## **Supporting Information**

## Synthesis of tri-level hierarchical SAPO-34 zeolite with intracrystalline micro-meso-macroporosity showing superior MTO performance

Qiming Sun,<sup>a‡</sup> Wang Ning,<sup>a‡</sup> Guanqi Guo,<sup>a</sup> Xiaoxin Chen,<sup>a</sup> and Jihong Yu\*<sup>a</sup>

<sup>a</sup> State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China



Figure S1 The TG curves of conventional microporous SAPO-34 ( $S_M$ ) and hierarchically porous SAPO-34 ( $S_{H1}$ ,  $S_{H2}$ ,  $S_{H3}$ , and  $S_{H4}$ ) catalysts.



**Figure S2** Selectivity of ethylene versus time-on-stream over conventional microporous SAPO-34 ( $S_M$ ) and hierarchically porous SAPO-34 ( $S_{H1}$ ,  $S_{H2}$ ,  $S_{H3}$ , and  $S_{H4}$ ) catalysts in MTO reaction. Experimental conditions: WHSV = 4 h<sup>-1</sup>, T = 723 K, catalyst weight = 300 mg.



**Figure S3** Selectivity of propylene versus time-on-stream over conventional microporous SAPO-34 ( $S_M$ ) and hierarchically porous SAPO-34 ( $S_{H1}$ ,  $S_{H2}$ ,  $S_{H3}$ , and  $S_{H4}$ ) catalysts in MTO reaction. Experimental conditions: WHSV = 4 h<sup>-1</sup>, T = 723 K, catalyst weight = 300 mg.



**Figure S4** Products distribution of conventional microporous SAPO-34 catalyst ( $S_M$ ) in MTO reaction. Experimental conditions: WHSV = 4 h<sup>-1</sup>, T = 723 K, catalyst weight = 300 mg.



**Figure S5** Products distribution of hierarchically porous SAPO-34 catalyst ( $S_{H1}$ ) in MTO reaction. Experimental conditions: WHSV = 4 h<sup>-1</sup>, T = 723 K, catalyst weight = 300 mg.



**Figure S6** Products distribution of hierarchically porous SAPO-34 catalyst ( $S_{H2}$ ) in MTO reaction. Experimental conditions: WHSV = 4 h<sup>-1</sup>, T = 723 K, catalyst weight = 300 mg.



**Figure S7** Products distribution of hierarchically porous SAPO-34 catalyst ( $S_{H3}$ ) in MTO reaction. Experimental conditions: WHSV = 4 h<sup>-1</sup>, T = 723 K, catalyst weight = 300 mg.



**Figure S8** Products distribution of hierarchically porous SAPO-34 catalyst ( $S_{H4}$ ) in MTO reaction. Experimental conditions: WHSV = 4 h<sup>-1</sup>, T = 723 K, catalyst weight = 300 mg.



**Figure S9** Hydrogen transfer index (HTI,  $C_3H_8/C_3H_6$ ) values of methanol conversion over conventional microporous SAPO-34 (S<sub>M</sub>) and hierarchically porous SAPO-34 (S<sub>H1</sub>, S<sub>H2</sub>, S<sub>H3</sub>, and S<sub>H4</sub>) catalysts. Experimental conditions: WHSV = 4 h<sup>-1</sup>, T = 723 K, catalyst weight = 300 mg.

Samples	TOS (min)	Selectivity (%)							
		$\mathrm{CH}_4$	$C_2H_4$	$C_2H_6$	$C_3H_6$	$\mathrm{C_{3}H_{8}}$	$C_4$	$C_5^+$	$C_2^{=}+C_3^{=}$
S <sub>M</sub>	6	1.4	33.9	0.5	41.2	4.2	15.1	3.7	75.1
	66*	1.6	41.0	0.7	38.8	2.8	11.4	3.7	79.8
S <sub>H1</sub>	6	1.2	36.5	0.5	39.4	3.5	14.4	4.5	75.6
	186*	2.8	47.8	0.6	35.1	1.4	8.9	4.8	82.9
S <sub>H2</sub>	6	1.3	36.0	0.5	39.6	3.5	14.6	5.1	75.6
	306*	2.7	49.3	0.5	34.2	0.9	8.9	3.5	83.5
S <sub>H3</sub>	6	1.0	33.1	0.5	41.1	3.8	16.0	4.5	74.2
	386*	2.7	51.1	0.5	33.1	0.9	8.4	3.3	84.2
$\mathrm{S}_{\mathrm{H4}}$	6	1.5	39.4	0.5	38.5	2.4	13.6	4.1	77.9
	226*	2.3	48.2	0.5	34.9	1.1	9.3	3.7	83.1

Reaction conditions: WHSV = 4  $h^{-1}$ , T =723K, catalyst weight = 300 mg.

\* Lifetime: the reaction duration with > 99.9% methanol conversion.

**Table S2** The variations of coke formation in methanol conversion over conventional microporous SAPO-34 ( $S_M$ ) and hierarchically porous SAPO-34 ( $S_{H1}$ ,  $S_{H2}$ ,  $S_{H3}$ , and  $S_{H4}$ ) catalysts.

Catalysts	$S_{M}$	$\mathbf{S}_{\mathrm{H1}}$	$\mathbf{S}_{\mathrm{H2}}$	$S_{\rm H3}$	$\mathbf{S}_{\mathrm{H4}}$
Coke (%, g/gcat)	16.95	22.39	23.06	23.07	21.18
TOS (min)	126	246	366	486	286
R <sub>coke</sub> (mg/min) (1)	0.403	0.273	0.189	0.142	0.222
$P_{coke}(g/gMeOH)(2)$	0.020	0.014	0.009	0.007	0.011

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

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