Electronic Supplementary Information (ESI)

Organosilane surfactant-directed synthesis of hierarchical porous SAPO-34 catalysts with excellent MTO performance

Qiming Sun,[a] Ning Wang,[a] Dongyang Xi,[a] Miao Yang,[b] and Jihong Yu*[a]

[a] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China

[b] National Engineering Laboratory for Methanol to Olefins, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China.

Contents

A. Materials and Methods

The reagents used were aluminum iso-propoxide ($Al(OPr^i)_3$ (99.5 wt%, Beijing Reagents Company), phosphoric acid (H_3PO_4, 85 wt%, Beijing Chemical Works), morpholine (Mor) (98.5%, Tianjin Guangfu fine chemical research institute), tetraethylorthosilicate (TEOS) (Beijing Chemical Works), [3-(trimethoxysilyl)propyl]octadecyldimethyl-ammonium chloride (TPOAC) (Nanjing Robit Co., Ltd.)

Hierarchical porous SAPO-34 catalysts (S_{H1} and S_{H2}). The hierarchical porous SAPO-34 catalysts (SH_1 and SH_2) were synthesized from the starting gels with the optimized molar compositions of $1.0Al_2O_3$: $1.0P_2O_5$: 3.0Mor: $0.6SiO_2$: $80H_2O$: *x*TPOAC (*x*=0.1 and 0.15) under hydrothermal conditions at 180 ° C by using morpholine (Mor) as the template for micropore and TPOAC for mesopore. Typically, the TPOAC was firstly mixed with Mor solution and deionized water at room temperature with fast stirring overnight until dissolved completely. The finely ground $Al(OPr^i)_3$ was added into the mixture slowly and then stirred for 2 h continuously. Phosphoric acid was then added dropwise to the resultant solution, followed by a continuous stirring for 2 h. Finally, TEOS was added slowly. The reaction mixture was further stirred for 1 h and was then transferred into a 100 mL Teflon-lined stainless steel autoclave. The crystallization was conducted in a conventional oven at 180 °C for 3 days under static conditions. The as-synthesized solid products were centrifuged, washed with water and ethanol for several times, and then dried at 80 °C in the oven overnight, followed by calcination at 600 °C for 8 h.

Conventional microporous SAPO-34 catalyst (S_M). The conventional microporous SAPO-34 (S_M) was synthesized from the starting gel with the molar composition of $1.0Al_2O_3$: $1.0P_2O_5$: 3.0Mor: $0.6SiO_2$: $80H_2O$. Typically, the finely ground $Al(OPr^i)_3$ was firstly mixed with Mor solution and deionized water at room temperature and then stirring for 2 h constantly. Phosphoric acid was then added dropwise to the resultant solution, followed by a continuous stirring for 2 h. Finally, TEOS was added slowly. The reaction mixture was further stirred for 1 h and was then transferred into a 100 mL Teflon-lined stainless steel autoclave. The crystallization was conducted in a conventional oven at 180 °C for 3 days under static conditions. The as-synthesized solid products were centrifuged, washed with water and ethanol for several times, and then dried at 80 °C in the oven overnight, followed by calcination at 600 °C for 8 h.

B. Characterizations

The crystallinity and phase purity of the samples were characterized by powder X-ray diffraction on a Rigaku D-Max 2550 diffractometer using Cu Kα radiation (λ = 1.5418 Å). The crystal size and morphology were measured by a scanning electron microscopy (SEM) using a JSM-6510 (JEOL) electron microscope. Transmission electron microscopy (TEM) images were recorded with a Tecnai F20 electron microscope. Thermogravimetric (TG) analysis was performed on a Perkin-Elmer TGA7 unit in air at a heating rate of 10 K min^{-1} from room temperature to 800 °C in air. Thermogravimetric and differential thermal analysis (TG-DTA) were carried out on a NETZSCH STA 449C in air at a heating rate of 20 K/min from room temperature to 800 ° C. Chemical compositions were determined with inductively coupled plasma (ICP) analyses carried out on a Perkin-Elmer Optima 3300 DV ICP instrument. Elemental analyses were conducted on a Perkin-Elmer 2400 elemental analyzer. Infrared (IR) spectrum was recorded by Nicolet Impact 410 FTIR infrared instrument. 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. The temperature-programmed desorption of ammonia (NH_3-TPD) experiments were performed using a Micromeritics AutoChem II 2920 automated chemisorption analysis unit with a thermal conductivity detector (TCD) under helium flow. All NMR experiments were performed on a Varian Infinity plus 400WB spectrometer with BBO MAS probe operating at a magnetic field strength of 9.4 T. The resonance frequencies in this field strength were 161.9, 104.2, 79.5 and 400.1 MHz for ^{31}P, ^{27}Al, ^{29}Si and ^{1}H respectively. Chemical shifts were referenced to 1.0 M $Al(NO_3)_3$ for ^{27}Al, 85% H_3PO_4 for ^{31}P, and 2,2-dimethyl-2-ilapentane-5-sulfonate sodium salt (DSS) for ^{29}Si and ^{1}H. The spinning rates of the samples at the magic angle were 4, 10, 6 and 8 kHz for ^{29}Si, ^{27}Al, ^{31}P, and ^{1}H, respectively.

C. Catalytic tests and carbon deposit analyses.

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 773 K in a N_2 flow of 30 mL/min for 1 h before starting each reaction run and then the temperature was adjusted to reaction temperature of 673 K. The methanol was fed by passing the carrier gas (15 mL/min) through a saturator containing methanol at 40 °C, which gave a WHSV of 2.0 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 19091-Q04, 30m × 320µm × 10µm). The schematic of catalytic test set-up is shown in Scheme S1. 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 Perkin-Elmer TGA7 at a heating rate of 10 K min^{-1} from room temperature to 800 °C under air flow.

D. Supplementary Figures and Tables

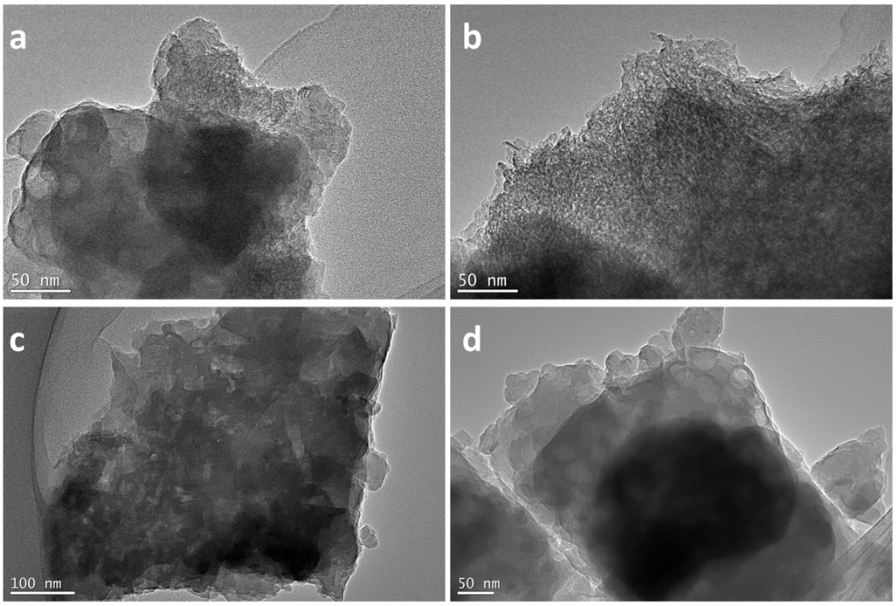


Fig. S1 TEM images of hierarchical porous SAPO-34 catalysts S_{H1} (a, b) and S_{H2} (c, d)

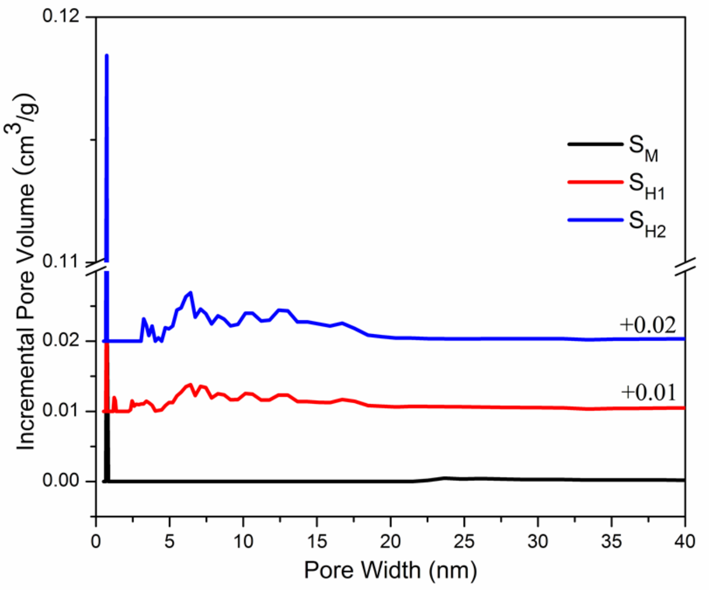


Fig. S2 DFT pore size distribution curves of conventional microporous SAPO-34 (S_M) and hierarchical porous SAPO-34 (S_{H1} and S_{H2}) catalysts.

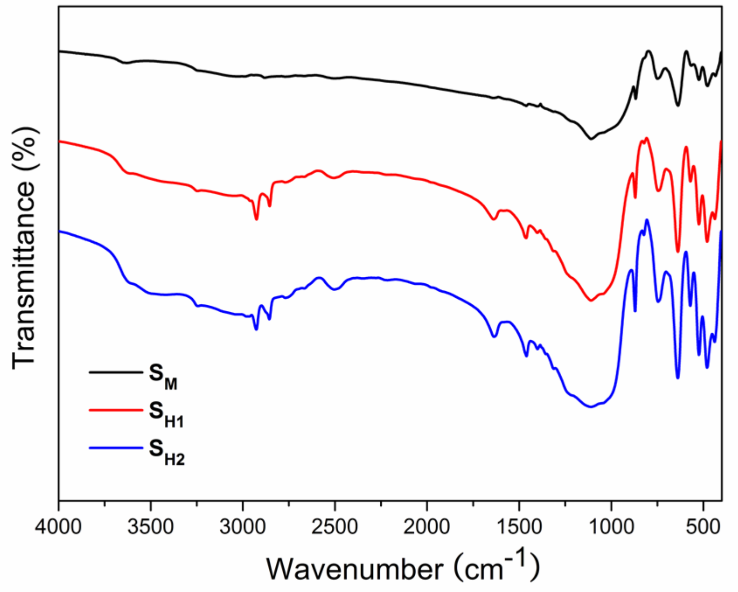


Fig. S3 FT-IR spectra of conventional microporous SAPO-34 (S_M) and hierarchical porous SAPO-34 (S_{H1} and S_{H2}) catalysts.

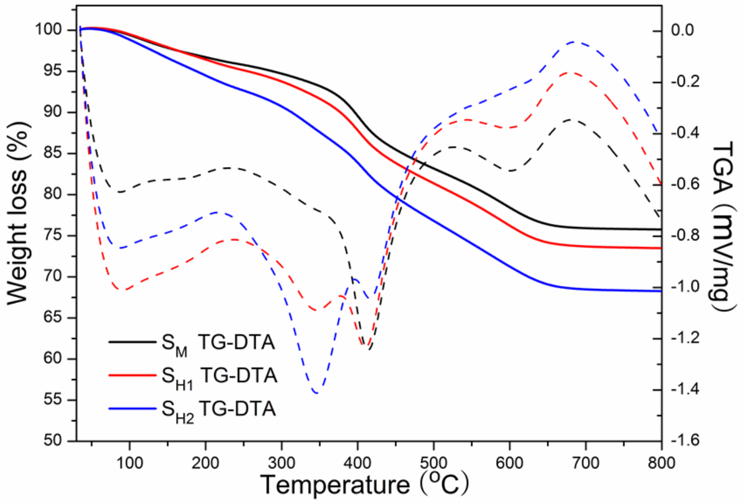


Fig. S4 The TG-DTA curves conventional microporous SAPO-34 (S_M) and hierarchical porous SAPO-34 (S_{H1} and S_{H2}) catalysts.

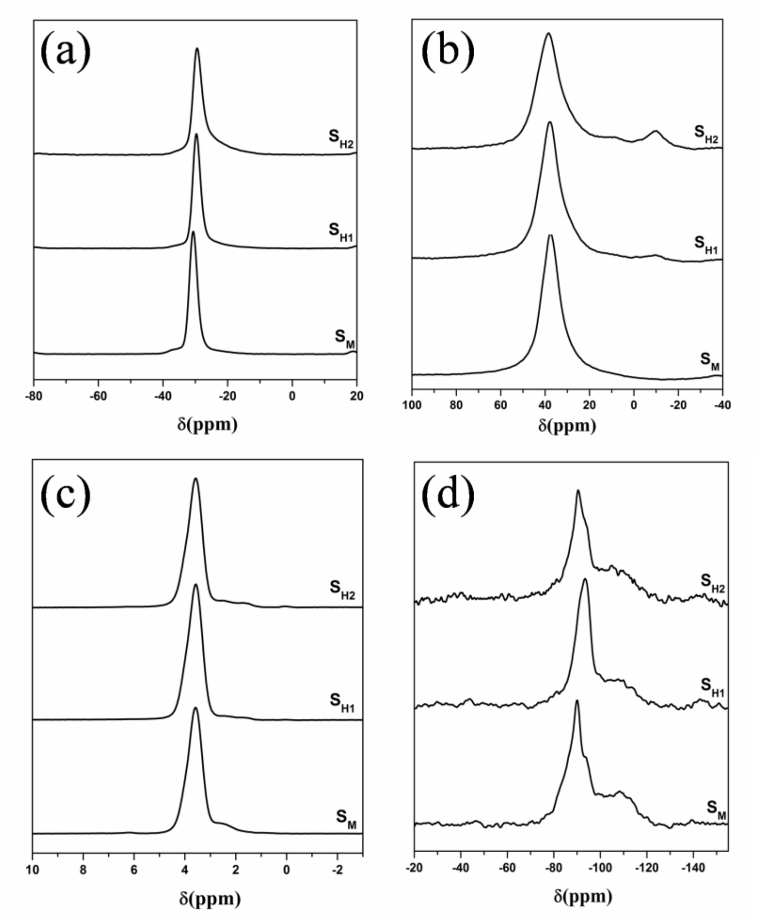


Fig.S5 (a) ^{31}P, (b) ^{27}Al, (c) ^{1}H and (d) ^{29}Si MAS NMR spectra of conventional microporous SAPO-34 (S_M) and hierarchical porous SAPO-34 (S_{H1} and S_{H2}) catalysts.

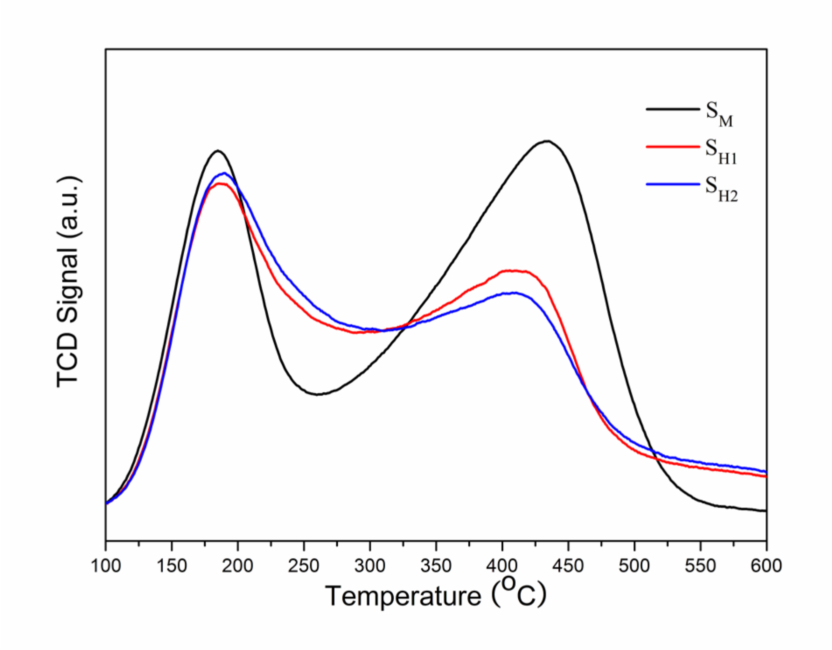


Fig. S6 NH_3-TPD profiles of conventional microporous SAPO-34 (S_M) and hierarchical porous SAPO-34 (S_{H1} and S_{H2}) catalysts.

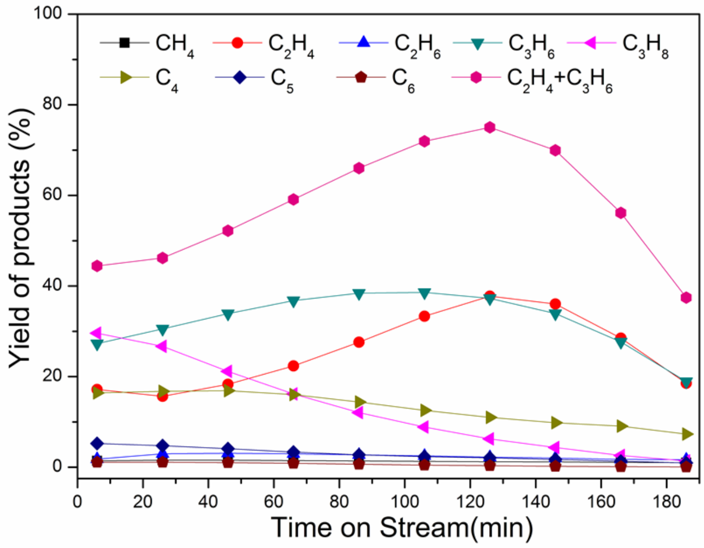


Fig. S7 Products distribution of conventional microporous SAPO-34 catalyst (S_M) in MTO reaction. Experimental conditions: WHSV = 2 h^{-1}, T = 673 K, catalyst weight = 300 mg.

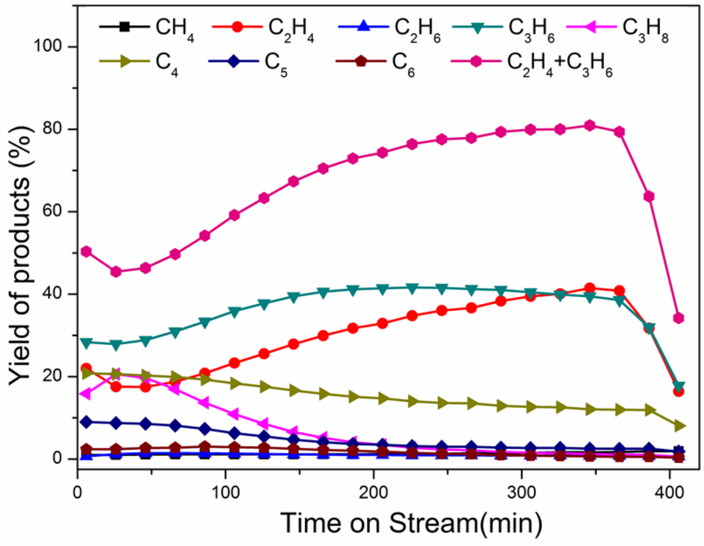


Fig. S8 Products distribution of hierarchical porous SAPO-34 catalyst (S_{H1}) in MTO reaction. Experimental conditions: WHSV = 2 h^{-1}, T = 673 K, catalyst weight = 300 mg.

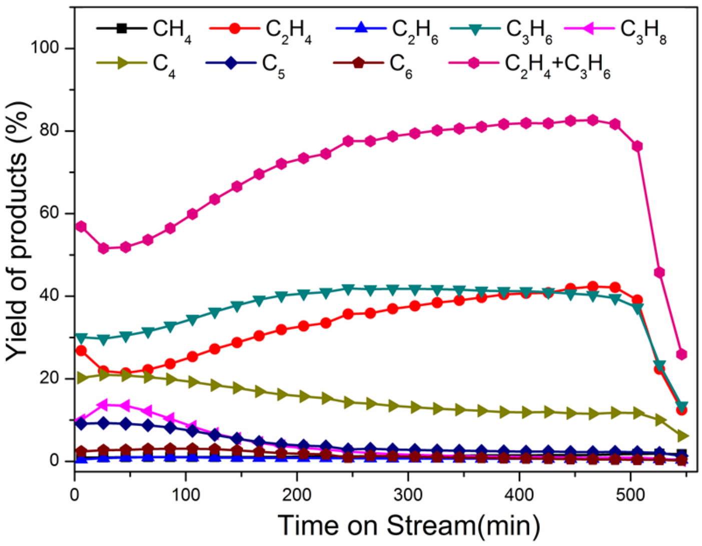


Fig. S9 Products distribution of hierarchical porous SAPO-34 catalyst (S_{H2}) in MTO reaction. Experimental conditions: WHSV = 2 h^{-1}, T = 673 K, catalyst weight = 300 mg.

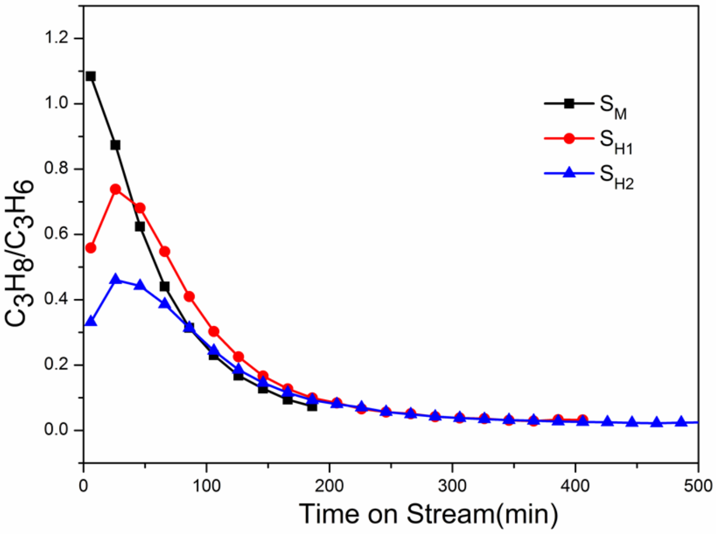
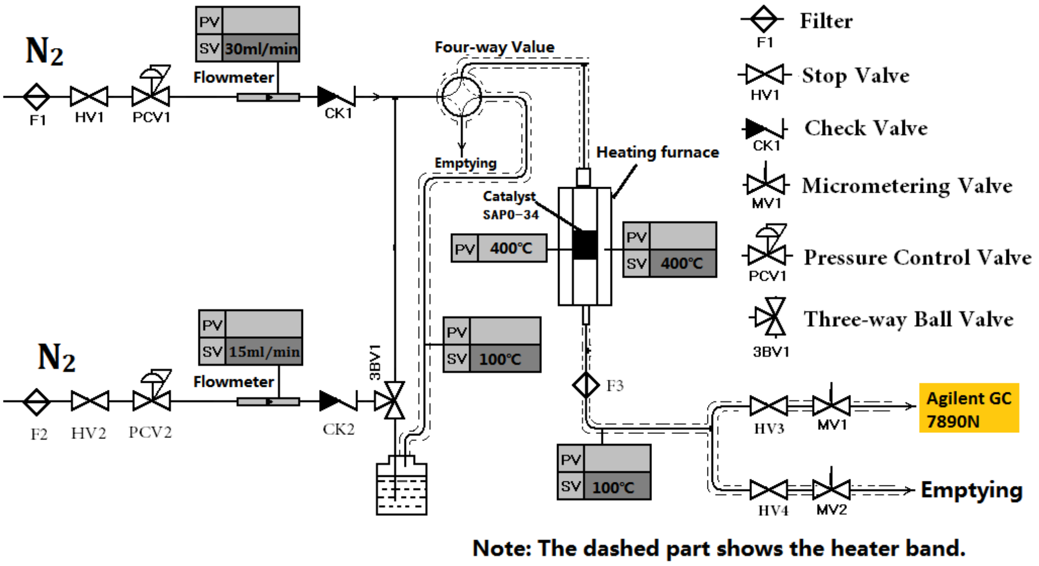


Fig. S10. Hydrogen transfer index (HTI, C_3H_8/C_3H_6) value of methanol conversion over conventional microporous SAPO-34 (S_M) and hierarchical porous SAPO-34 (S_{H1} and S_{H2}) catalysts.



Scheme S1 Schematic of catalytic test set-up of MTO reaction.

Table S1 MTO results on conventional microporous SAPO-34 (S_M) and hierarchical porous SAPO-34 (S_{H1} and S_{H2}) catalysts.

Sample	TOS (min)	Selectivity（%）							
		CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4	C_5^+	$C_2^=+C_3^=$
S_M	6	1.4	17.1	1.8	27.3	29.6	16.4	5.2	44.4
	106*	1.3	33.3	2.5	38.6	8.9	12.5	2.3	71.9
S_{H1}	6	1.0	22.0	0.7	28.4	15.8	20.8	9.0	50.4
	346*	1.6	41.5	0.8	39.6	1.2	12.1	2.5	81.1
S_{H2}	6	0.9	26.8	0.5	30.1	10.0	20.2	9.1	56.9
	466*	1.5	42.4	0.6	40.3	0.9	11.5	2.2	82.7

Reaction conditions: WHSV = 2 h^{-1}, T = 673 K,
* Lifetime: the reaction duration with > 99.9% methanol conversion.

Table S2 The variation of coke formation in methanol conversion over conventional microporous SAPO-34 (S_M) and hierarchical porous SAPO-34 (S_{H1} and S_{H2}) catalysts.

Catalysts	S_M	S_{H1}	S_{H2}
Coke (%, g/gcat)	20.68	23.96	24.91
TOS(MIN)	186	426	566
R_{coke} (mg/min) (1)	0.334	0.169	0.132
P_{coke} (g/gMeOH) (2)	0.033	0.017	0.013

R_{coke}(g/min) = coke amount(g)/reaction time (min) (1);

P_{coke}(g/g) = coke amount (g)/methanol feedstock (g) (2).