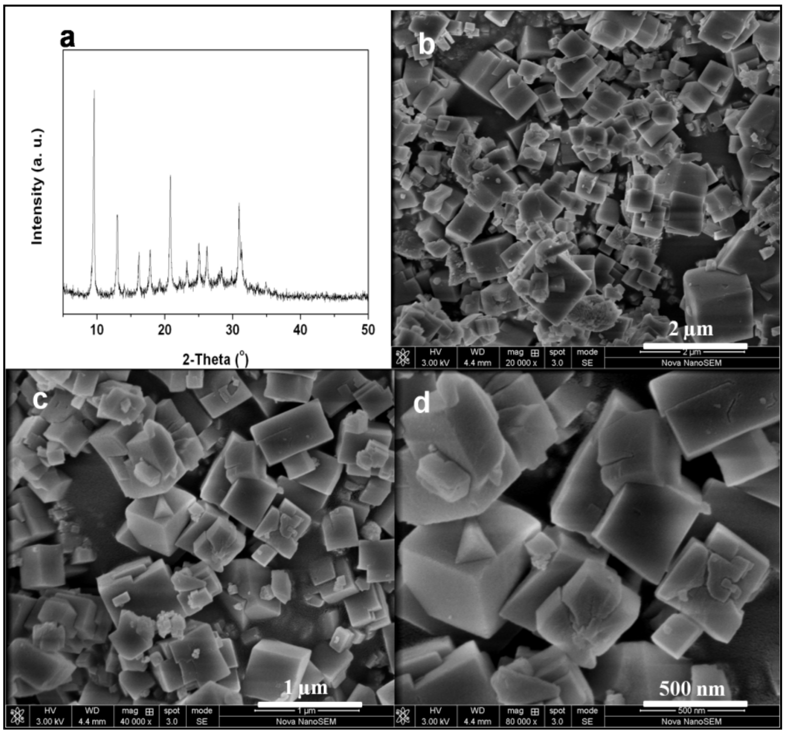

Fig. S4 (a) XRD pattern and (b,c,d) SEM images of TM-SAPO-34 (E).

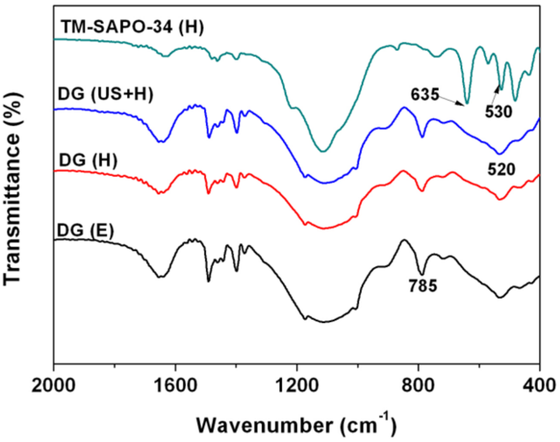

Fig. S5 FT-IR spectra of DG (E), DG(H), DG (US+H) and TM-SAPO-34 (H).

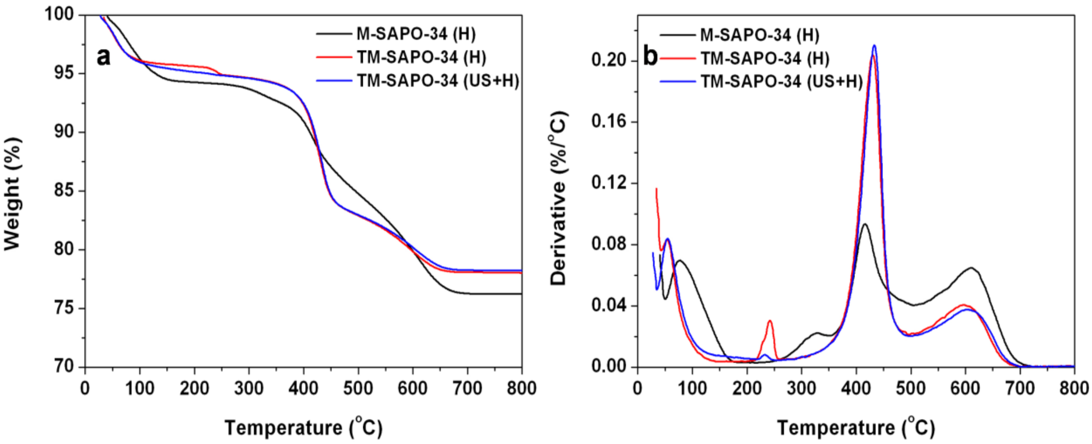

Fig. S6 TG-DTG curves of as-synthesized M-SAPO-34(H), TM-SAPO-34(H) and TM-SAPO-34 (US+H).

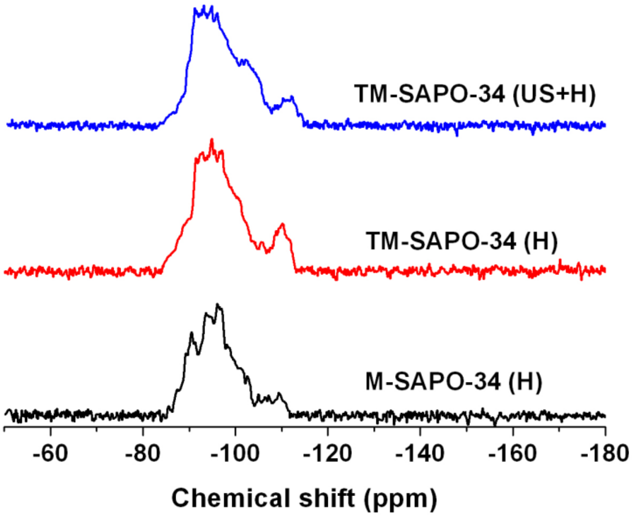

Fig. S7 ^{29}Si MAS NMR spectra of the synthesized samples.

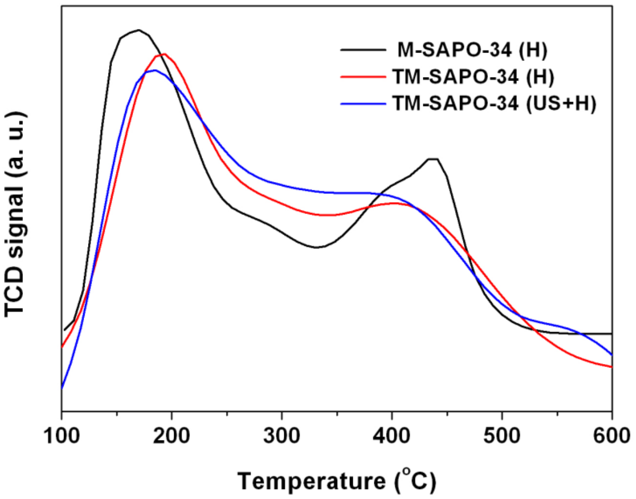

Fig. S8 NH_3 temperature programmed desorption (TPD) spectra of M-SAPO-34(H), TM-SAPO-34(H) and TM-SAPO-34 (US+H).

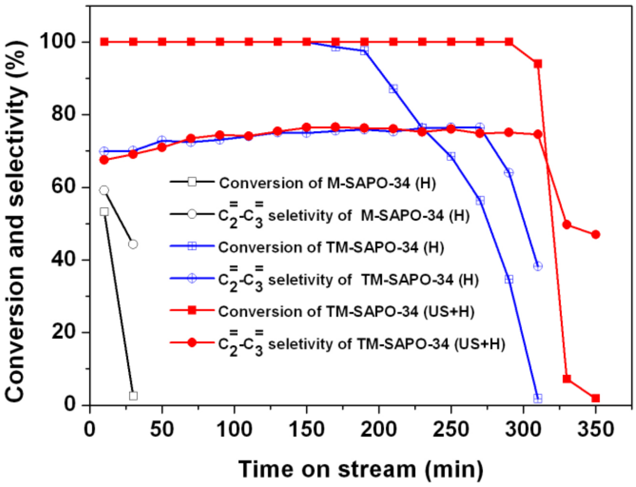

Fig. S9 Methanol conversion and selectivity of C_2H_4 plus C_3H_6 in the MTO reaction on the M-SAPO-34 (H), TM-SAPO-34 (H) and TM-SAPO-34 (US+H). Reaction conditions: 450 °C, WHSV = 2.35 h^{-1}

Table S3 MTO results on M-SAPO-34(H), TM-SAPO-34(H) and TM-SAPO-34 (US+H)[a]

Sample	Lifetime/min	Selectivity						
		CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	$C_2^=$-$C_3^=$
M-SAPO-34 (H)	10	10.1	35.2	0.9	23.9	0.2	17.2	59.1
TM-SAPO-34 (H)	270	5.5	42.8	1.5	33.5	0.8	11.1	76.3
TM-SAPO-34 (US+H)	310	4.2	41.0	1.6	35.5	1.2	11.5	76.5

a: Reaction condition: WHSV=2.35 h^{-1}, 450 °C; Lifetime: breakthrough point, described as 50% methanol conversion.

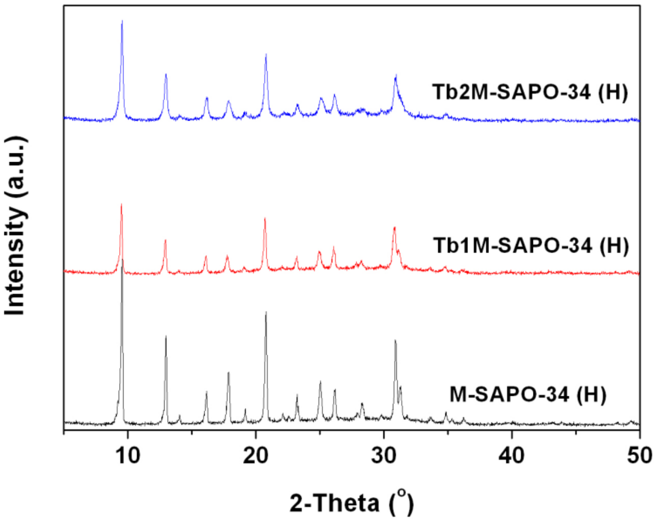

Fig. S10 XRD patterns of M-SAPO-34(H) (extracted from Fig. 2a), Tb1M-SAPO-34(H) and Tb2M-SAPO-34(H).

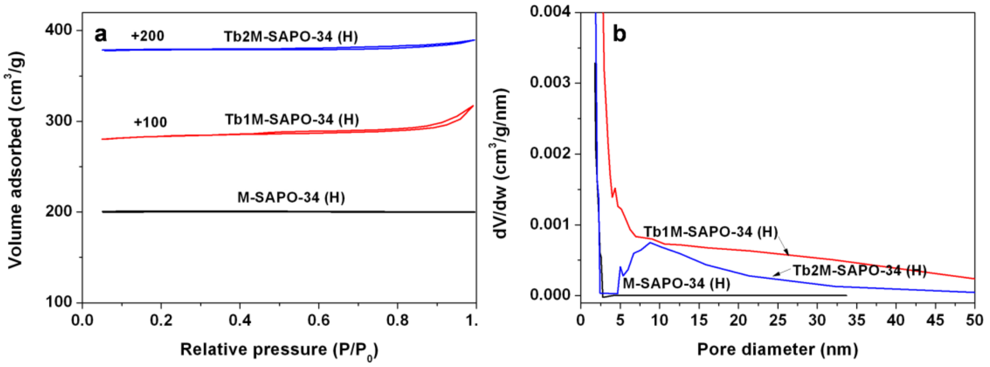

Fig. S11 (a) N_2 adsorption-desorption isotherms and (b) the corresponding pore size distributions of M-SAPO-34(H) (extracted from Fig. S3), Tb1M-SAPO-34(H) and Tb2M-SAPO-34 (H).

Table S4 Textural properties of M-SAPO-34(H) (extracted from Table S2), Tb1M-SAPO-34(H) and Tb2M-SAPO-34(H).

Sample	S_{BET} (m^2g^{-1})	$^aV_{micro}$ (cm^3g^{-1})	V_{total} (cm^3g^{-1})	$^bV_{meso}$ (cm^3g^{-1})
M-SAPO-34 (H)	599	0.30	0.31	0.01
Tb1M-SAPO-34 (H)	553	0.26	0.33	0.07
Tb2M-SAPO-34 (H)	535	0.26	0.29	0.03

^{a}Calculated from the t-plot method. ^{b} Vmeso = $V_{ads,P/P0=0.99}$ -V_{micro}.

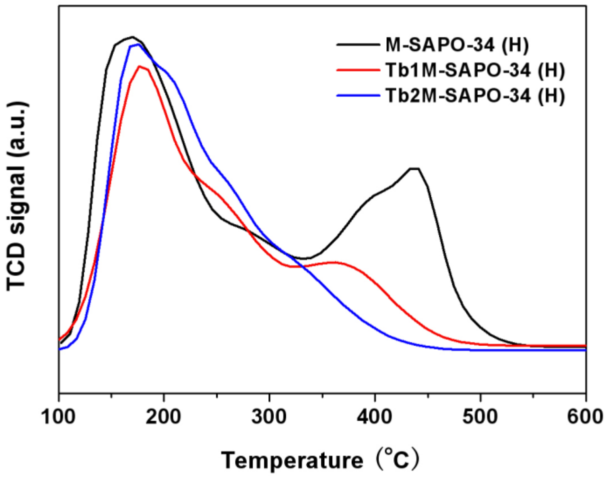

Fig. S12 NH_3 temperature programmed desorption (TPD) spectra of M-SAPO-34 (H) (extracted from Fig. S8), Tb1M-SAPO-34 (H) and Tb2M-SAPO-34 (H).

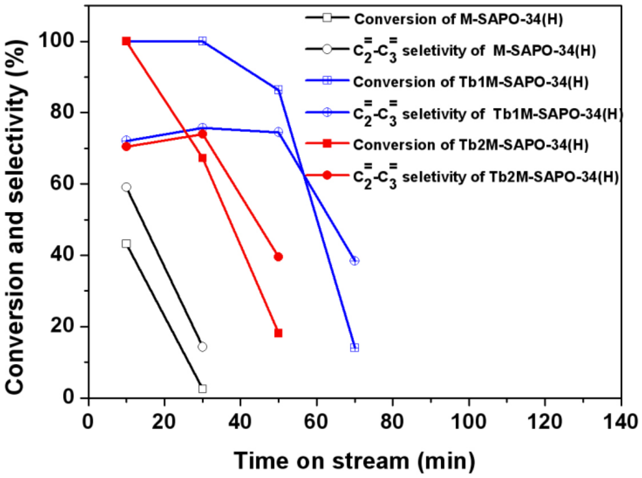

Fig. S13 Methanol conversion and selectivity of C_2H_4 plus C_3H_6 in the MTO reaction on the M-SAPO-34 (H) (extracted from Fig. S9), Tb1M-SAPO-34 (H) and Tb2M-SAPO-34 (H). Reaction conditions: 450 ^{o}C, WHSV = 2.35 h^{-1}

Table S5 MTO results on M-SAPO-34(H) (extracted from Table S3), Tb1M-SAPO-34(H) and Tb2M-SAPO-34(H)^{a}.

Sample	Lifetime/min	Selectivity						
		CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	$C_2^=$-$C_3^=$
M-SAPO-34 (H)	10	10.1	35.2	0.9	23.9	0.2	17.2	59.1
Tb1M-SAPO-34 (H)	50	5.1	44.8	1.6	31.0	0.9	11.3	75.8
Tb2M-SAPO-34 (H)	30	6.5	41.3	1.4	34.3	0.3	11.6	75.6

a: Reaction condition: WHSV=2.35 h^{-1}, 450 ^{o}C; Lifetime: breakthrough point, described as 50% methanol conversion.

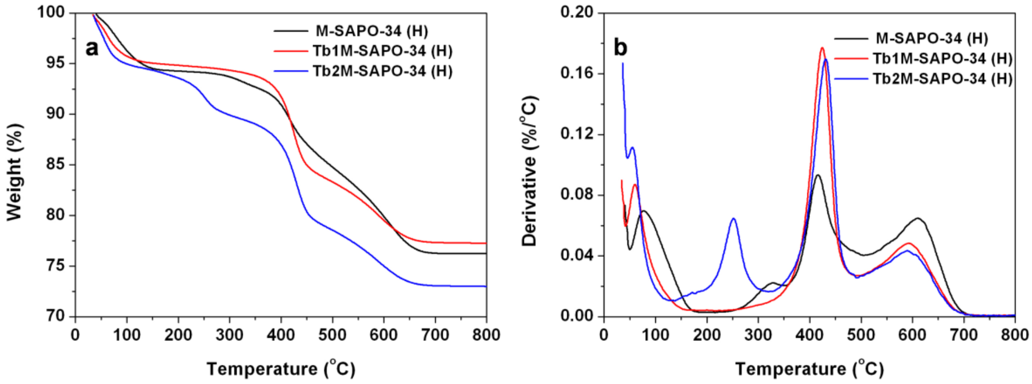

Fig. S14 TG-DTG curves of as-synthesized M-SAPO-34 (H) (extracted from Fig. S6), Tb1M-SAPO-34 (H) and Tb2M-SAPO-34 (H).