

Electronic Supplementary Information (ESI)

A low-temperature approach to synthesize low-silica SAPO-34 nanocrystals and their application in the Methanol-to-Olefins (MTO) reaction

Beibei Gao,^{ab} Miao Yang,^a Yuyan Qiao,^{ab} Jinzhe Li,^a Xiao Xiang,^{ab} Pengfei Wu,^{ab} Yingxu Wei,^a Shutao Xu,^a
Peng Tian,^{*a} and Zhongmin Liu^{*a}

*^a 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. Fax: 0086-411-84379289; Tel: 0086-411-
84379998; E-mail: tianpeng@dicp.ac.cn ; liuzm@dicp.ac.cn*

^b University of Chinese Academy of Sciences, Beijing 100049, P. R. China

Table S1 Synthesis conditions and compositions of reference samples synthesized under higher crystallization temperatures

Sample	Gel composition			T/°C	t/h	Product	Molar composition ^a
	a TEA	b TEABr	c SiO ₂				
H1	1.8	1.5	0.5	160	48	SAPO-34/18 intergrowth	—
H2	2.0	1.5	0.5	200	48	SAPO-34/18 intergrowth	Al _{0.451} P _{0.418} Si _{0.131}
H3	2.0	1.5	0.25	200	48	SAPO-5 +SAPO-34/18 intergrowth	Al _{0.484} P _{0.444} Si _{0.072}
H4 ^b	2.0	-	0.4	200	24	SAPO-34	Al _{0.499} P _{0.418} Si _{0.083}
H5 ^b	2.0	-	0.2	170	72	SAPO-34	Al _{0.490} P _{0.441} Si _{0.069}

^a Determined by X-ray fluorescence(XRF) analysis. ^b TEAOH was used as the template in the synthesis gel. Sample H4 has ~1μm crystal size and higher Si content. Sample H5 has nanscaled size and comparable Si content as low-temperature sample L5.

Table S2 Summary of the XPS results of SAPO-34 crystals

Sample	Crystallization temperature	Molar composition		R ^a
		XRF	XPS	
L5 ^b	120 °C	Al _{0.510} P _{0.423} Si _{0.067}	Al _{0.450} P _{0.474} Si _{0.076}	1.13
L5-10 ^b	120 °C	Al _{0.495} P _{0.437} Si _{0.068}	Al _{0.456} P _{0.473} Si _{0.071}	1.04
1 (sample R1) ^c	200 °C	Al _{0.486} P _{0.434} Si _{0.080}	Al _{0.453} P _{0.341} Si _{0.206}	2.58
2 (sample 10 with lower surface Si enrichment) ^c	200 °C	Al _{0.504} P _{0.420} Si _{0.076}	Al _{0.484} P _{0.391} Si _{0.124}	1.63
3 (SAPO-34 precursor) ^d	200 °C	Al _{0.448} P _{0.351} Si _{0.200}	Al _{0.307} P _{0.246} Si _{0.447}	2.24
4 (sample 2 after recrystallization) ^d	200 °C	Al _{0.485} P _{0.379} Si _{0.136}	Al _{0.398} P _{0.383} Si _{0.219}	1.61

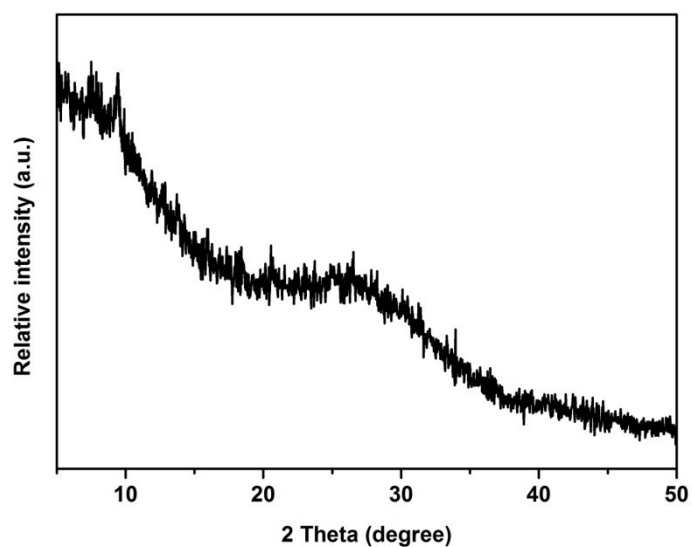
^a The surface enrichment index R is defined as $[\text{Si}/(\text{Si}+\text{P}+\text{Al})]_{\text{surface}}/[\text{Si}/(\text{Si}+\text{P}+\text{Al})]_{\text{bulk}}$ to indicate the degree of surface Si enrichment degree. ^b Samples obtained in this work. ^c SAPO-34 synthesized in the our previous work [1]. ^d SAPO-34 synthesized in our previous work [2].

Table S3 Synthesis conditions and compositions of low-silica nano SAPO molecular sieves

Sample	Gel composition ^a			Seeds (wt%)	Product	Molar composition	
	xTEA	yTEABr	zSiO ₂			XRF ^b	XPS ^c
L5-5	1.8	1.5	0.5	5	SAPO-34	Al _{0.514} P _{0.423} Si _{0.063}	—
L5-10	2.0	1.5	0.5	10	SAPO-34	Al _{0.495} P _{0.437} Si _{0.068}	Al _{0.456} P _{0.473} Si _{0.071}
L5-20	1.8	1.5	0.5	20	SAPO-34	Al _{0.513} P _{0.422} Si _{0.065}	—

^a x TEA: y TEABr: 0.8 Al₂O₃: 1.0 P₂O₅: z SiO₂: 50 H₂O (120°C, 48h). ^b Determined by X-ray fluorescence(XRF) analysis.

^c Determined by X-ray photoelectron spectroscopy (XPS) compositional analysis.

**Fig.S1** XRD pattern of the prepared milled seeds.

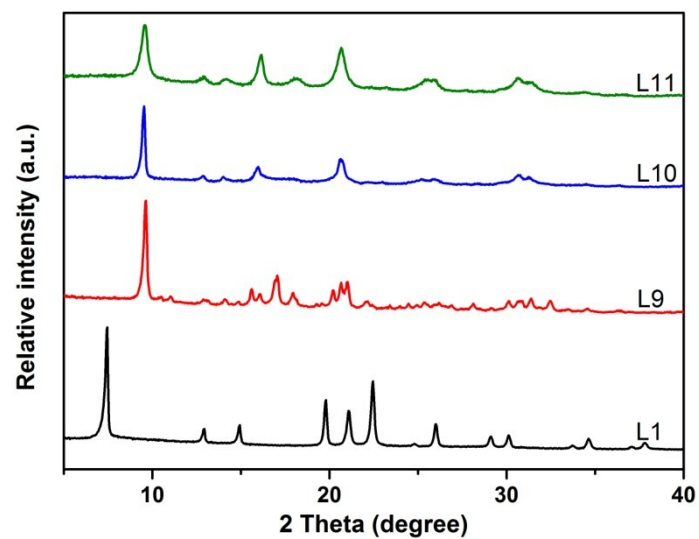


Fig. S2 XRD patterns of as-synthesized SAPO samples.

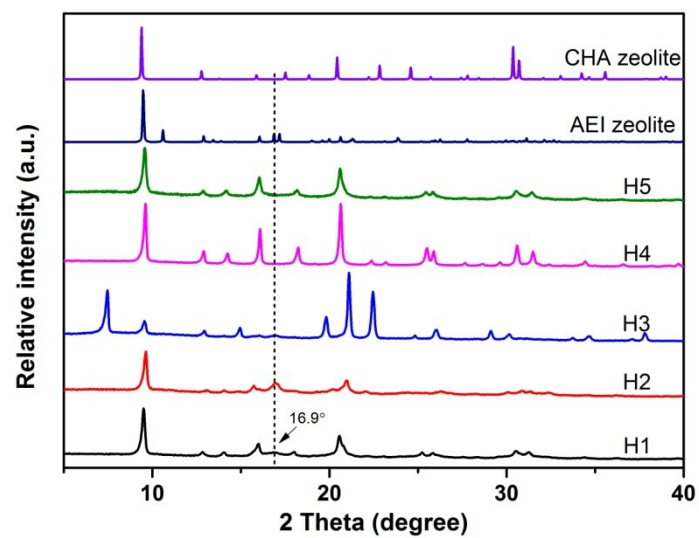


Fig. S3 XRD patterns of as-synthesized reference samples obtained at higher temperature. The emergence of small peak around 16.9° in the patterns indicates the formation of SAPO-34/18 (CHA/AEI) intergrowth in samples H1-H3.

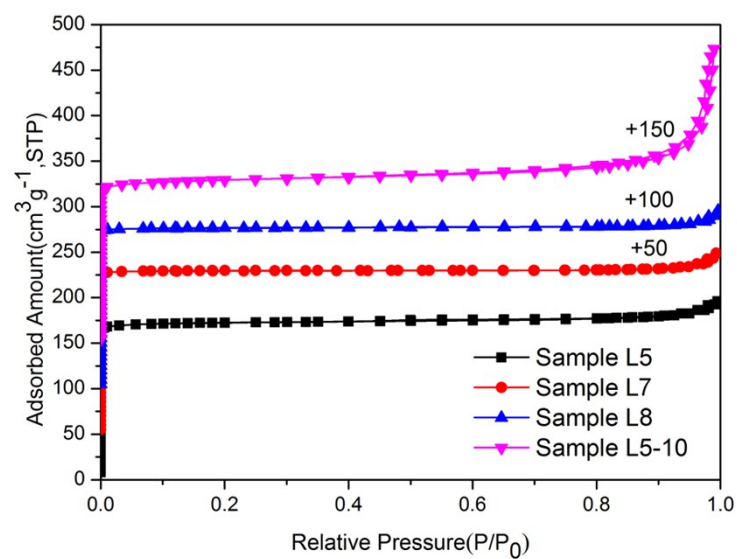


Fig. S4 N_2 adsorption-desorption isotherms of low-silica SAPO-34 samples (the isotherms of sample L7, L8, L5-10 are vertically offset by 50, 100 and 150 $cm^3 g^{-1}$, respectively).

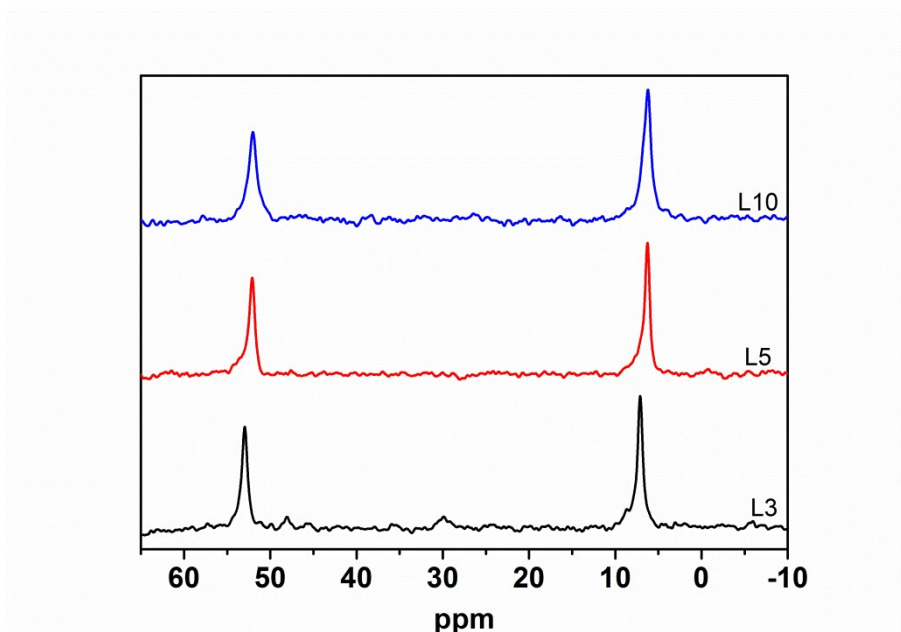


Fig. S5 ^{13}C MAS NMR spectra of as-synthesized low-silica samples.

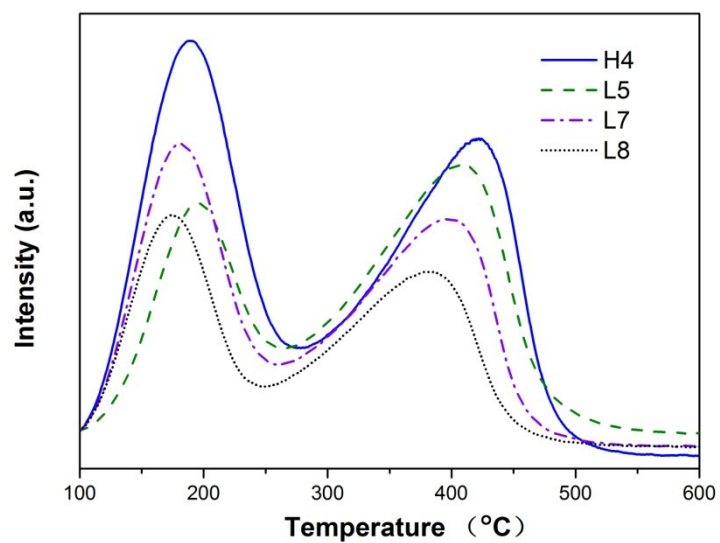


Fig. S6 NH₃-TPD profiles of selected SAPO samples.

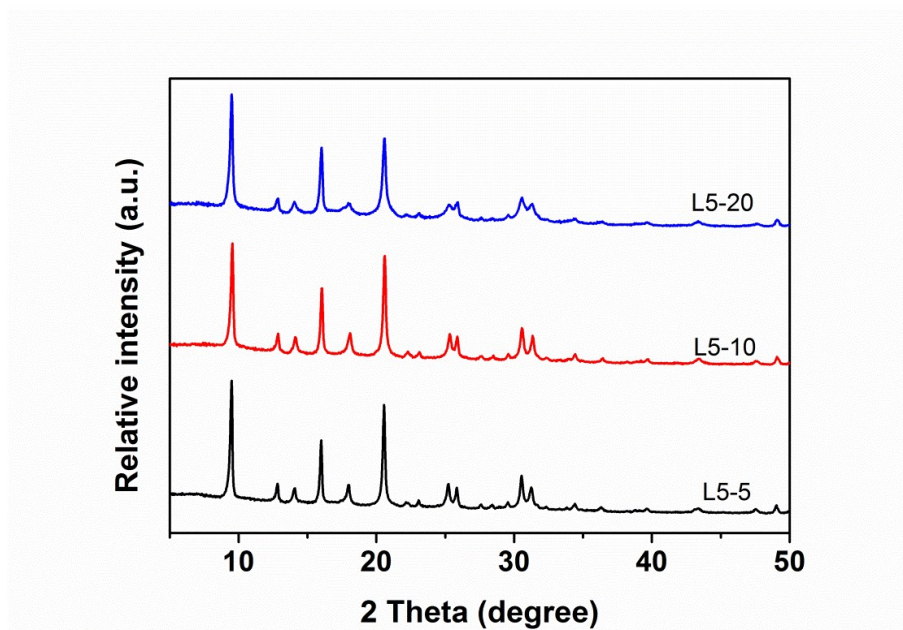


Fig. S7 XRD patterns of low-silica SAPO-34 nanocrystals synthesized under the assistance of seeds.

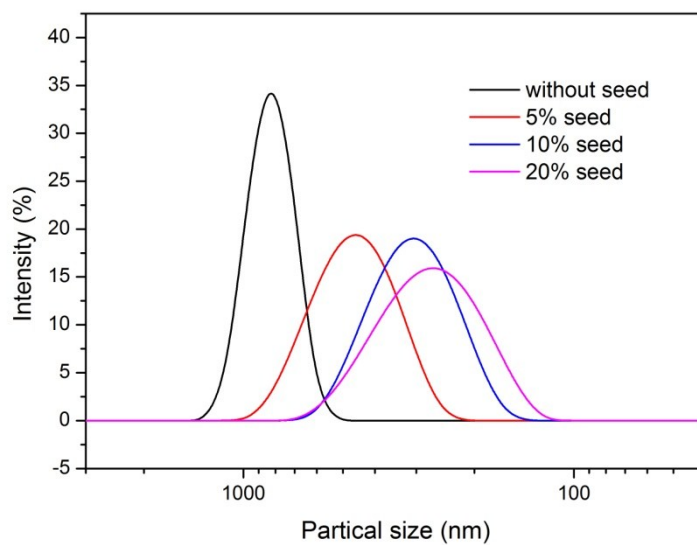


Fig. S8 . Intensity-weighted size distribution curve of SAPO-34 samples with different amounts of seeds.

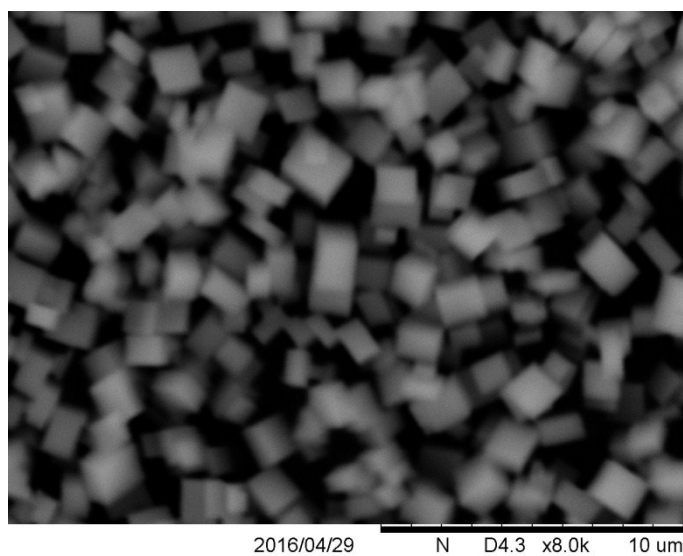


Fig. S9 SEM image of sample H4.

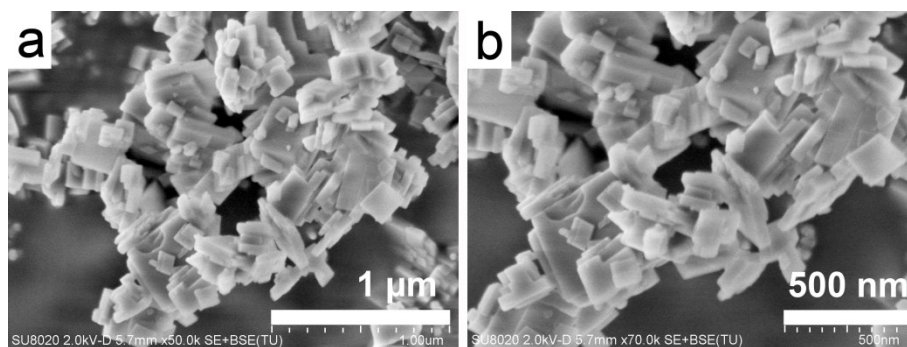


Fig. S10 SEM images of sample H5.

Reference

1. D. Fan, P. Tian, S. Xu, D. Wang, Y. Yang, J. Li, Q. Wang, M. Yang and Z. Liu, *New J. Chem.*, 2016, **40**, 4236-4244.
2. M. Yang, P. Tian, C. Wang, Y. Yuan, Y. Yang, S. Xu, Y. He and Z. Liu, *Chem. Commun.*, 2014, **50**, 1845-1847.