Electronic Supplementary Material (ESI) for ChemComm.

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Silicoaluminophosphate-11 (SAPO-11) Molecular Sieve Synthesized by a Grinding Synthesis Method

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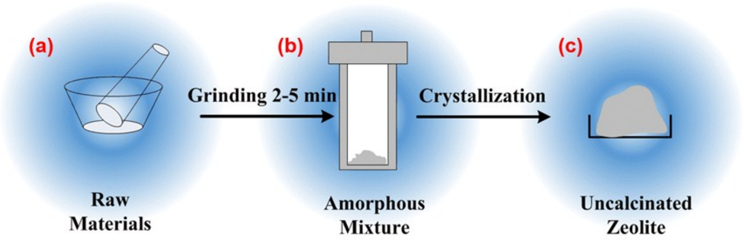
Contents

A. Materials and methods

Synthesis of SAPO-11@G. SAPO-11@G was synthesized by the grinding synthesis method (GSM) following the procedure in Scheme 1.The chemical composition of the amorphous mixture applied is 1.0 P_2O_5: 1.0 Al_2O_3: 0.4 SiO_2: 1.0 DPA. Pseudo-boehmite (1.45 g, Industrial grade, 70 wt.% Al_2O_3, Yantai Henghui Petrochemical Co., Ltd), phosphoric acid (2.31 g, Analytical reagent, 85 wt.% H_3PO_4, Xirong Petrochemical Co., Ltd), di-propylamine (DPA) (1.11 g, Chemical reagent, Sinopharm Chemical Reagent Corporation), and colloidal silica (0.80 g, Industrial grade, 30 wt.% SiO_2, Qingdao Haiyang Petrochemical Co., Ltd) were mixed in a mortar. After grinding for 5 min, the amorphous mixture is obtained, which is viscous wrapping the water from the raw materials (i.e., physically adsorbed water on pseudo-boehmite, H_3PO_4 solution, and colloidal silica). The amorphous mixture was transferred in an autoclave and subjected to crystallization (200 ^oC, 4-24 h). The final product was washed by deionized water and activated at 600 ^oC for 4 h and named as SAPO-11@G. Suffix @G represents the sample obtained by the GSM.

Synthesis of SAPO-11@H. A reference sample under classical hydrothermal method was synthesized. In a typical synthesis, the chemical composition of the amorphous mixture applied is 1.0 P_2O_5: 1.0 Al_2O_3: 0.4 SiO_2: 1.0 DPA. A mixture of pseudo-boehmite (4.37 g) and phosphoric acid (6.92 g) with distilled water (50 g) was stirred for 2 h. Then, DPA (3.34 g) was added drop by drop. Subsequently, the mixture was stirred for 2 h followed by adding colloidal silica (2.4 g). After stirring for 2 h, the pH value of resulting hydrogel was mixed in the range of 5.0-5.5. Finally, the resulting hydrogel was transferred into autoclave and subjected to crystallization (200 ^oC, 24 h). The final product was washed by deionized water and activated at 600 ^oC for 4 h and named as SAPO-11@H. Suffix @H represents the sample obtained by hydrothermal method.



Scheme 1. SAPO molecular sieves synthesized by the GSM: (a) preparation of amorphous mixture consisting of pseudo-boehmite, H_3PO_4, colloidal silica, and DPA for 2-5 min, (b) crystallization at static conditions at 200 ^{o}C for 4-24 h, and (c) separation of crystalline samples.

Hydrothermal treatment of SAPO-11@G and SAPO-11@H. Hydrothermal treatment was carried out at 380 °C for 4 h with a flow of deionized water at the rate of 1.0 g min^{-1} at atmospheric pressure**.** Samples were put in ceramic bowls. Steam can go through from the bottom of the ceramic bowls.

Synthesis of CeAPO-11. Pseudo-boehmite (1.45 g), phosphoric acid (2.31 g), DPA (2.23 g), and $Ce(NO_3)_3 \cdot nH_2O$ (0.20 g, Analytical reagent, Sinopharm Chemical Reagent Corporation) were added in a mortar. After grinding for 5 min, the wet gel was put in the autoclave for crystallization (200 ^{o}C, 4-24 h). The crystalline product was washed by deionized water and subjected to activation at 600 ^{o}C for 4 h.

Synthesis of AlPO-11. Pseudo-boehmite (1.45 g), phosphoric acid (2.31 g), and DPA (2.23 g) were added in a mortar. After grinding for 5 min, the wet gel was put in the autoclave for crystallization (200 ^{o}C, 4-24 h). The crystalline product was washed by deionized water and subjected to activation at 600 ^{o}C for 4 h.

Preparation of catalysts Pt/SAPO-11@G and Pt/SAPO-11@H. Pt/SAPO-11@G and reference catalyst (i.e., Pt/SAPO-11@H) were prepared based on the reference[1]. Next, Pt/SAPO-11@H and Pt/SAPO-11@G were prepared with a Pt loading of 0.3 wt% via incipient impregnation[1] with H_2PtCl_6 solution with a size of 20-40 mesh were obtained via a pellet presser, followed by drying at 110 ^{o}C for 2 h and calcination at 400 ^{o}C for 4 h.

B. Characterizations

XRD patterns were measured with an X' Pert PRO MPD diffractometer (P A Nalytical B.V. Netherlands) with Cu Kα radiation (λ = 0.15418 nm), operating at 40 kV, 40 mA, and scanning speed of 10 ° min^{-1}. Relative crystallinity is calculated by the sum of peaks areas at 2θ=8.0-8.5° and 20.0-23.5°. The morphology of the samples was observed with scanning electron microscopy (Hitachi S-4800, Japan HQ) with an acceleration voltage of 0.5-30 kV. The samples were covered by a conductive layer (gold). N_2 adsorption-desorption measurements were carried out with an ASAP 2020 Micromeritics instrument. The specific surface area was obtained with Brunauer Emmet Teller (BET) analysis. Total pore volume was calculated based on the amount of the nitrogen adsorbed at P/P_0=0.99. Micropore volume was obtained by the t-plot analysis. Magic angle spinning nuclear magnetic resonance (MAS NMR) spectra of ^{27}Al and ^{31}P were measured with a Bruker Advance 400 spectrometer. ^{29}Si and ^{1}H/^{29}Si cross-polarization (CP) solid-state MAS NMR on a Bruker Avance III-HD 500 (11.7 T) spectrometer operating at 99.3 MHz, using zirconia rotors of 4-mm outer diameter spun at 12 kHz. For ^{29}Si MAS NMR, a single pulse excitation (30° flip angle) is used with a recycle delay of 30 s. For ^{1}H/^{29}Si CP MAS NMR, a contact time of 5 ms and a recycle delay of 2 s are used. Transmission electron microscopy (TEM) images of catalysts and element mapping were obtained with JEOL JEM2100UHR instrument operating at 120 kV. Particle size of Pt (D) was randomly selected to reflect their actual size. Pt spherical particles were measured at diametrical direction.

$$D = d \pm SE$$

$$SE = \sqrt{\frac{\sum_{1}^{N} (x_i - d)^2}{N-1}}$$

d： mean value of selected particles

SE: standard error

N: number of selected particles

x_i: the particle size of selected particles ($i \leq N$)

The UV-Vis diffuse reflectance spectra (UV-Vis DRS) were recorded with a Jena Specord 210 Plus UV-Vis spectrophotometer using $BaSO_4$ as a reference. Temperature-programmed desorption of ammonia (NH_3-TPD) was conducted to determine the acidity of samples with chemisorption (ASAP 2920, Micromeritics).

C. Hydroisomerization evaluation.

The hydroisomerization of n-hexane (Sinopharm Chemical Reagent Co., Ltd.) was carried out in a fixed-bed micro-reactor. In each run, catalysts (2.0 g) were loaded into the reactor and the reactant n-hexane was fed into the reactor by a syringe pump. Prior to the reaction, the catalyst was pre-reduced in hydrogen flow for 4 h. Catalysts were tested at 340-380 ^{o}C and 2 MPa. The weight hourly space velocity (WHSV) is 1.0 h^{-1} and the mole ratio of hydrogen to n-hexane was selected as 4.0. The reactant and products were analyzed on-line by a gas chromatograph (Agilent 7820) equipped with a flame ionization detector.

D. Supplementary figures and tables.

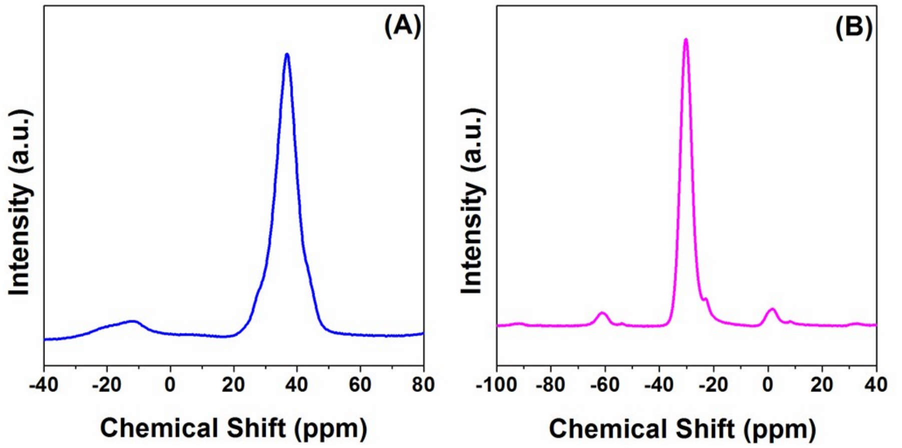


Fig. S1 ^{27}Al (A) and ^{31}P (B) MAS NMR spectra of SAPO-11@G heated for 4 hours.

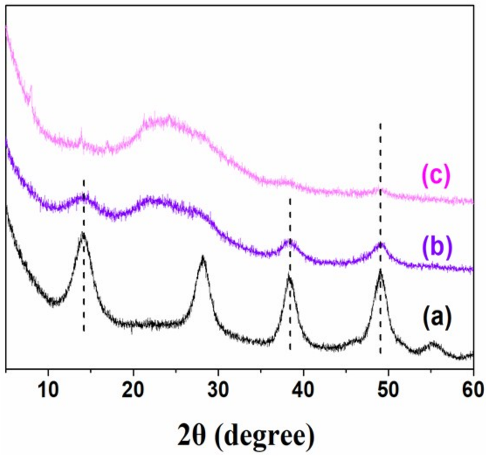


Fig. S2 XRD patterns of: pseudo-boehmite (a), SAPO-11@H heating for 1.5 h (b), and SAPO-11@G heating for 1.5 h (c).

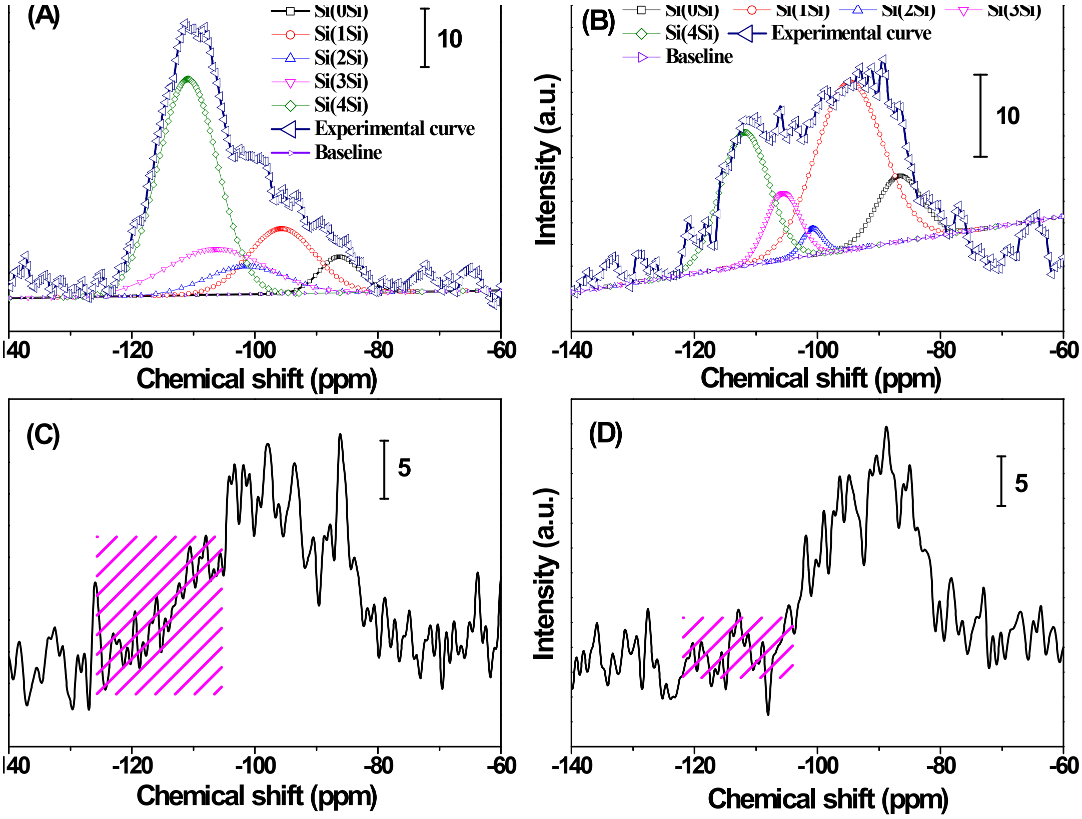


Fig. S3 Gaussian fitting of ^{29}Si MAS NMR spectra of SAPO-11@G (A) and SAPO-11@H (B) and ^{1}H/^{29}Si CP MAS NMR spectra of SAPO-11@G (C) and SAPO-11@H (D)

Chemical shift of resonance signals at -112, -106, -101, -95, -86 ppm represents Si(4Si), Si(3Si), Si(2Si), Si(1Si), and Si(0Si) species, respectively. Slash area in Figures C and D represents the resonance signals of Si(4Si) under the condition of ^{1}H/^{29}Si CP MAS NMR spectra.

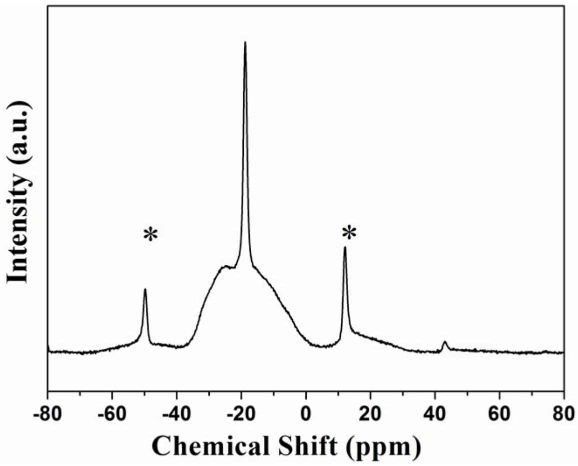


Fig. S4 ^{31}P MAS NMR spectrum of SAPO-11@G heating for 2 h (Note: *is the spinning sideband).

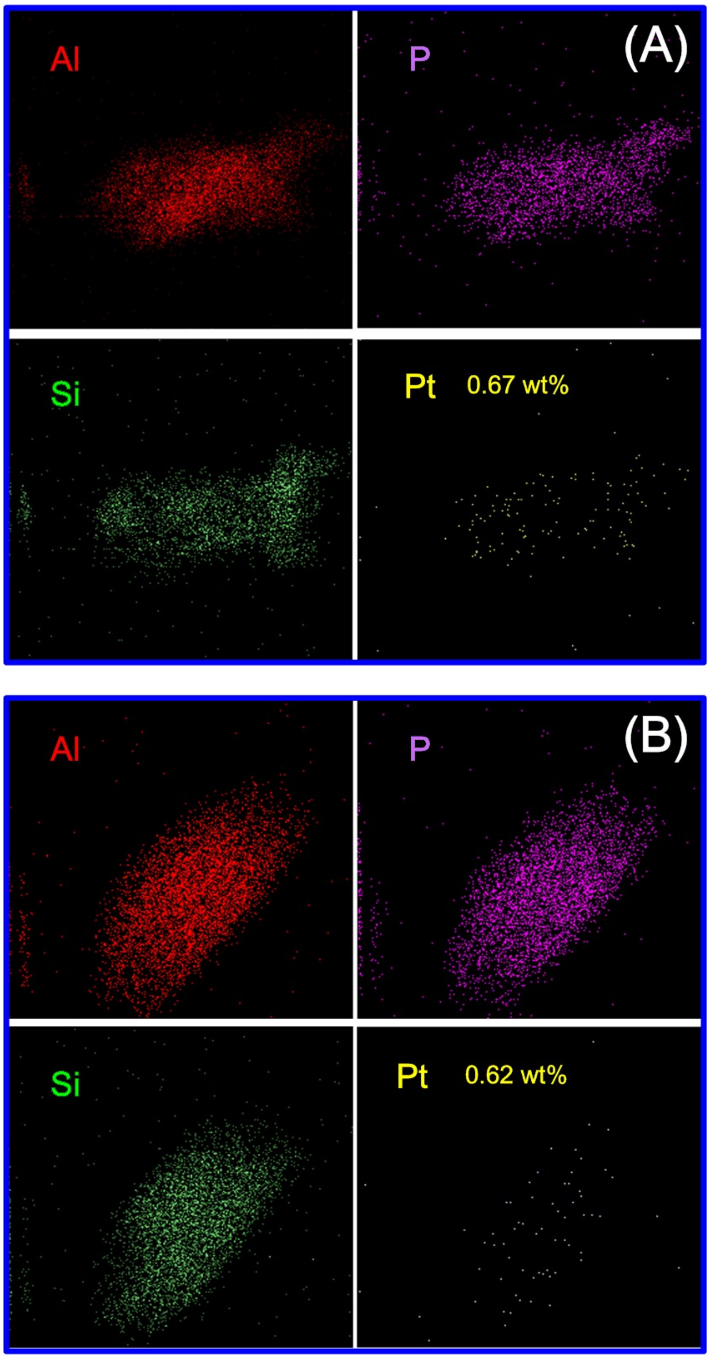


Fig. S5 Elemental mapping spectra of SAPO-11@G (A) and SAPO-11@H (B).

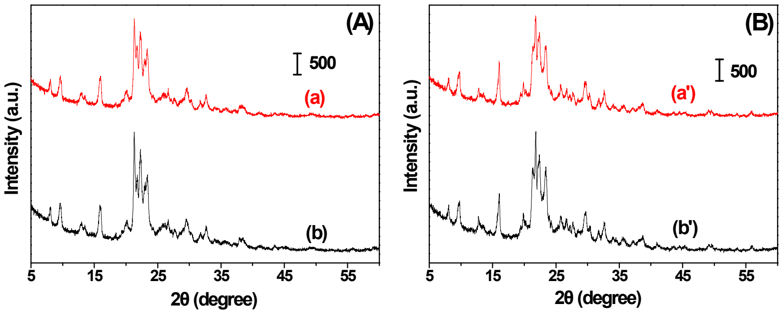


Fig. S6 XRD patterns of SAPO-11@H (A) and SAPO-11@G (B) before (a and a’) and after (b and b’) hydrothermal treatment.

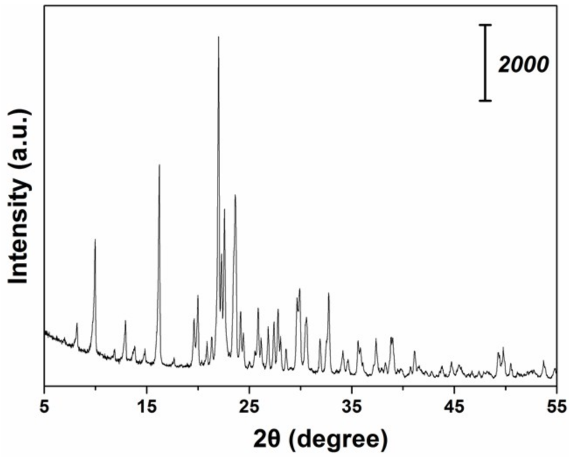


Fig. S7 XRD pattern of AlPO-11 molecular sieve.

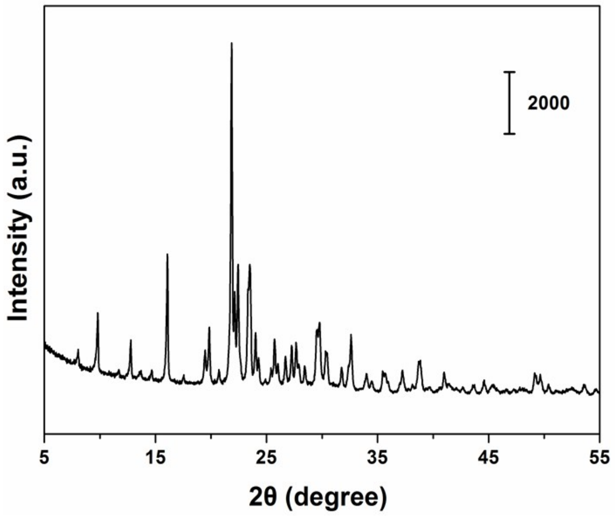


Fig. S8 XRD pattern of CeAPO-11 molecular sieve.

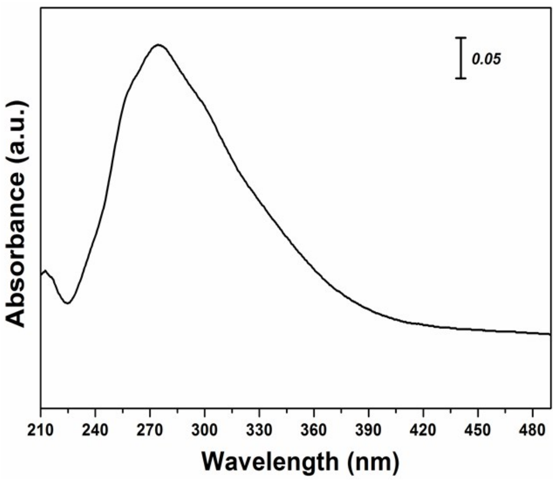


Fig. S9 UV-Vis diffuse reflectance spectrum of CeAPO-11 molecular sieve.

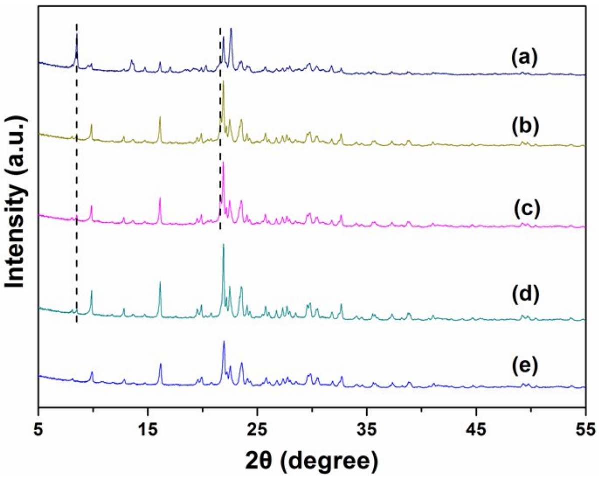


Fig. S10 XRD patterns of CeAPO-11 synthesized at pH=4.5 (a), 5.5 (b), 6.5 (c), 7.0 (d), and 8.0 (e).

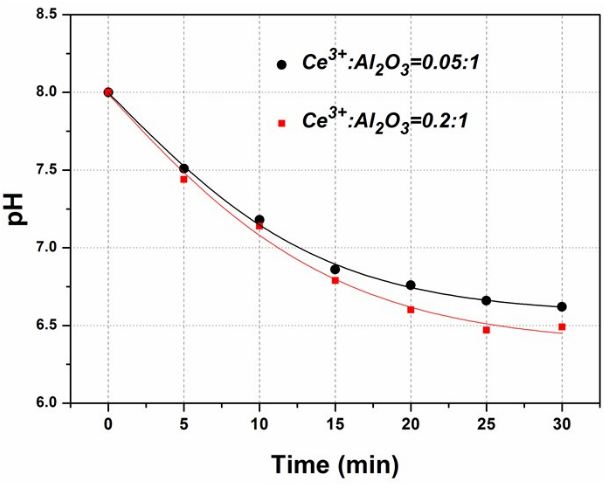


Fig. S11 Variation of pH value during the preparation of dry gel (water was removed under heating at 100 °C for 30 min).

Table S1 Pore structure of SAPO-11@G and SAPO-11@H

Samples	BET surface area (m^2/g)	Micropore surface area (m^2/g)	Micropore volume (cm^3/g)	Mesopore volume (cm^3/g)
SAPO-11@G	211	169	0.09	0.10
SAPO-11@H	198	169	0.09	0.06

Table S2 Elemental composition of SAPO-11@G and SAPO-11@H

Samples	*Elemental composition (atomic percent, %)			
	Al	P	Si	O
SAPO-11@G	19.41	15.32	6.03	59.24
SAPO-11@H	19.91	16.99	4.45	58.65

*Measured by EDS

Table S3 Phosphorous species in ^{31}P MAS NMR spectra

Chemical shift (ppm)	Phosphorous species	Reference
-20~-30	Longer polymeric phosphate chains and extra-framework aluminum phosphate as well as highly condensed polyphosphate species	[2, 3]
-18	Long-range ordering layered phase as an intermediate of AlPO-11	[4]
-14	Middle groups in pyrophosphates or short-chain polyphosphate species	[5]
-8	Terminal $[PO_4]^{3-}$ groups in polyphosphoric species	[6]
0	Residual phosphorus compound	[7]

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