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Supporting information

A top-down approach to prepare silicoaluminophosphate molecular sieve nanocrystals with improved catalytic property

Miao Yang,[a] Peng Tian,[a] Chan Wang,[a,b] Yangyang Yuan,[a,b] Yue Yang,[a] Shutao Xu,[a] Yanli He,[a] 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; * E-mail: liuzm@dicp.ac.cn*

[b] *University of Chinese Academy of Sciences, Beijing, P. R. China*

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Sample Preparation:

1.Synthesis of conventional SAPO molecular sieves.

Typical synthesis of SAPO-34 precursor: an SAPO gel with a molar composition of diethylamine/Al_2O_3/P_2O_5/SiO_2/H_2O = 2.0/1/1/0.8/50 was prepared by mixing pseudo-boehmite (72.5 wt%), water, phosphoric acid (85 wt%), silica sol (30.1 wt%), and diethylamine in sequence. The crystallization was conducted in a stainless steel autoclave at 200 ºC for 48 h under rotation. The as-synthesized product was washed and recovered through filtration, and dried at 110 ºC overnight.

Typical synthesis of SAPO-5 precursor: an SAPO gel with a molar composition of triethylamine/Al_2O_3/P_2O_5/SiO_2/H_2O = 1.2/1/1/0.4/60 was prepared by mixing pseudo-boehmite (72.5 wt%), water, phosphoric acid (85 wt%), silica sol (30.1 wt%), and triethylamine in sequence. The mixture was charged into a stainless steel autoclave, sealed, and heated to 200 ºC under rotation for 24 h. The as-synthesized product was washed and recovered through filtration, and dried at 110 ºC overnight.

Typical synthesis of SAPO-35 precursor: an SAPO gel with a molar composition of hexamethyleneimine/Al_2O_3/P_2O_5/SiO_2/H_2O = 1.5/1/1/0.3/55 was prepared by mixing pseudo-boehmite (72.5 wt%), water, phosphoric acid (85 wt%), silica sol (30.1 wt%) and hexamethyleneimine in sequence. The mixture was charged into a stainless steel autoclave, sealed, and heated to 200 ºC under rotation for 48 h. The as-synthesized product was washed and recovered through filtration, and dried at 110 ºC overnight.

2.**Milling treatment**: 6.0 g as-made SAPO-34/5/35 was calcined at 600 ºC for 300 min, after that it was dispersed into water and milled at 550 rpm/min for 360 min using a planetary ball mill (QM-3SP2, Nanjing China) with agate beads mixture in diameter of 3, 6 and 10 mm. After milling, the mud was collected and dried at 110 ºC overnight.

3. Recrystallization

For SAPO-34: 2.1 g milled sample was charged into 21 g solution consisted of H_3PO_4, pseudo-boehmite (72.5 wt%), triethylamine, and H_2O with the composition of triethylamine/Al_2O_3/P_2O_5/H_2O = 3.5-3.8/1/1/55-150. The mixture was hydrothermally crystallized at 180-200 ºC for 3-24 h. The product was washed and recovered by centrifugation, and dried at 110 ºC overnight.

Recrystallization in mother liquid: a mother liquid was first obtained after the SAPO-34 synthesis from the mixture of triethylamine, pseudo-boehmite (72.5 wt%), H_3PO_4, silica gel, and H_2O with the molar ratio of triethylamine/Al_2O_3/P_2O_5/SiO_2/H_2O = 3.5/1/1/0.3/55. Then, 3.0g milled SAPO-34 precursor was charged into 30.0 g mother liquid. The mixture was hydrothermally crystallized at 180 ºC for 2 h. The product was washed and recovered through centrifugation, and dried at 110 ºC overnight.

For the composition analysis of the mother liquid, 20 g of mother liquid was dried and calcined at 600 ºC for 300 min. The solid was collected and weighted. The solid content was calculated to be 11%. XRF analysis for the solid showed that it consisted of Al_2O_3 31.3 wt%, P_2O_5 65.6 wt% and 3.0 wt% SiO_2.

For SAPO-5: 0.25 g milled SAPO-5 precursor was charged into 2.5 g solution consisted of triethylamine, Al_2O_3, H_3PO_4 and H_2O with the composition of triethylamine/Al_2O_3/P_2O_5/H_2O = 1.9/1/1.2/150. The mixture was hydrothermally crystallized at 150 ºC for 2 h. The product was washed and recovered by centrifugation, and dried at 110 ºC overnight.

For SAPO-35: 0.2 g milled SAPO-35 precursor was charged into 2.0 g solution consisted of H_3PO_4, hexamethyleneimine, and H_2O with the composition of hexamethyleneimine/P_2O_5/H_2O = 5.8/1/128. The mixture was hydrothermally crystallized at 200 ºC for 2 h. The product was washed and recovered by centrifugation, and dried at 110 ºC overnight.

Characterization: The chemical composition of the solid samples was determined with a Philips Magix-601 X-ray fluorescence (XRF) spectrometer. The crystal morphology was observed by scanning electron microscopy TM3000 (Hitachi) and field emission scanning electron microscopy (Hitachi SU8020). The thermal analysis was performed on a TA Q-600 analyzer with a temperature-programmed rate of 10 ºC/min under an air flow of 100 ml/min. The powder X-ray diffraction (XRD) data were recorded on a PANalytical X'Pert PRO X-ray diffractometer with Cu Kα radiation (λ = 1.54059 Å) operating at 40 mA and 40 kV. Textural properties of the calcined samples were determined by N_2 adsorption/desortption at 77 K on a Micromeritics ASAP 2020 system. The total surface area was calculated based on the BET equation. The micropore volume and micropore surface area were evaluated using the t-plot method. Mesopore volume and mesopore surface area were evaluated by Barret–Joyner–Halenda (BJH) method. 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 were 104.2, 161.9 and 79.4 MHz for ^{27}Al, ^{31}P and ^{29}Si 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. The spinning rates of the samples at the magic angle were 4, 10, and 6 kHz for ^{29}Si, ^{27}Al and ^{31}P, respectively. The temperature-programmed desorption of ammonia (NH_3-TPD) was carried out with an Autochem 2920 equipment (Micromeritics). The calcined samples (200 mg, 40-60 mesh) was activated at 650 ºC for 60 min (10 ºC /min) in He, and then cooled down and saturated with ammonia at 150 ºC for 30 min. After the samples were purged with He (30 ml/min) for 30 min, the measurements of the desorbed NH_3 were performed from 150 to 650 ºC (10 ºC /min) under He (30 ml/min). X-ray photoelectron spectroscopy (XPS) was used to analyze the change of surface composition measured by VG ESCALAB MK2 X-ray photoelectron spectrometer.

Catalytic testing: MTO reaction was carried out with a fixed-bed reactor at atmospheric pressure. 1.2 g of catalyst (20-40 mesh) was loaded into the reactor. The sample was activated in a flow of nitrogen at 550 ºC for 1 h, and then the temperature was

reduced to a reaction temperature 450 ºC. The methanol solution (weight ratio of CH_3OH/H_2O was 40/60) was pumped into the reactor after nitrogen was turned off. The weight hourly space velocity (WHSV) was 4 h^{-1}. The reaction products were analyzed using on online gas chromatograph (Agilent GC 7890N), equipped with a flame ionization detector (FID) and PoraplotQ-HT capilliary column. The conversion and selectivity were calculated on CH_2 basis. Dimethyl ether (DME) was considered as reactant in the calculation.

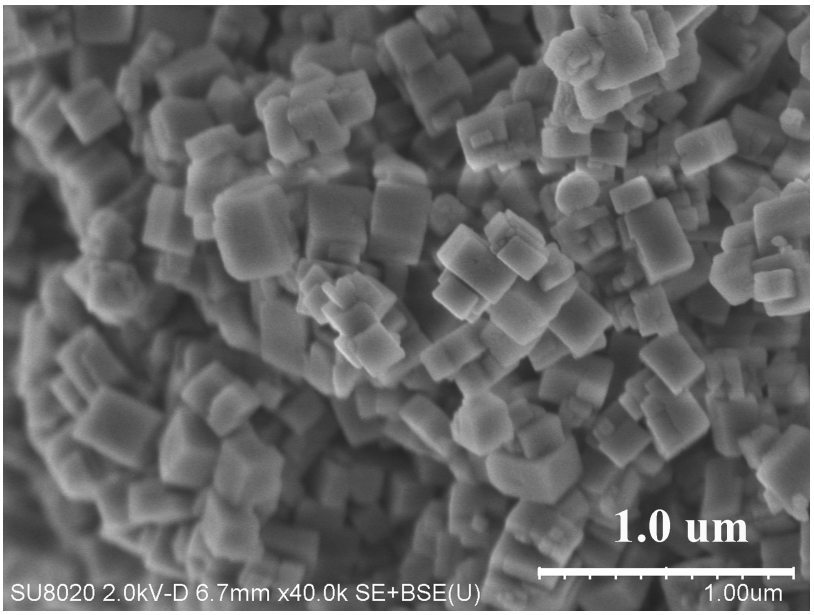

Fig. S1 SEM image of SAPO-34 recrystallized in a self-made solution with composition of $1.0P_2O_5$: $1.0Al_2O_3$: 3.5TEA: $55H_2O$ at 200 ^oC for 24 h (sample 6).

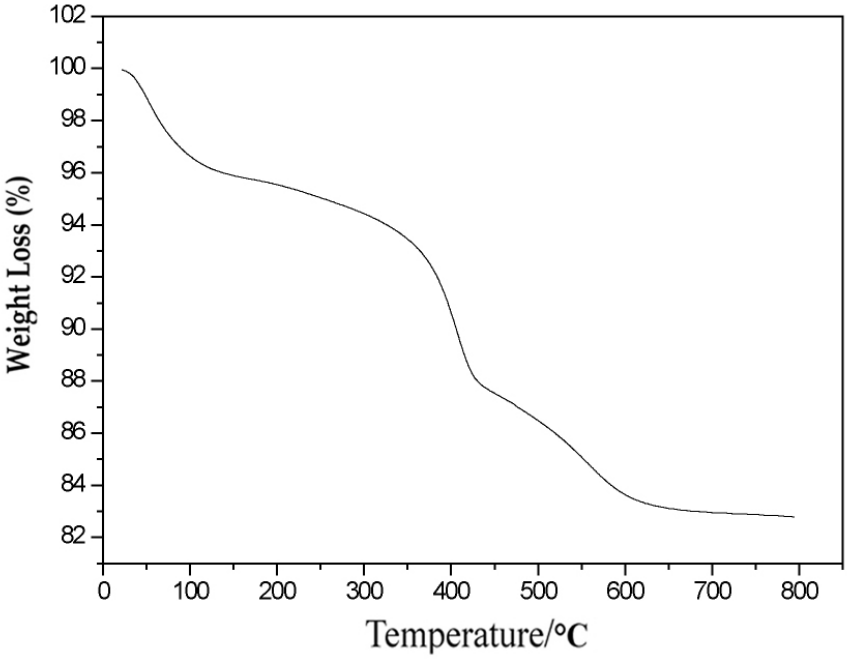

Fig. S2 TG curve of recrystallized SAPO-34 (sample 2).

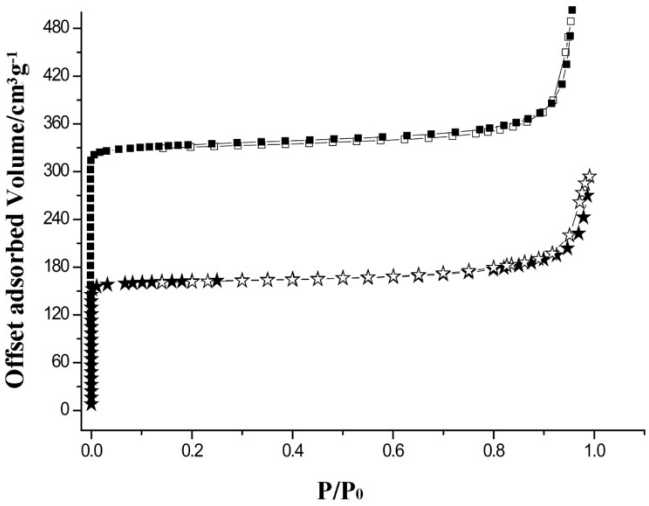

Fig. S3 N_2 adsorption (solid) and desorption (empty) isotherms of sample 2 (■,□) and 6(★, ☆).

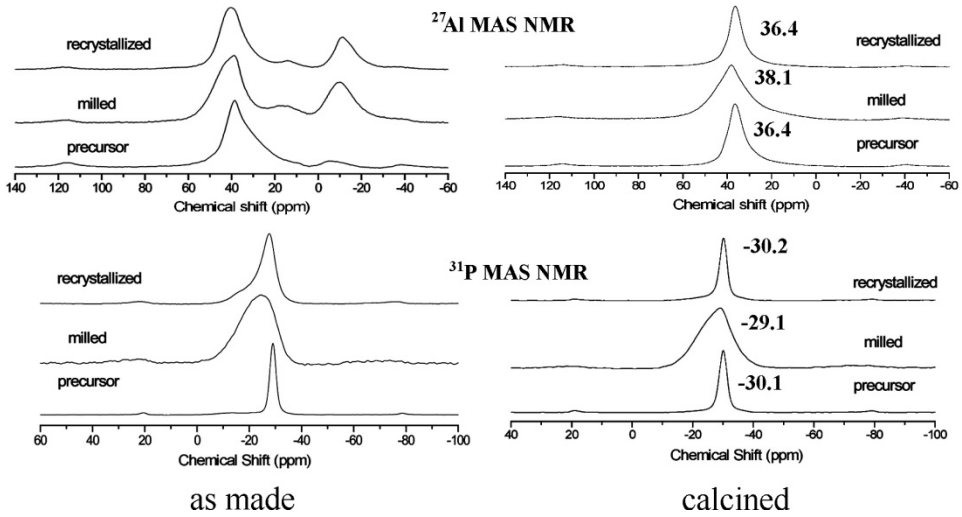

Fig. S4 ^{27}Al and ^{31}P MAS NMR spectra of SAPO-34 precursor, milled SAPO-34, and recrystallized SAPO-34 (sample 2).

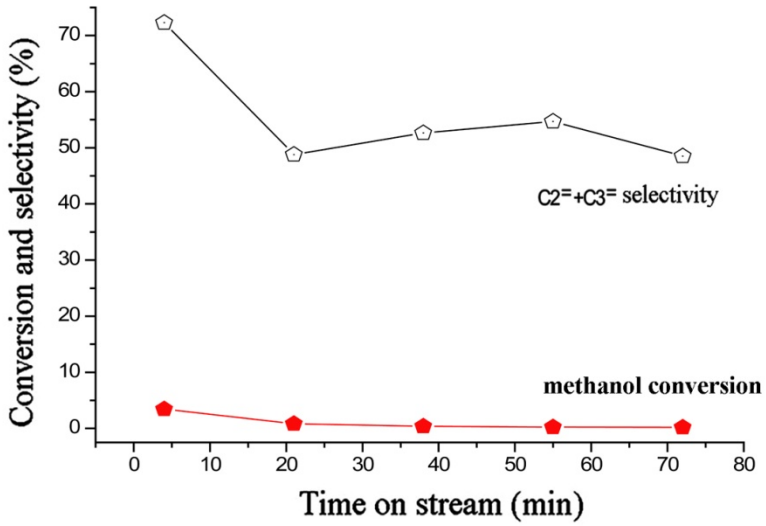

Fig. S5 Methanol conversion and selectivity of C_2H_4 plus C_3H_6 in the MTO reaction on the milled SAPO-34. Reaction condition: 450 ºC, WHSV = 4.0 h^{-1}, 40 wt% methanol solution.

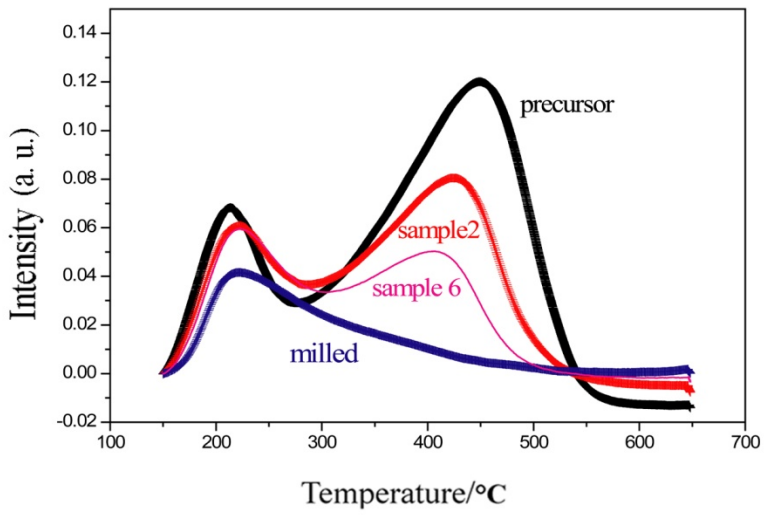

Fig.S6 NH_3-TPD profiles of precursor, milled and recrystallized SAPO-34s (sample 2 and sample 6).

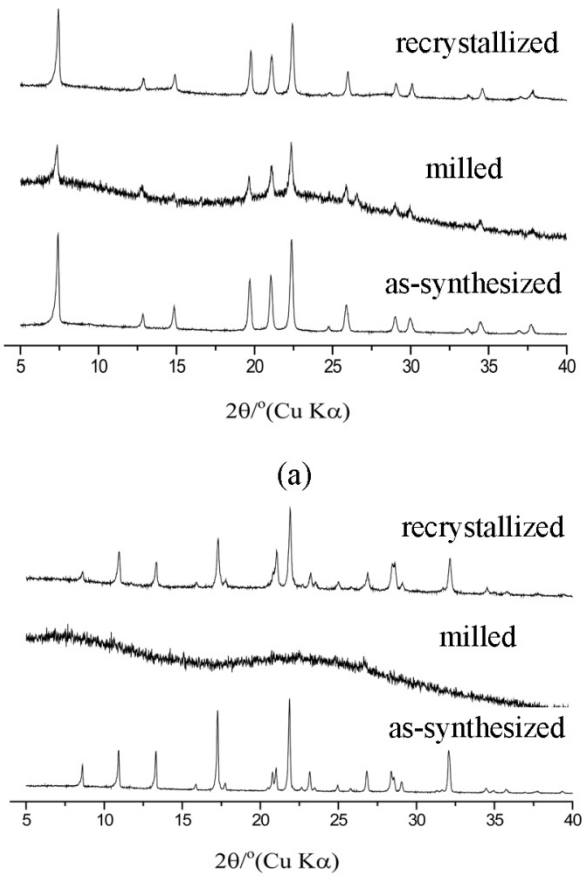

Fig. S7 XRD patterns of SAPO-5 (a) and SAPO-35(b) in the three stages.

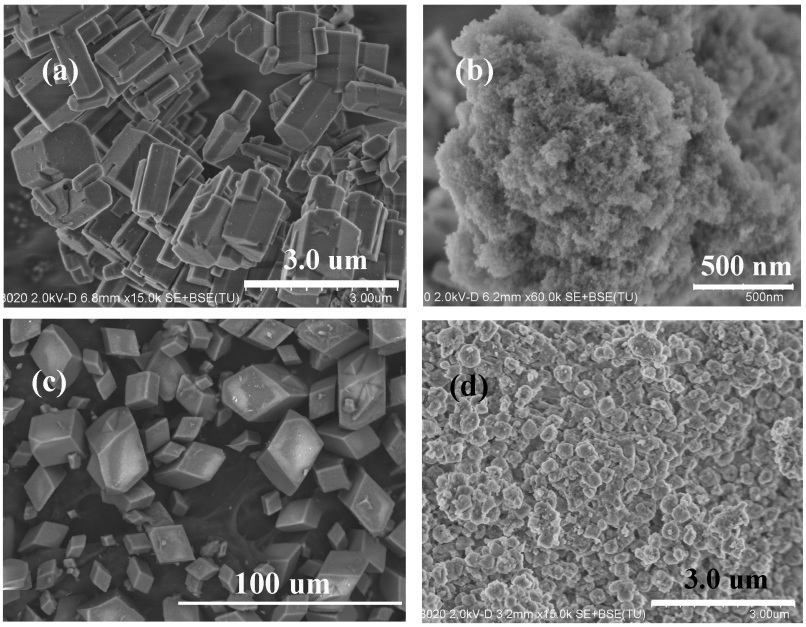

Fig. S8 SEM images of SAPO-5 precursor (a), recrystallized SAPO-5 (b), SAPO-35 precursor (c) and recrystallized SAPO-35 (d).

Table S1 MTO results on the SAPO-34 precursor and recrystallized products [a]

Samples	Lifetime [b] (min)	Selectivity (wt %)							
		CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4^+	C_5^+	$C_2H_4+C_3H_6$
SAPO-34 precursor	38	1.3	35.1	1.6	36.5	6.3	13.1	4.4	71.6
Sample 2	224	2.8	46.3	0.5	36.2	0.6	9.9	3.2	82.6
Sample 6	258	2.6	47.2	0.5	36.0	0.5	9.3	2.7	83.2
SAPO-34-TEA [c]	140	1.3	42.4	0.8	38.7	2.5	11.2	3.1	81.1

[a] Reaction conditions: WHSV = 4 h^{-1}, T = 450 ^{o}C, 40 wt% methanol-water solution; [b] Lifetime: the reaction duration with >99.5% methanol conversion. [c] SAPO-34 hydrothermally synthesized with TEA as a template for compare. Its bulk composition ($Al_{0.486}Si_{0.080}P_{0.434}O_2$) is similar to that of sample 6.

Table S2 Textural properties of samples

Samples	Surface area (m^2/g)			Pore volume (cm^3/g)		
	T-plot	External	BET	Micropore	Mesopore	Total
SAPO-34 precursor	567.2	29.5	609.5	0.30	0.04	0.34
Milled SAPO-34	8.2	27.2	35.4	0	0.07	0.07
Sample 2	479.3	50.8	530.1	0.22	0.20	0.42
Sample 6	499.2	41.8	541.0	0.23	0.22	0.45