

Supplementary Information

In-Situ Growth-Etching Approach to the Preparation of Hierarchically Macroporous Zeolites with High MTO Catalytic Activity and Selectivity

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Figure S1. TEM image of a fragment of the hierarchically macroporous SAPO-34 synthesized with $\text{HF}/\text{Al}_2\text{O}_3 = 2.7$.

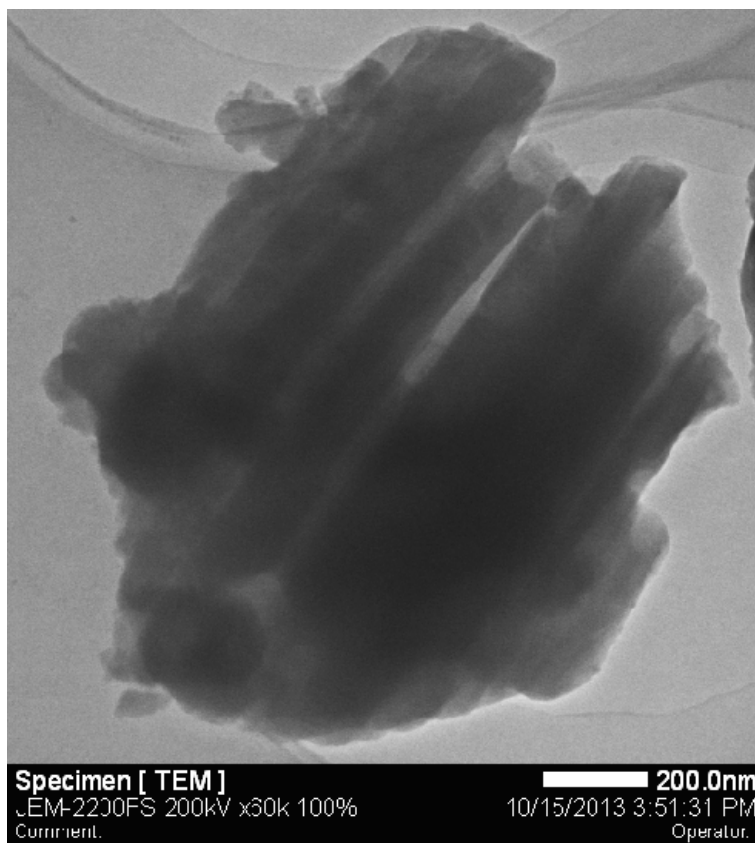


Figure S2. The XRD patterns of the hierarchically macroporous SAPO-34 synthesized with $\text{HF}/\text{Al}_2\text{O}_3 = 1.9$ crystallized at 6 h, 12 h, 18 h and 24 h. Crystals crystallized at 6 h and 12 h are separated after the autoclaves are immediately quenched by water, while crystals crystallized at 18 h and 24 h are separated after the autoclaves are naturally cooled down to room temperature.

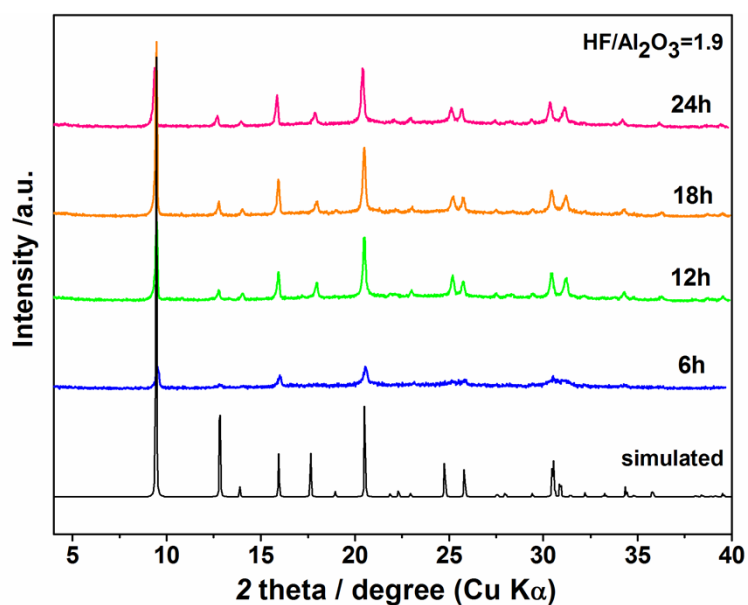


Figure S3. SEM images of the hierarchically macroporous SAPO-34 synthesized with HF/Al₂O₃ of 1.9 from crystallization time at 6h (a)-(e), 12h (f)-(g) and 18h (h). Crystals at 6h and 12h were separated after the autoclaves are immediately quenched by water, while crystals at 18 h are separated after the autoclave is naturally cooled down to room temperature. The crystals shown in (b)-(e) are from the batch crystals of (a). The denoted part with the circle in (h) means big hole in the middle of the surface. a), f), g), h) were taken at 5mm working distance and b), c), d), e) were taken at 7mm working distance with 2.5keV accelerating voltage and 2kV stage bias.

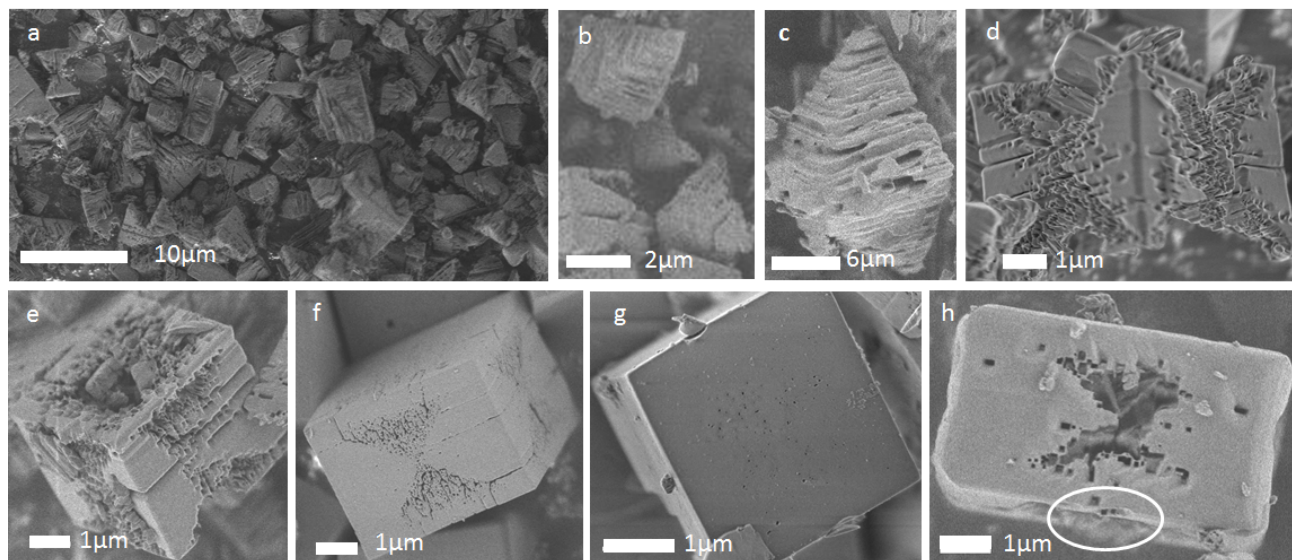


Figure S4. SEM images of hierachically macroporous $\text{AlPO}_4\text{-5}$ (AFI) synthesized by using the one-step hydrothermal method via in-situ growth-etching assisted by HF.

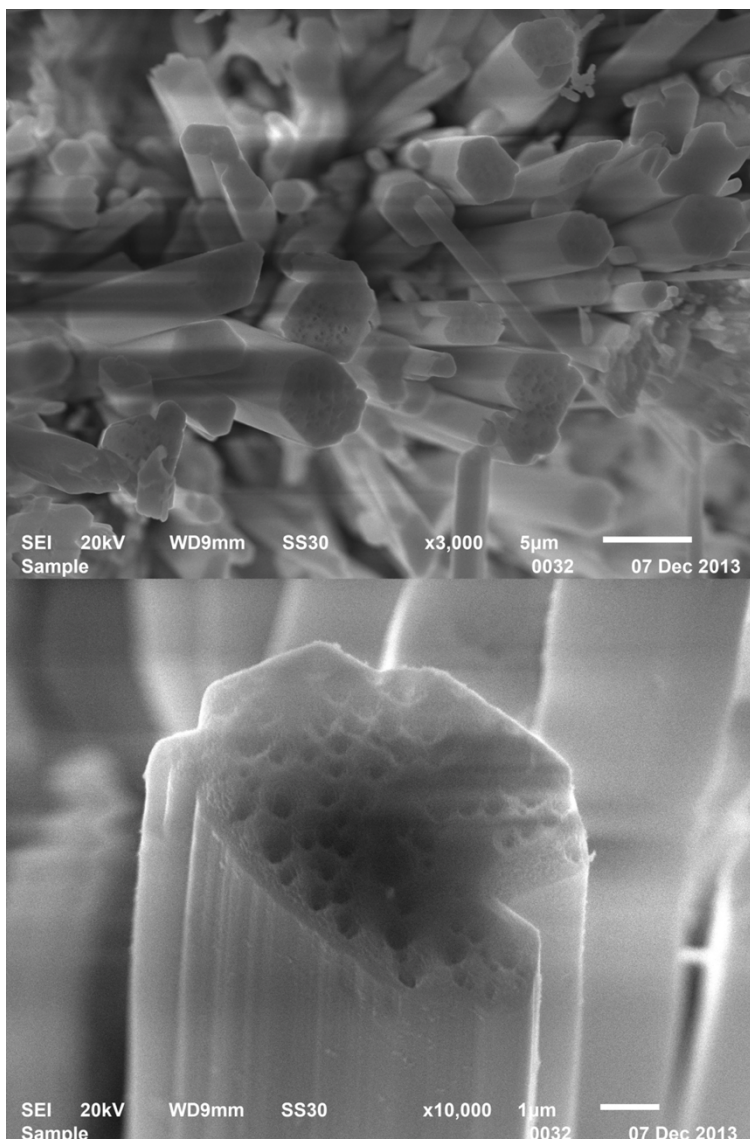


Figure S5. Pore diameter distribution of the hierarchically macroporous SAPO-34 synthesized with HF/Al₂O₃ of 1.9 determined by mercury porosimetry measurement.

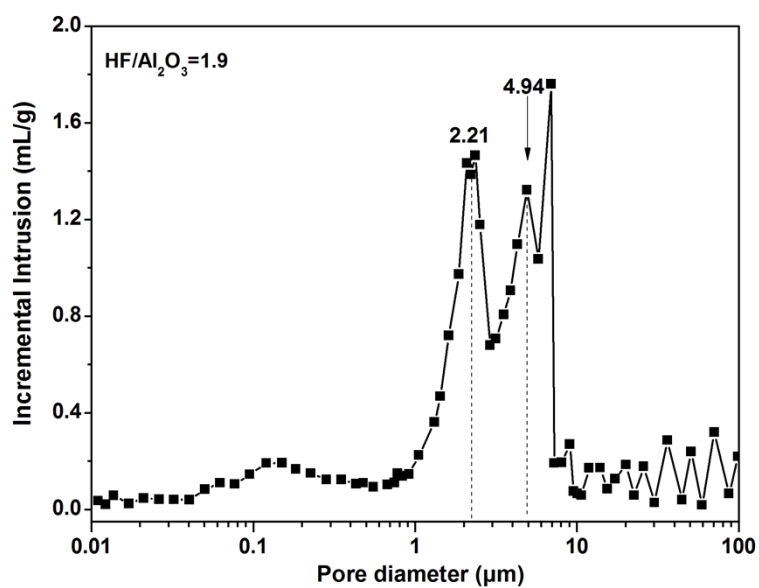


Figure S6. Product selectivity of the hierarchically macroporous and conventional SAPO-34 catalysts for MTO conversion at 400 °C.

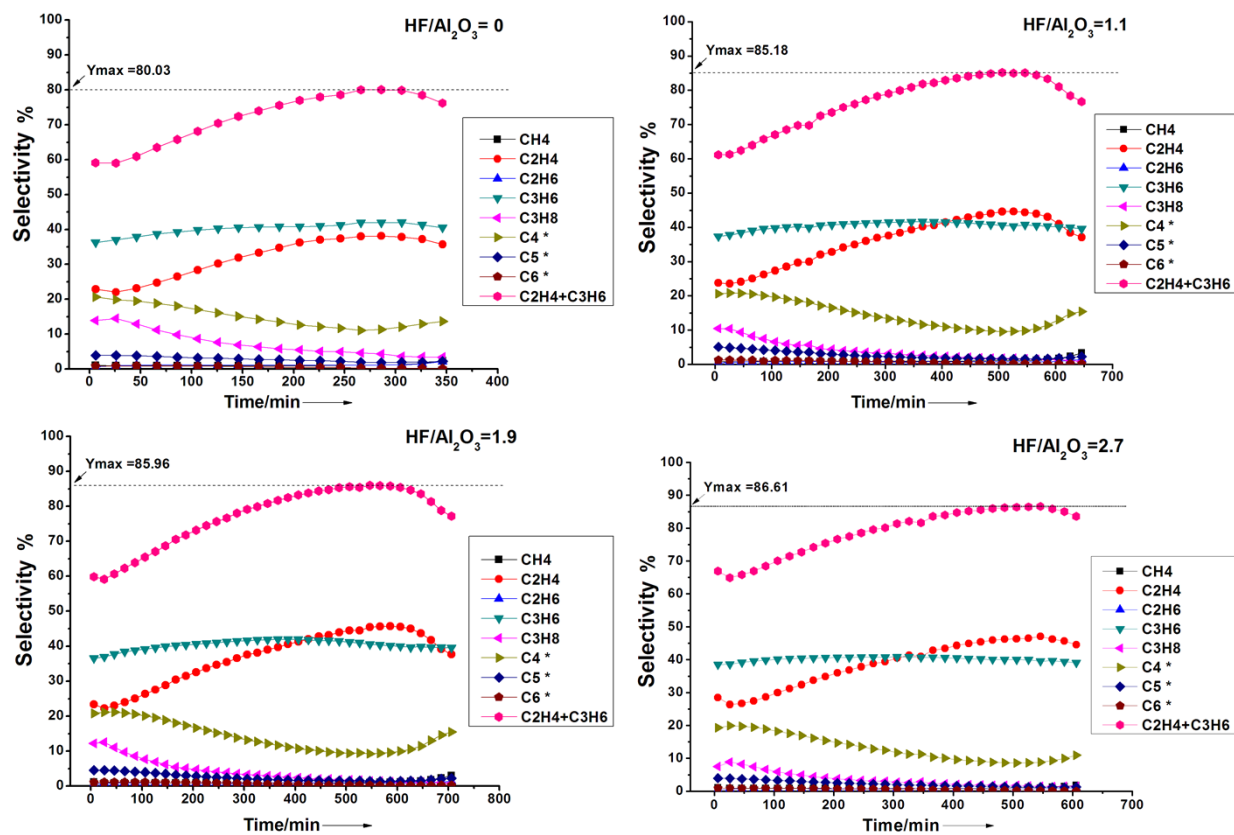


Table S1. Molar compositions measured by ICP^a and surface Si/(Al+P+Si) ratios measured by SEM-EDS^b for the hierarchically macroporous and conventional SAPO-34.

samples	molar composition ^a	Si/(Al+P+Si) ratio ^b (surface)
HF/Al ₂ O ₃ =0	Si _{0.09} Al _{0.46} P _{0.45} O ₂	0.10
HF/Al ₂ O ₃ =1.1	Si _{0.09} Al _{0.46} P _{0.45} O ₂	0.08
HF/Al ₂ O ₃ =1.9	Si _{0.10} Al _{0.46} P _{0.44} O ₂	0.08
HF/Al ₂ O ₃ =2.7	Si _{0.09} Al _{0.46} P _{0.45} O ₂	0.07

Table S2. Molar compositions measured by ICP and by SEM-EDS for SAPO-34 samples synthesized with HF/A₂O₃ of 1.9 at different crystallization time. ^a Samples are separated after the autoclaves are immediately quenched by water; ^b Samples are separated after the autoclaves are naturally cooled down to room temperature.

Crystallization	Composition(ICP)	SEM-EDS
6h	Si _{0.11} Al _{0.44} P _{0.45} O ₂	Si _{0.07} Al _{0.47} P _{0.46} O ₂
12h	Si _{0.11} Al _{0.45} P _{0.44} O ₂	Si _{0.08} Al _{0.46} P _{0.46} O ₂
18h ^a	Si _{0.11} Al _{0.45} P _{0.44} O ₂	Si _{0.08} Al _{0.46} P _{0.46} O ₂
18h ^b	Si _{0.11} Al _{0.46} P _{0.43} O ₂	Si _{0.09} Al _{0.46} P _{0.45} O ₂
24h ^a	Si _{0.11} Al _{0.46} P _{0.43} O ₂	Si _{0.08} Al _{0.45} P _{0.47} O ₂
24h ^b	Si _{0.10} Al _{0.47} P _{0.43} O ₂	Si _{0.08} Al _{0.45} P _{0.47} O ₂

Table S3. Yields of main products versus time-on-stream for MTO reaction over the hierarchically macroporous SAPO-34 catalysts as compared with the conventional catalyst.

Samples	TOS (min)	Selectivity (%)*							
		CH ₄	C₂H₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₄ *	C ₅ *	C ₂ H ₄ +C ₃ H ₆
HF/Al ₂ O ₃ =0	226	1.0	36.2	1.1	40.8	5.4	12.6	2.4	77.0
HF/Al ₂ O ₃ =1.1	486	1.0	42.9	0.8	41.2	2.0	10.2	1.7	84.1
HF/Al ₂ O ₃ =1.9	526	0.9	43.2	0.8	41.6	1.9	9.8	1.5	84.8
HF/Al ₂ O ₃ =2.7	446	0.9	44.3	0.8	40.4	2.1	9.6	1.6	84.7

*100% The methanol conversion with the highest (ethylene + propylene) selectivity