Electronic Supporting Information for:

Tailored synthesis of nanosized SAPO-34 via time-controlled silicon release enabled by organosilane precursor

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A. Synthesis and method

Materials: The reagent used were pseudoboehmite (70 wt% Al_2O_3, Aluminum Corporation of China), phosphoric acid (85wt%, Shanghai Lingfeng Chemical Reagent Co. Ltd.), tetraethylammonium hydroxide (TEAOH) (35wt%, Shanghai Cainorise Chemicals Co., Ltd), tetraethyl orthosilicate (TEOS, 28 wt % SiO_2, Shanghai Lingfeng Chemical Reagent Co. Ltd), Phenyltrimethoxysilane (PTMS, 97%, Gelest, Co,. Ltd), Tris(hydroxymethyl)aminomethane (TCI, >99.0%). These chemicals were used as provided without further purifications.

Synthesis: Hierarchical SAPO-34 named SAPO-34-PTMS was prepared using PTMS as solely silicon source. The molar composition of synthesis gel was 1.0 Al_2O_3: 1.0 P_2O_5: 0.6 PTMS: 2.0 TEAOH: 50H_2O. In a typical synthesis, 2.19 g pseudoboehmite was mixed with 3.46 g H_3PO_4 and 4.60 g deionized water. 1.84 g PTMS was added after digesting for 7 h. 12.64 g TEAOH was added dropwise after stirring another 2 h. The mixture was further stirred for 4 h to give a homogeneous gel. The synthesis gel was transferred to a 100 mL Teflon lined stainless steel autoclave for crystallization. Crystallization was conduct at 200 ºC under tumbling of 50 rpm for 72 h. The product was centrifuged, washed thoroughly with water before drying at 80 ºC for 6 h and calcination was done at 550 ºC for 6 h. To investigate the crystallization, part of the gel was sampled at various crystallization intervals and denoted by using synthesis time as suffix. For example, SAPO-34-PTMS-3h represent the sample was hydrothermal treated for 3h.

SAPO-34-In was synthesized by adding crystal growth modifier after precrystallization for 6 h. The preparation of synthesis and crystallization condition were identical to SAPO-34-PTMS. After precrystallization, the gel was quenched and 0.003 mole (0.363 g) tris(hydroxymethyl)aminomethane was added then stirred for 6 h to allow homogeneity. The final molar composition was 1.0 Al_2O_3: 1.0 P_2O_5: 0.6 Si: 2.0 TEAOH: 50H_2O: 0.2 tris(hydroxymethyl)aminomethane. A resumed crystallization was conduct for another 66 h to afford fully crystallization.

A series samples were synthesized with various PTMS amount. The PTMS amount used were 0.2, 0.3 and 0.4 in molar recipe. Other procedure was same as the SAPO-34-PTMS.

Conventional counterpart SAPO-34-C was synthesized using TEOS as silicon source, the other condition and handing were identical to SAPO-34-PTMS.

B. Characterization techniques

X-ray diffraction (XRD) patterns were gathered using a Rigaku 2550VB/PC diffractometer operating at 40 kV and 100 mA with Cu Kα X-ray source (λ = 1.5418 Å). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were captured on NOVA Nano SEM450 and JEL-2011 (JEOL) instruments, respectively. N_2 physisorption measurements were conducted on an ASAP 2020 HD (Micromeritics, USA) analyzer at -196 ºC, all samples were degas at 350 ºC for 4 h under vacuum before measurements. The surface areas were determined by the Brunauer-Emmett-Teller (BET) method. Micropore volumes and surfaces were derived from a *t*-plot approach, pore size distribution was derived from adsorption branch using Barret-Joyner-Halenda (BJH) method and the total pore volume values were estimated by the adsorption at a relative pressure p/p_0 = 0.99. Ammonium temperature programed desorption (NH_3-TPD) measurements were performed on a Chemisorb 2720 analyzer. The samples were pretreated at 600 °C for 1 h under He flow before saturated with ammonium at 100 °C. The profiles collected between 100 °C and 600 °C at a ramp of 10 $°C \cdot min^{-1}$. Elementary composition was measured by inductively coupled plasma optical emission spectrometry (ICP) on an IRIS 1000 instrument. ^{29}Si, ^{13}C ^{27}Al and ^{31}P solid state magic angle spinning nuclear magnetic resonance (MAS NMR) measurements were carried out on a Bruker 600 MHz instrument. ^{13}C and ^{29}Si liquid NMR spectra were collected on Bruker avance III 400 instrument. The chemical shifts of ^{31}P, ^{27}Al, and ^{29}Si were referenced to 85 wt% H_3PO_4, 1M $Al(NO_3)_3$ aqueous solution, and tetramethylsilane, respectively.

C. Catalytic assessment

Methanol to olefin conversion (MTO) was carried out on a fix bed reactor at atmospheric pressure. 2.00 g catalyst (20-40 mesh) was preheated at 550 °C for 3h under N_2 flow before reaction. The pure methanol was pumped into preheater to transform the liquid into vapor and then flow though the catalysts. Reaction temperature was 460 °C and the methanol weight hourly space velocity (WHSV) was 6 h^{-1}. The products were analyzed by an on-line gas chromatograph equipped with a flame ionization detector.

D. Supplementary Figures and Tables

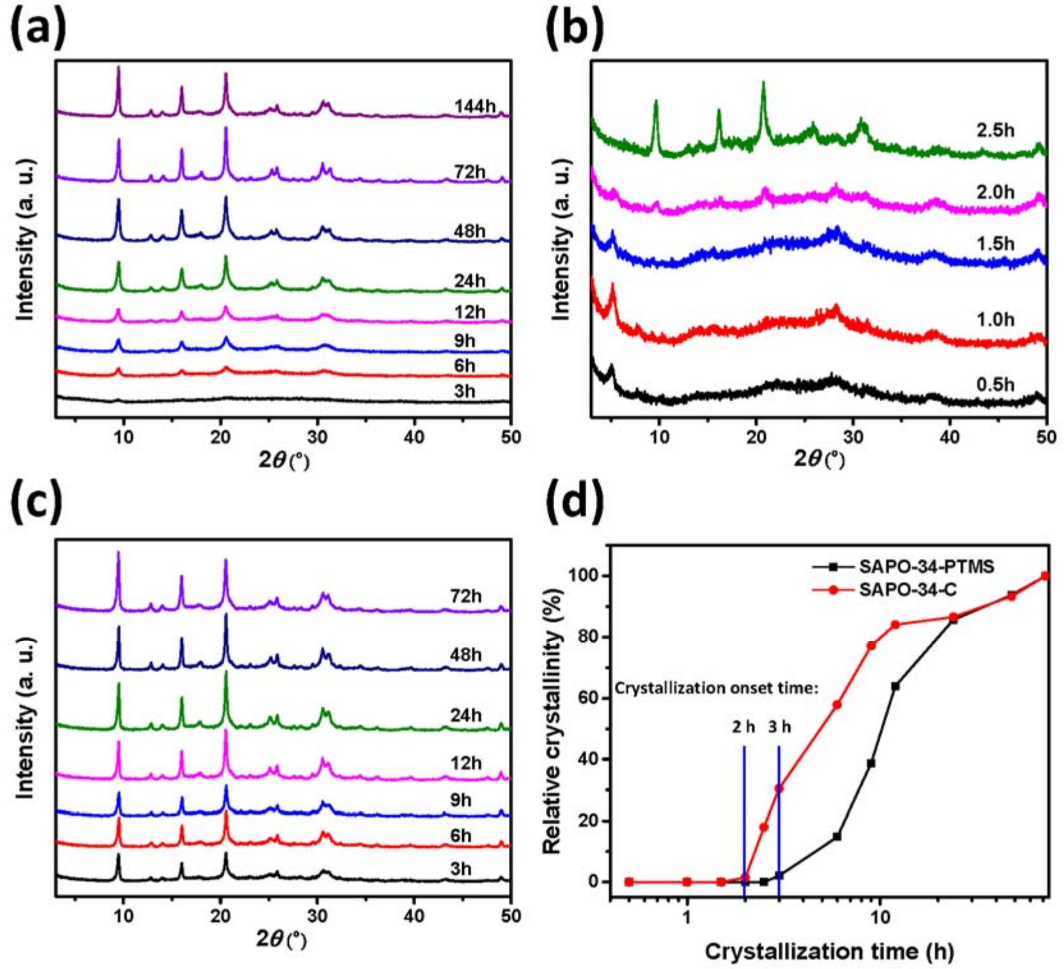

Fig S1 Time-dependent XRD patterns of SAPO-34-PTMS (a), SAPO-34-C (b, c), relative crystallinity evolution with crystallization tome (d)[a]

[a] Relative crystallinity calculation based on the area of peaks at 2θ = 9.5, 12.81, 16.0, 20.5, 25.8 and 30.50 °, the relative crystallinity of fully crystallized SAPO-34-C and SAPO-34-PTMS were set as 100%, respectively.

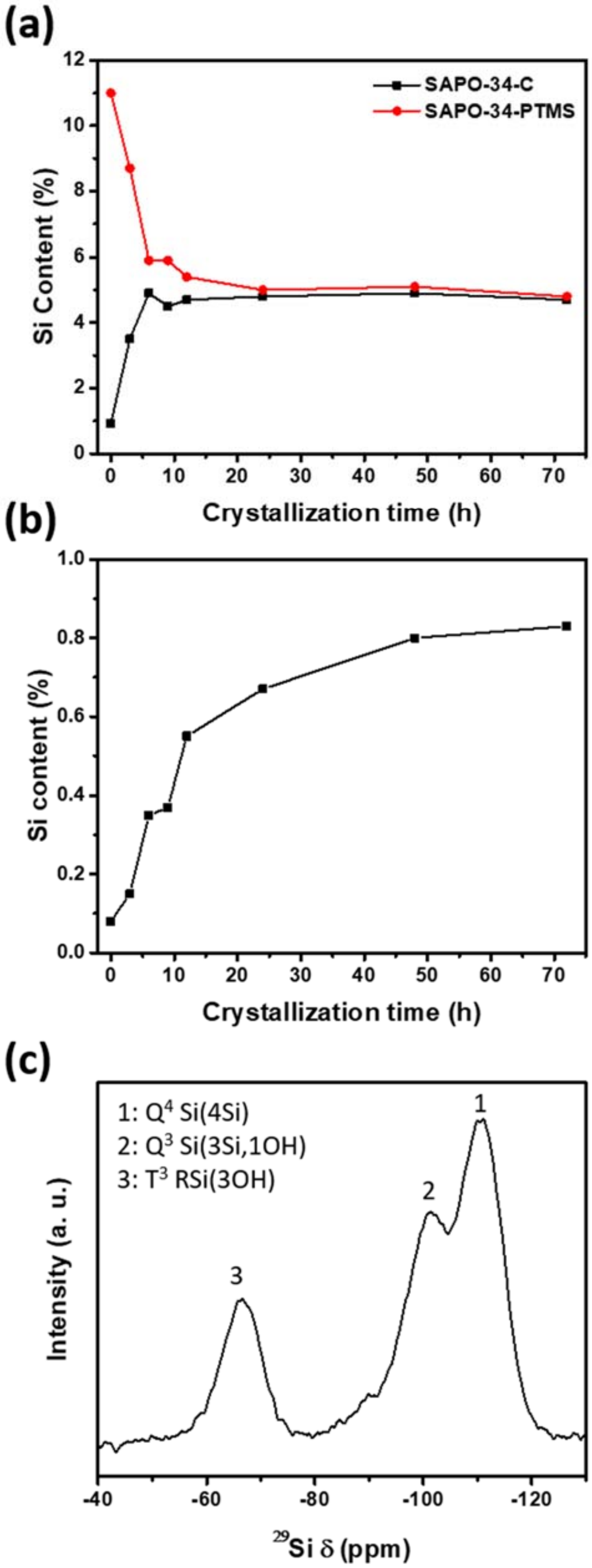

Fig S2 Si content evolution with crystallization time for SAPO-34-C and SAPO-34-PTMS (a), aqueous mother liquid (b), ^{29}Si CP MAS NMR spectrum for enriched mother liquor collected after crystallization for 6 h (c)

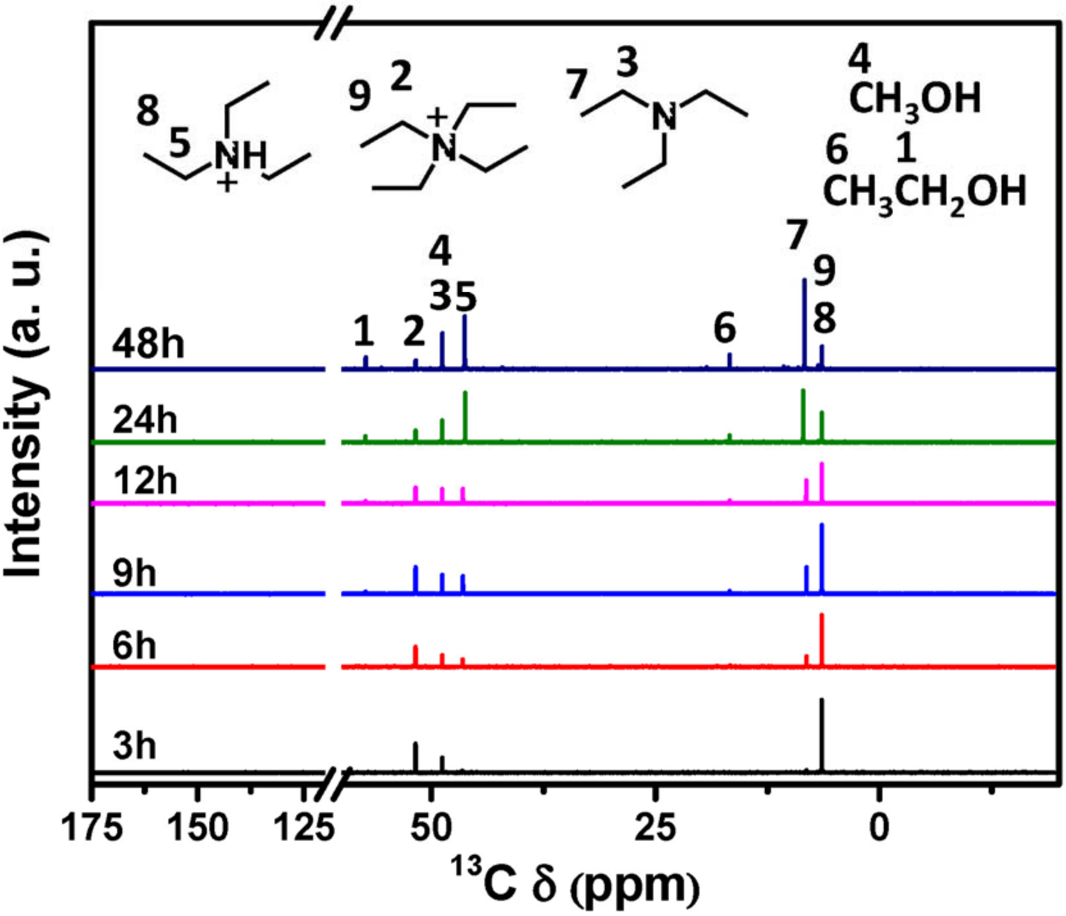

Fig S3 Time-dependent ^{13}C NMR spectra of aqueous mother liquor

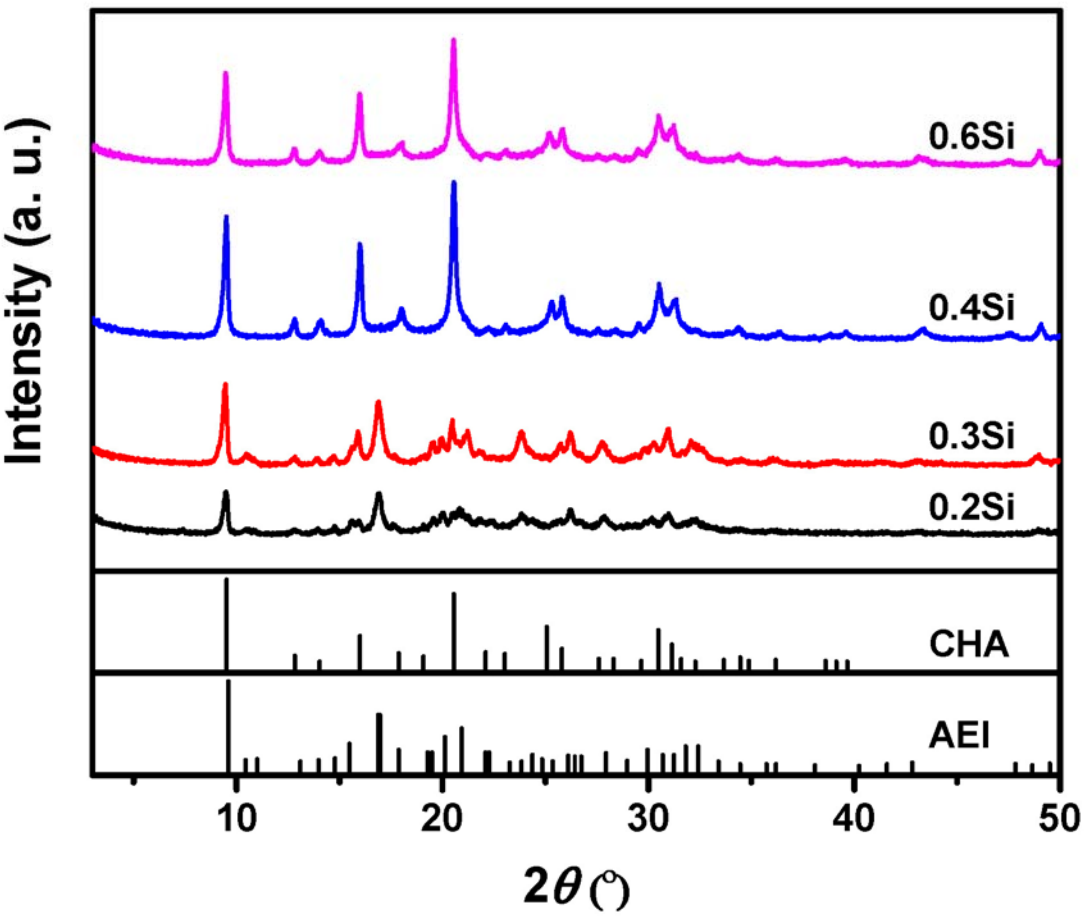

Fig S4 XRD patterns of samples synthesized with various PTMS content

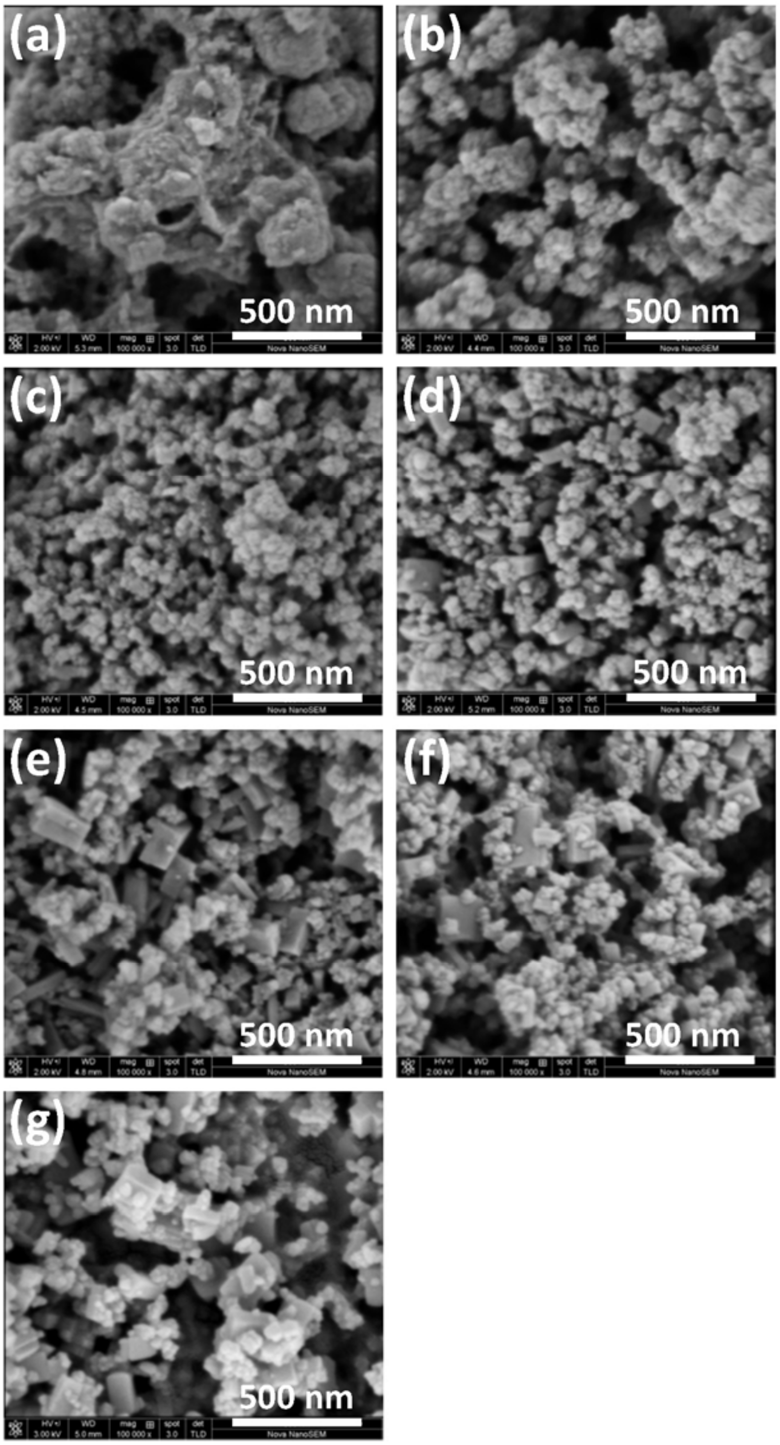

Fig S5 SEM images of SAPO-34-PTMS-3h (a), SAPO-34-PTMS-6h (b), SAPO-34-PTMS-9h (c), SAPO-34-PTMS-12h (d), SAPO-34-PTMS-24h (e), SAPO-34-PTMS-48h (f), SAPO-34-PTMS-72h (g)

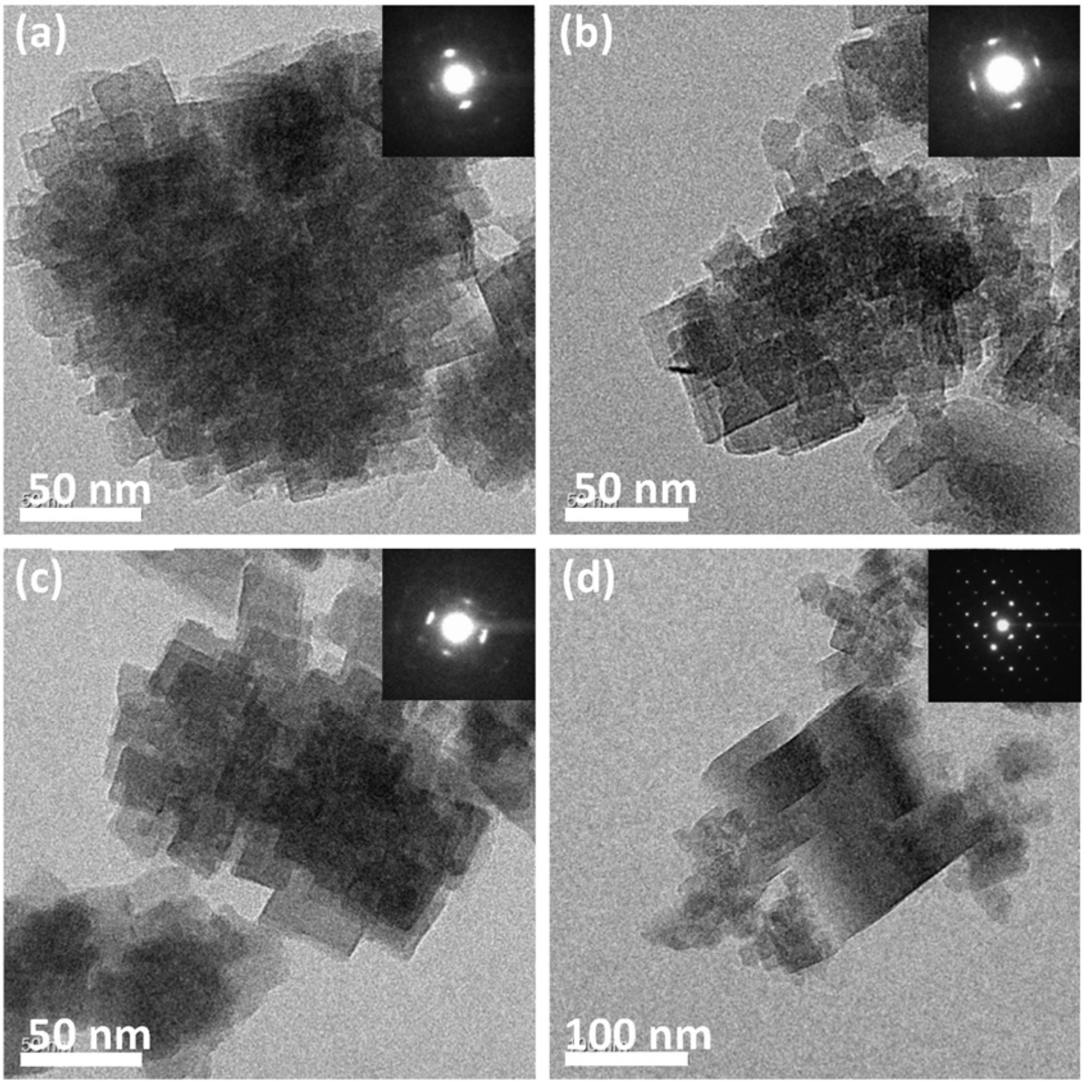

Fig S6 TEM images of SAPO-34-PTMS-6h (a), SAPO-34-PTMS-9h (b), SAPO-34-PTMS-12h (c), SAPO-34-PTMS-24h (d)

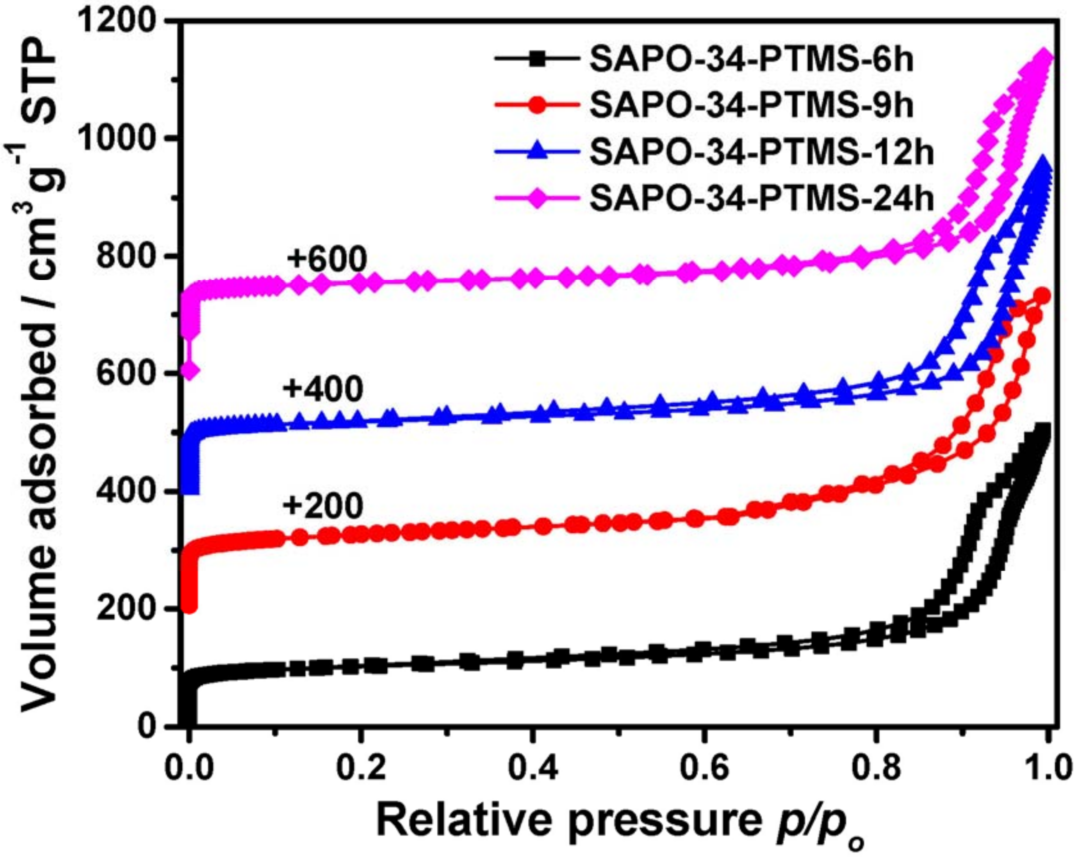

Fig S7 N_2 physisorption isotherms of SAPO-34-PTMS-6h, SAPO-34-PTMS-9h, SAPO-34-PTMS-12h, SAPO-34-PTMS-24h, respectively

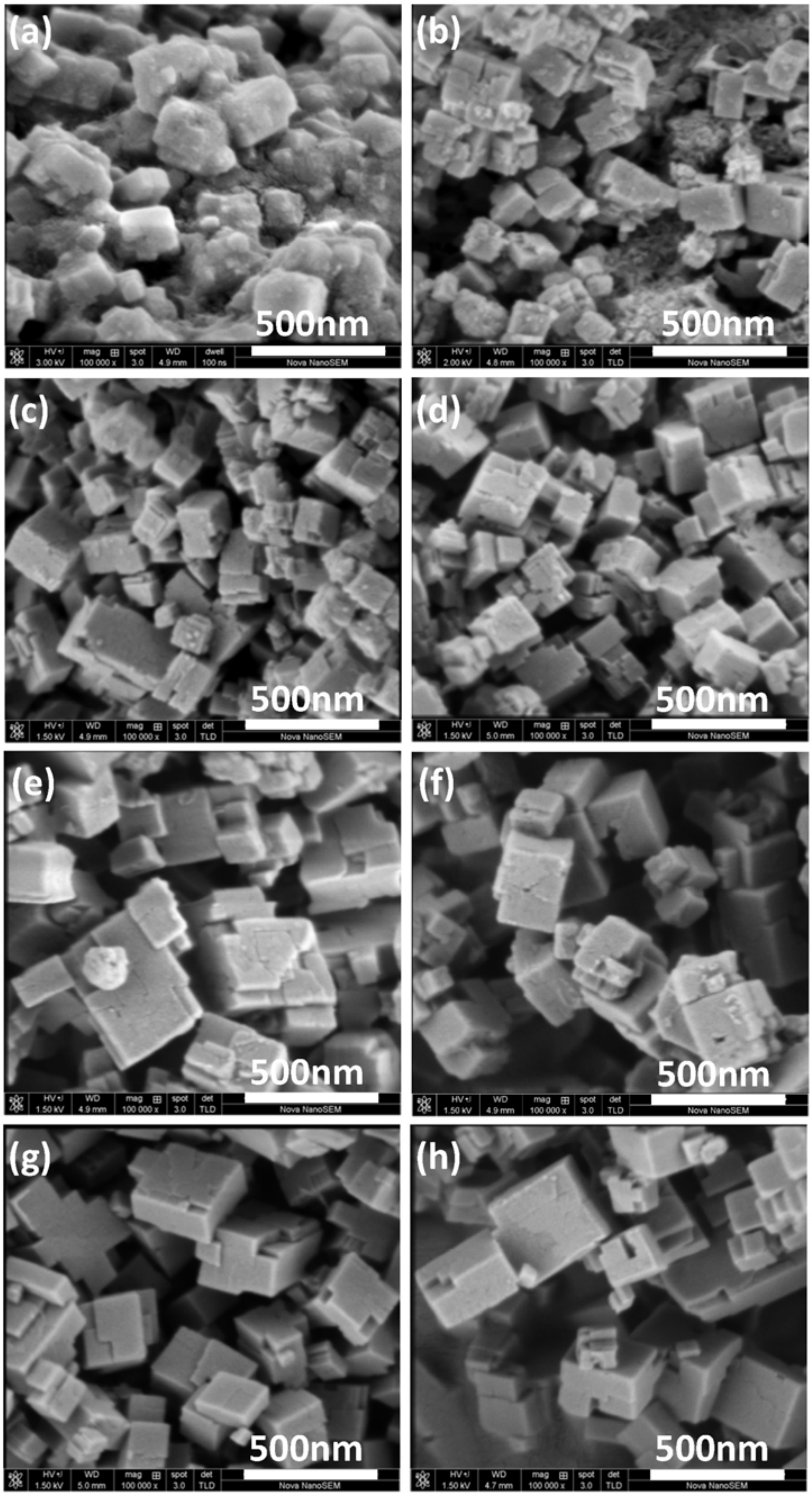

Fig S8 SEM images of SAPO-34-C-2.5h (a), SAPO-34-C-3h (b), SAPO-34-C-6h (c), SAPO-34-C-9h (d), SAPO-34-C-12h (e), SAPO-34-C-24h (f), SAPO-34-C-48h (g), SAPO-34-C-72h (h)

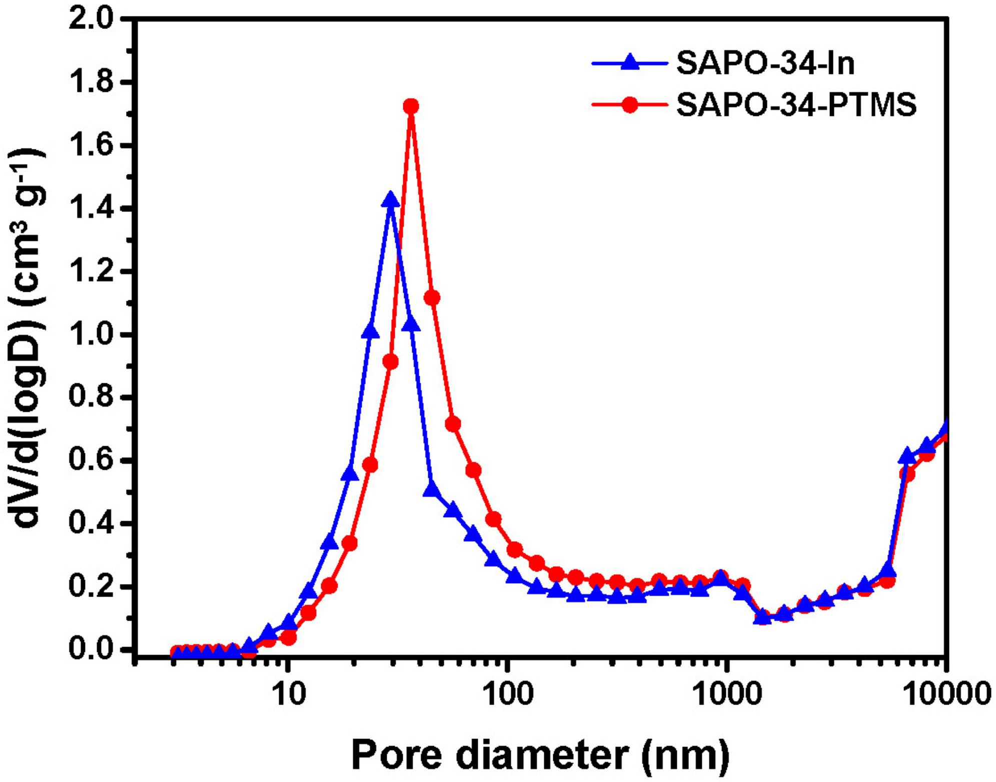

Fig S9 Mercury intrusion pore size distribution for SAPO-34-PTMS and SAPO-34In

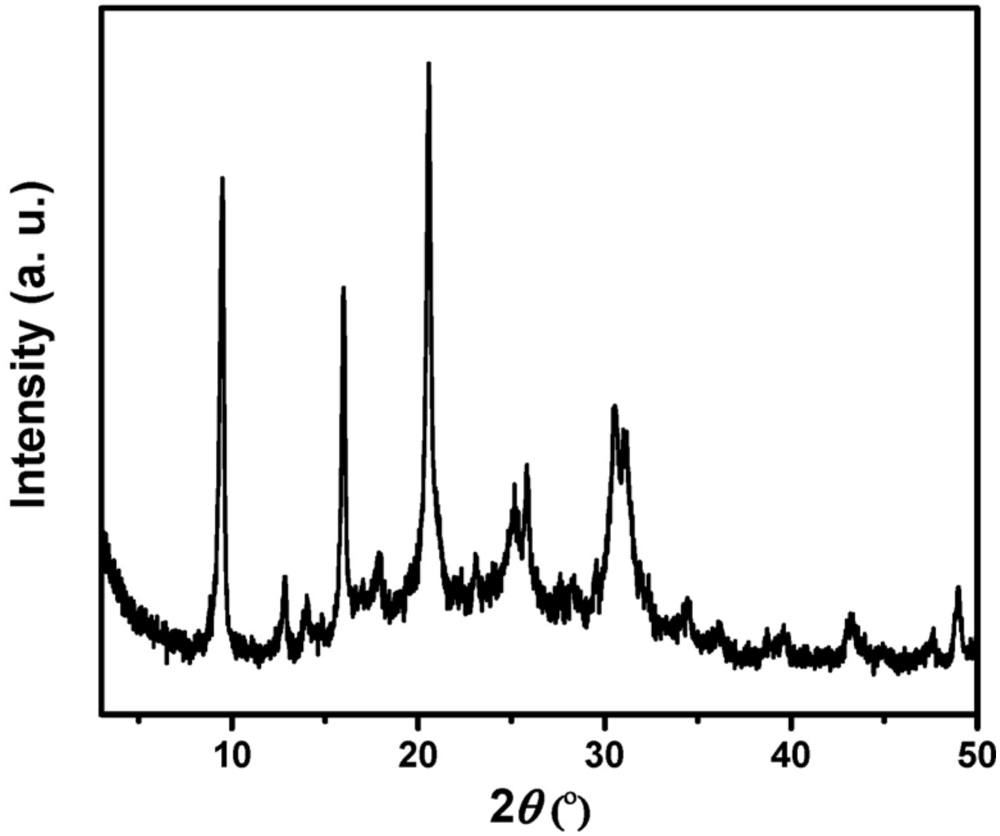

Fig S10 XRD pattern of SAPO-34-In

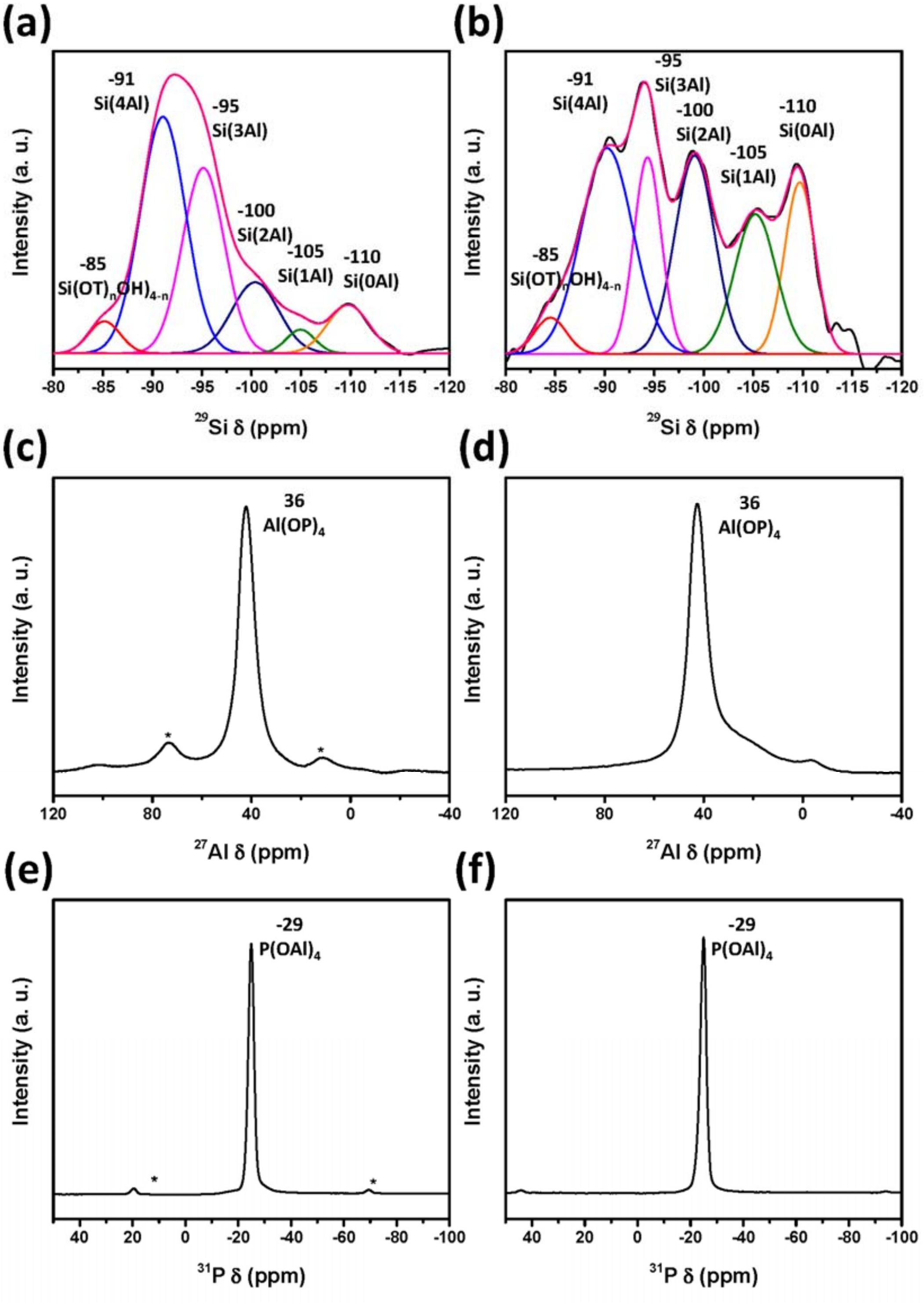

Fig S11 ^{29}Si (a, b), ^{31}P (c, d), ^{27}Al (e, f) MAS NMR spectra of SAPO-34-PTMS and SAPO-34-C, respectively

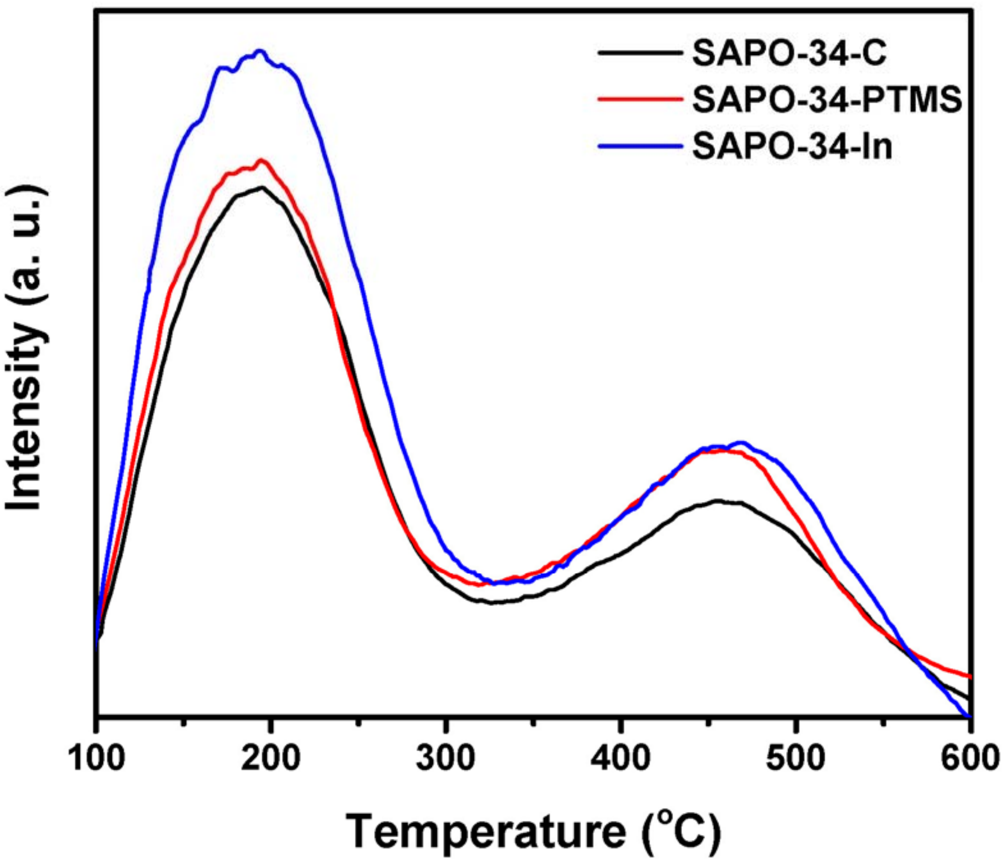

Fig S12 NH_3-TPD profiles for SAPO-34-C, SAPO-34-PTMS and SAPO-34-In

Table S1 Textural properties of hierarchical SAPO-34 after various hydrothermal

sample	S_{BET} ($\mathrm{m^2 \cdot g^{-1}}$)	S_{micro} ($\mathrm{m^2 \cdot g^{-1}}$)	S_{ext} ($\mathrm{m^2 \cdot g^{-1}}$)	V_{micro} ($\mathrm{cm^3 \cdot g^{-1}}$)	V_{total} ($\mathrm{cm^3 \cdot g^{-1}}$)
SAPO-34-PTMS-6h	385	280	141	0.11	0.86
SAPO-34-PTMS-9h	454	311	106	0.13	0.80
SAPO-34-PTMS-12h	473	350	104	0.14	0.78
SAPO-34-PTMS-24h	608	519	89	0.20	0.63

Table S2 Distribution of silicon atoms by deconvolution of different ^{29}Si MAS NMR spectra

sample	$Si(OT)_n(OH)_{4-n}$ (%)	Si(4Al) (%)	Si(3Al) (%)	Si(2Al) (%)	Si(1Al) (%)	Si(0Al) (%)
SAPO-34-PTMS	4.0	42.0	30.5	13.0	2.6	7.9
SAPO-34-C	3.2	29.6	15.0	21.8	16.0	14.4