Supporting information for

Creation of Hollow SAPO-34 Single Crystals by Alkaline or Acid Etching

Yuyan Qiao,[a,b] Miao Yang,[a] Beibei Gao,[a,b] Linying Wang,[a] Peng Tian,*[a] Shutao Xu,[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

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

Experimental Section

1. Chemical reagents

All chemical reagents were used without further purification. Orthophosphoric acid (85 wt%), diethylamine (DEA), NaOH and HCl (37 wt%) were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd.. Tetraethylammonium hydroxide (TEAOH, 35 wt%), tetramethylammonium hydroxide (TMAOH, 25 wt%) and tetrapropylammonium hydroxide (TPAOH, 25 wt%) were purchased from Runjing Chemical Co., Ltd.. The other chemical reagents used in the experiments included fumed silica (Shenyang Chemical Co., Ltd.), pseudoboehmite (67.5 wt%, CHINALCO), tetramethyl ethylenediamine (TMEDA, Sinopharm Chemical Reagent Co., Ltd.).

2. Preparation of SAPO molecular sieve precursors

Synthesis of SAPO-34 (SP34-P): an initial gel with a molar composition of 2.0 TEAOH / 0.5 TMEDA / 1.0 Al_2O_3 / 1.2 P_2O_5 / 1.0 SiO_2 / 60 H_2O was prepared by mixing pseudoboehmite, water, orthophosphoric acid, fumed silica, TEAOH and TMEDA in sequence. Milled SAPO-34 seeds (1 % gel weight) were finally added into the gel under stirring. The crystallization was conducted in a stainless steel autoclave at 200 ^oC for 16 h under rotation. The as-synthesized product was recovered through filtration, washed, and dried at 110 ^oC overnight.

Synthesis of SAPO-20: an initial gel with a molar composition of 1.5 TMAOH / 1.0 TMEDA / 1.0 Al_2O_3 / 1.0 P_2O_5 / 1.0 SiO_2 / 60 H_2O was prepared by mixing pseudoboehmite, water, orthophosphoric acid, fumed silica, TMAOH and TMEDA in sequence. Milled SAPO-34 seeds (1 % gel weight) were finally added into the gel under stirring. The crystallization was conducted in a stainless steel autoclave at 200 ^oC for 24 h under rotation. The as-synthesized product was recovered through filtration, washed, and dried at 110 ^oC overnight.

3. Alkaline or acid treatments

All the alkaline or acid treatments conditions were listed in Table 1. Typically, for alkaline treatment, 1 g SAPO-34 precursor was added to 12 g of 0.6 mol/L TEAOH solution. Then the mixture was mixed and heated in an autoclave at 180 ^oC for 1 h under rotation. The product was recovered through filtration, washed, and dried at 110 ^oC overnight. For acid treatment, the procedure was similar to the above.

4. Characterization

The powder X-ray diffraction (XRD) data were recorded on a PANalytical X'Pert PRO X-ray diffractometer with Cu Kα radiation (λ = 1.54059Å) operating at 40 mA and 40 kV. The crystal morphology was observed by field emission scanning electron microscopy (Hitachi SU8020).

Transmission electron microscopy (TEM) images were recorded with a JEM-2100 electron microscope. The bulk and surface compositions of samples were determined with Philips Magix-601 X-ray fluorescence (XRF) spectrometer and VG ESCALAB MK2 X-ray photoelectron spectrometer (XPS). Textural properties of the calcined samples were determined by N_2 adsorption/desorption at -196 ^oC on a Micromeritics ASAP 2020 system. All the solid state NMR experiments were performed on a Bruker AvanceIII 600 spectrometer equipped with a 14.1 T wide-bore magnet. The resonance frequencies were 156.4, 242.9 and 119.2 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-silapentane-5-sulfonate sodium salt (DSS) for ^{29}Si. ^{27}Al and ^{31}P MAS NMR experiments were performed on a 4 mm MAS probe with a spinning rate of 12 kHz. ^{27}Al MAS NMR spectra were recorded using one pulse sequence. A 200 scans were accumulated with a $\pi/8$ pulse width of 0.75 μs and a 2 s recycle delay. ^{31}P MAS NMR spectra were recorded using high-power proton decoupling. A 32 scans were accumulated with a $\pi/4$ pulse width of 2.25 μs and a 30 s recycle delay. ^{29}Si CP/MAS NMR spectra were recorded with a 4 mm MAS probe with a spinning rate of 8 kHz. A 4096 scans were accumulated with a contact time of 3 ms and a recycle delay of 2 s. The temperature-programmed desorption of ammonia (NH_3-TPD) was carried out with an Autochem 2920 equipment (Micromeritics). The calcined samples (100 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).

5. Catalytic testing

Alkylation of benzene with benzyl alcohol was performed in autoclave. 0.15 g of the catalyst was transferred to the 100 ml Parr reactor; Then 29.8 g benzene (99.5%) and 0.52 g benzyl alcohol (98%) were added in sequence resulting in a molar ratio of benzene to benzyl alcohol of 80. The reactor was purged with nitrogen and maintained a permanent pressure of 20–25 bars during the reaction, so the reactants could keep in the liquid phase at the reaction temperature of 140 ^oC. The mixture was stirred at 300 rpm throughout the run, which was determined to be sufficiently fast. After 1 h reaction, a small amount of liquid sample were withdrawn and analyzed by using GC–MS equipped with a capillary HP-5 (Agilent Technologies) column.

Table S1. Conditions for base and acid treatments of SAPO molecular sieves

Sample	Reagent	C[a]	LSR[b]	T(°C)	t(h)	R (r/min)[c]	Product	Solid yield
SP34-TEAOH	TEAOH	0.6	12	180	1	60	CHA	35%
SP34-TPAOH	TPAOH	0.6	12	180	1	60	CHA	38%
SP34-TMAOH	TMAOH	0.9	12	180	1	60	CHA	39%
SP34-DEA	DEA	1	10	180	1	60	CHA	42%
SP34-NaOH	NaOH	0.63	20	80	6	60	amorphous	48%
SP34-HCl	HCl	0.58	10	80	3	60	CHA	25%
SP34-HCl-i	HCl	0.96	10	180	1	60	amorphous	27%
SAPO-20-TMAOH	TMAOH	0.5	10	200	16	10	SOD	38%
SAPO-20-HCl	HCl	0.9	11	180	1	60	SOD+amorphous	22%

[a] The concentration of base or acid aqueous solution (mol/L). [b] Liquid to solid ratio (ml/g). [c] The tumbling speed during treatment.

Table S2. Bulk and surface compositions of the sample.

Sample	Product composition		R [c]
	Bulk [a]	Surface [b]	
SAPO-20	$Si_{0.209}Al_{0.435}P_{0.357}$	$Si_{0.488}Al_{0.284}P_{0.228}$	2.33

[a] Determined by XRF. [b] Determined by XPS. [c] $R=[Si/(Al+P+Si)]_{surface}/[Si/(Al+P+Si)]_{bulk}$

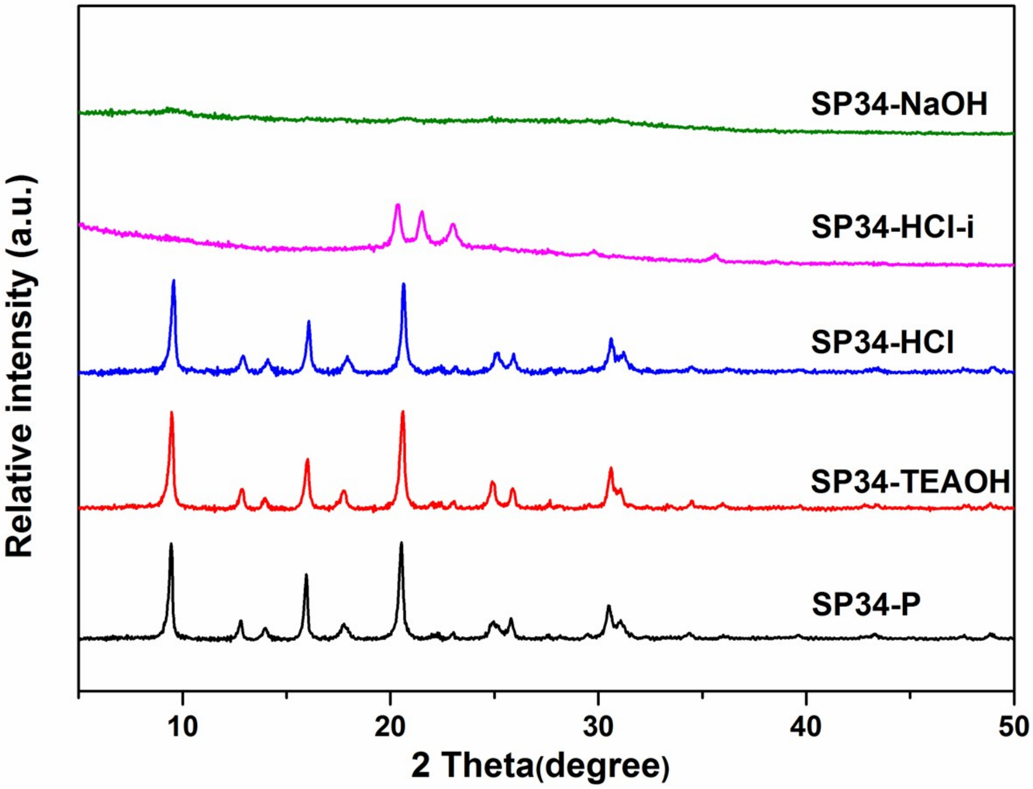

Figure S1. The XRD patterns of the samples.

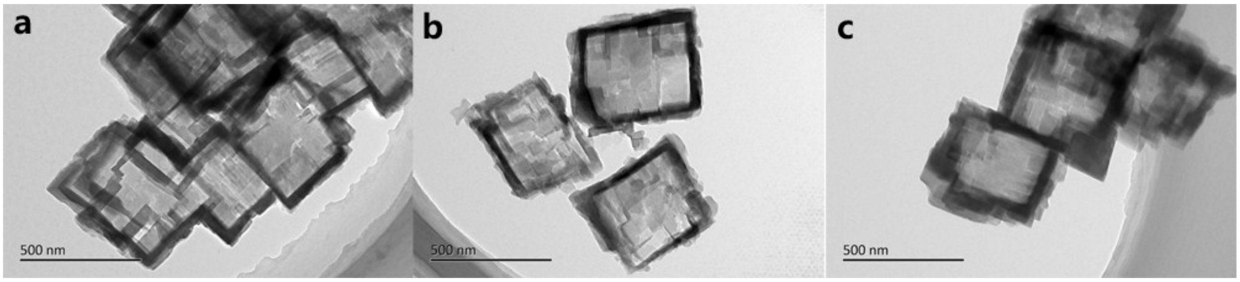

Figure S2. The TEM images of the base-treated samples: (a) SP34-TPAOH, (b) SP34-TMAOH, (c) SP34-DEA.

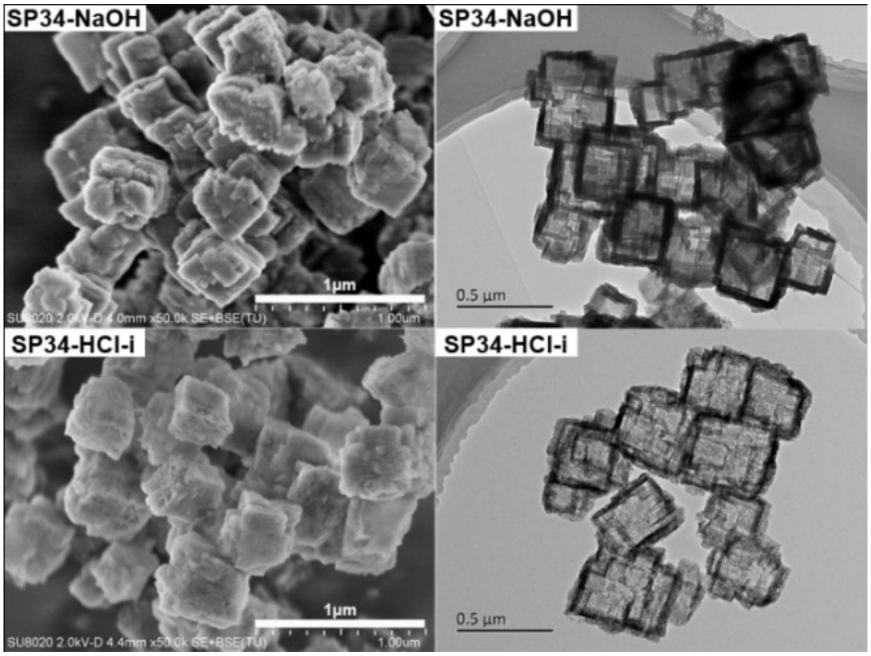

Figure S3. The SEM (left) and TEM (right) images of SP34-NaOH and SP34-HCl-i.

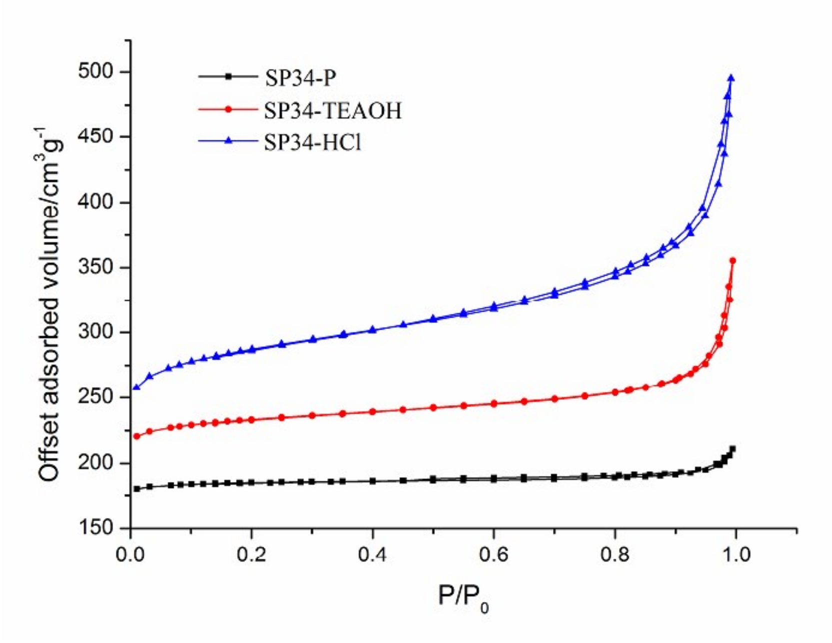

Figure S4. The N_2 adsorption-desorption isotherms of the samples.

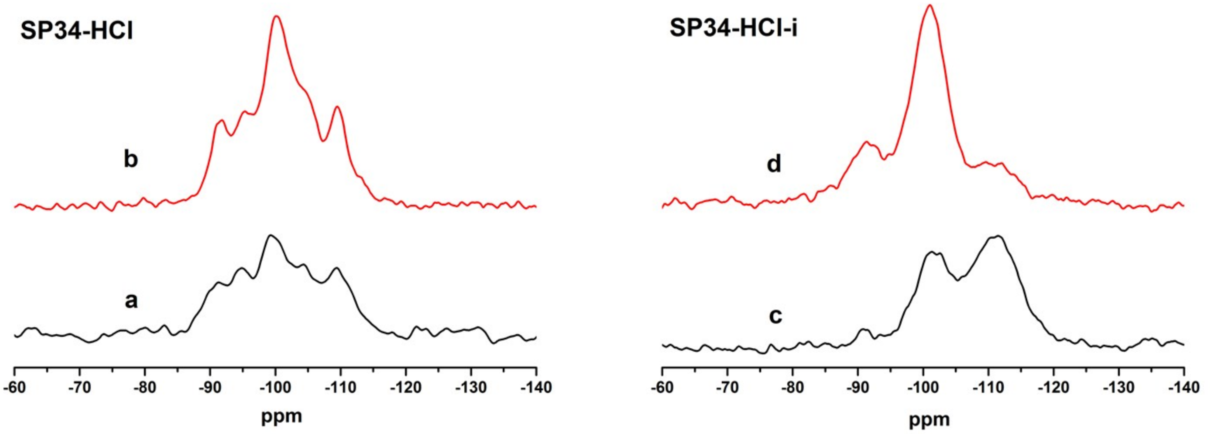

Figure S5. The ^{29}Si MAS NMR (a, c) and $^{1}H \rightarrow ^{29}Si$ CP MAS NMR (b, d) spectra of SP34-HCl and SP34-HCl-i.

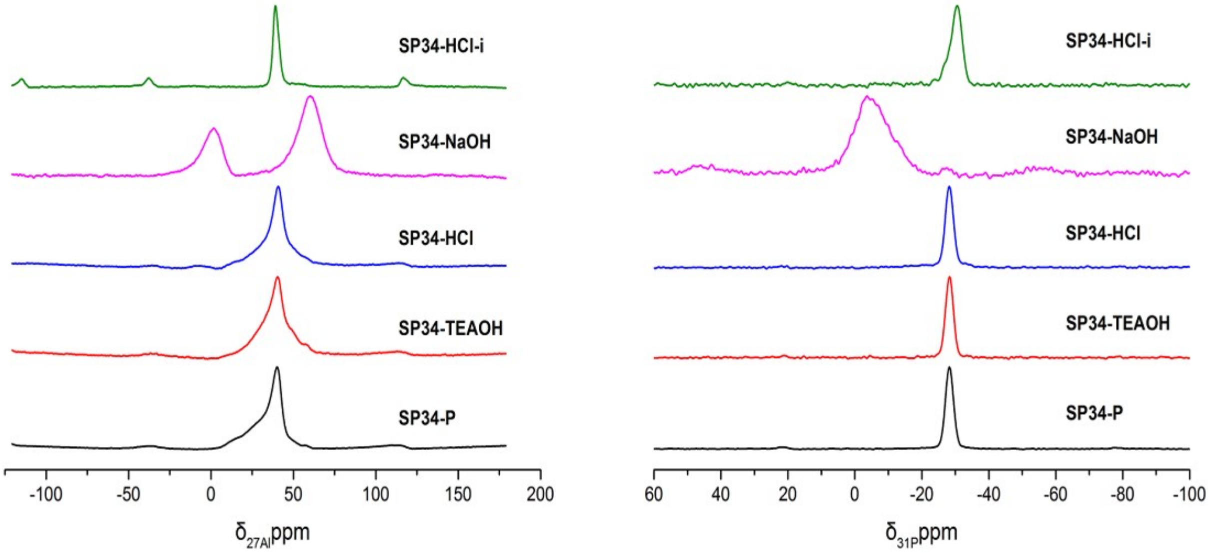

Figure S6. The ^{27}Al and ^{31}P MAS NMR spectra of the samples.

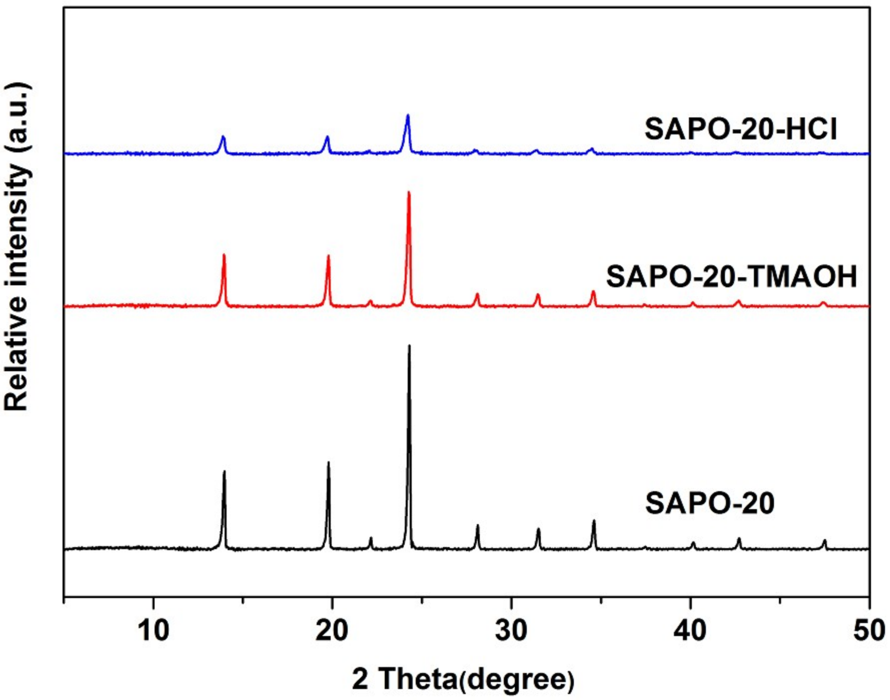

Figure S7. The XRD patterns of SAPO-20 and its acid/base-treated samples.

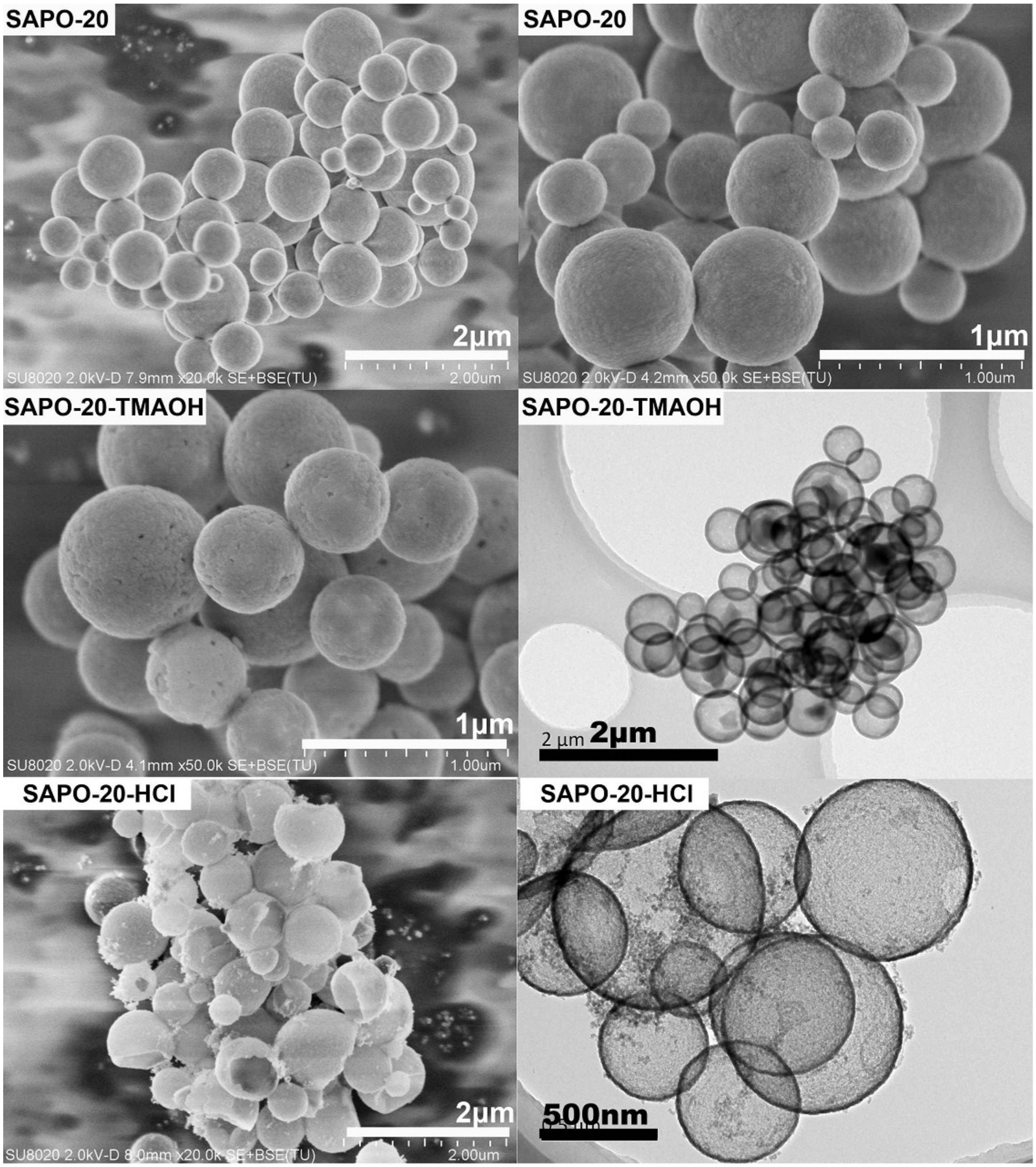

Figure S8. The SEM and TEM images of SAPO-20 and its acid/base-treated samples.

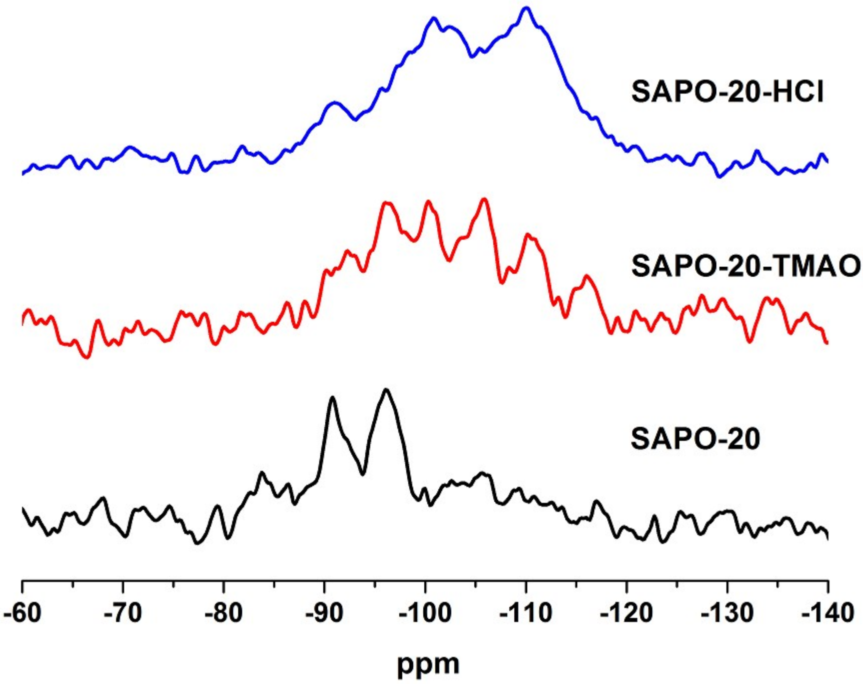

Figure S9. The ^{29}Si MAS NMR spectra of SAPO-20 and its acid/base-treated samples.

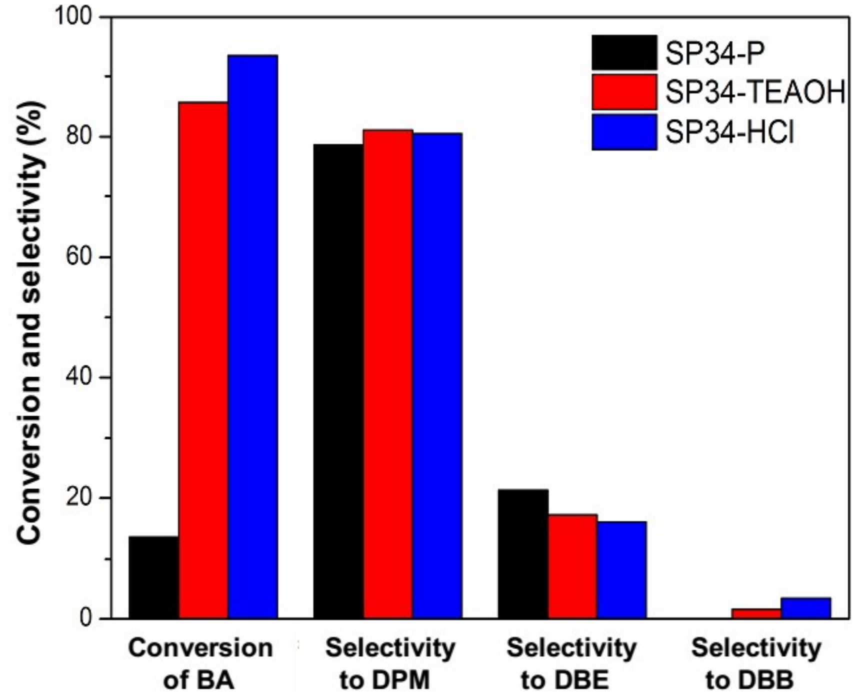

Figure S10. Results of alkylation of benzene with benzyl alcohol (BA) over the samples (DPM: diphenyl methane, DBE: dibenzyl ether, DBB: dibenzyl benzene).

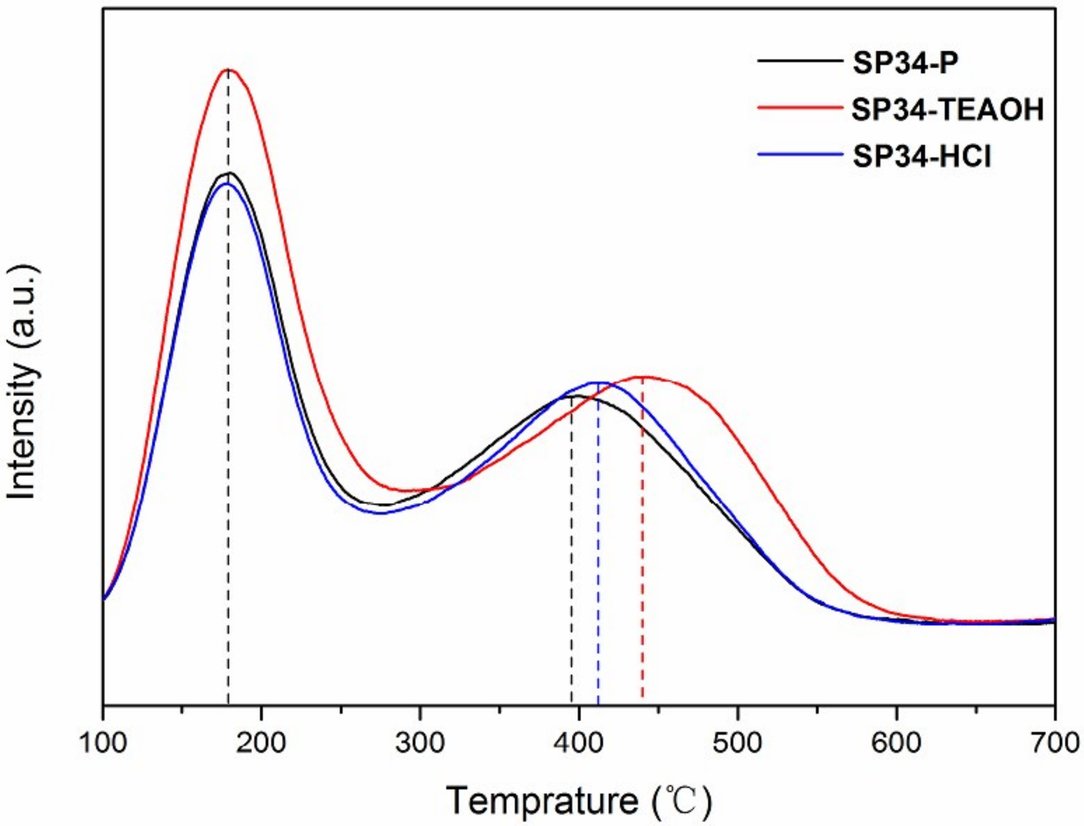

Figure S11. NH_3-TPD curves of the samples.