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不同结构导向剂合成不同硅含量 SAPO-34 分子筛的酸性质

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Acid Properties of SAPO-34 Molecular Sieves with Different Si Contents Templated by Various Organic Structure-Directing Agents

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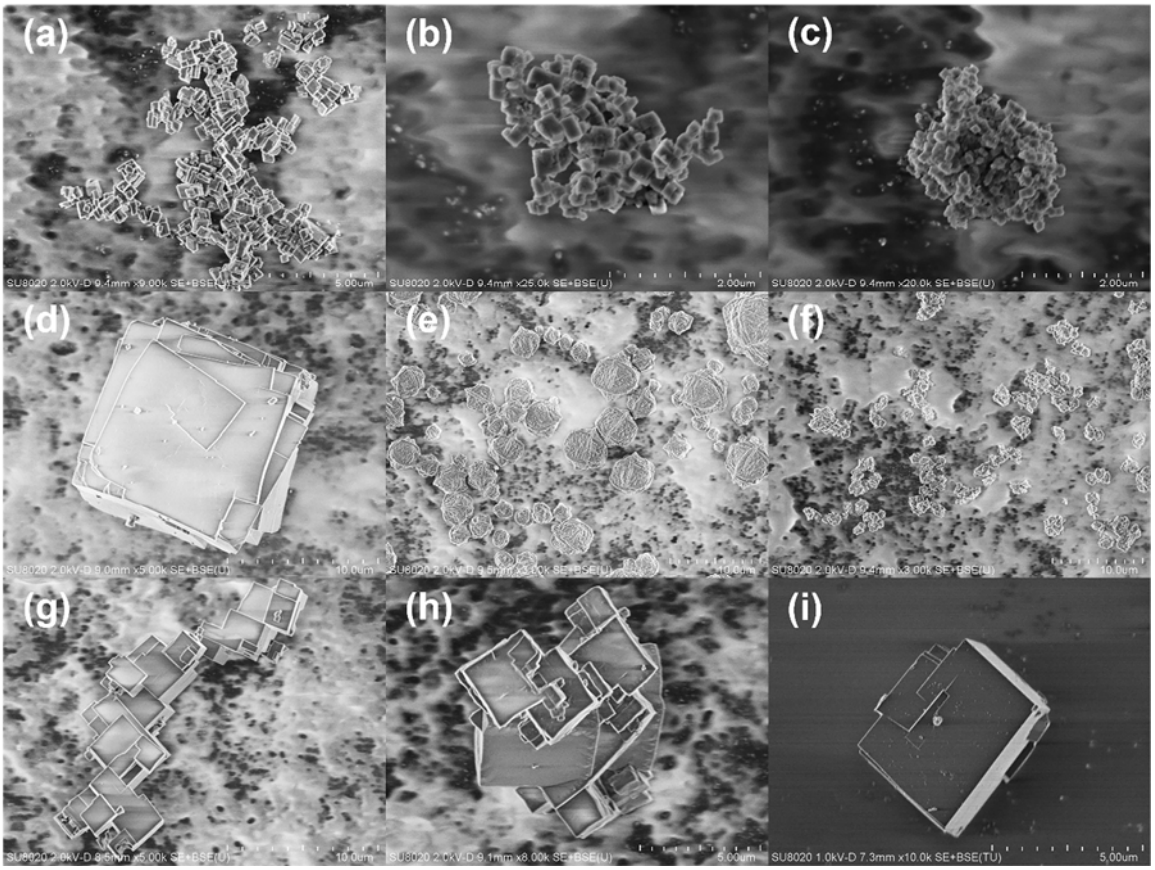

Fig. S1 SEM images of (a) SAPO-34-TEAOH-L, (b) SAPO-34-TEAOH-M, (c) SAPO-34-TEAOH-H, (d) SAPO-34-DIPA-L, (e) SAPO-34-DIPA-M, (f) SAPO-34-DIPA-H, (g) SAPO-34-nBA-L, (h) SAPO-34-nBA-H and (i) SAPO-34-MOR-M.

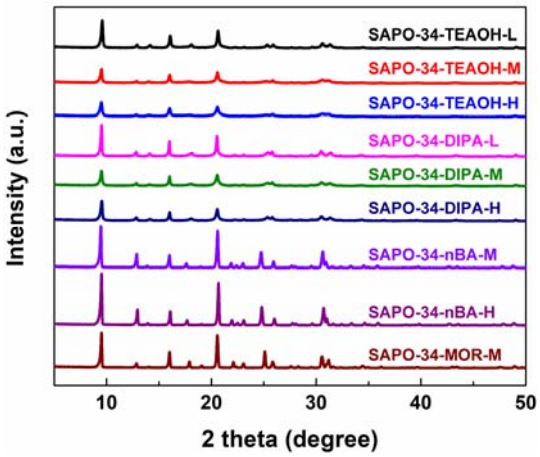

Fig. S2 Initial PXRD patterns of as-synthesis SAPO-34 samples.

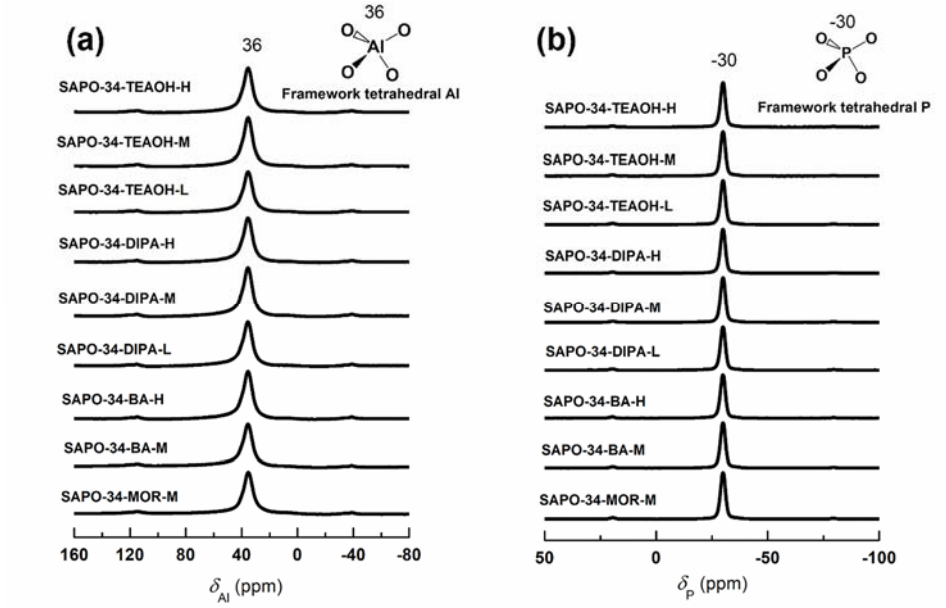

Fig. S3 (a) ^{27}Al and (b) ^{31}P MAS NMR of spectra proton-form SAPO-34s.

The chemical shifts of skeleton defects are present at 0.9–2.6 ppm in ^{1}H MAS NMR spectra, −75 – −85 ppm in ^{29}Si MAS NMR spectra, −15 ppm in ^{31}P MAS NMR spectra and 6–13 ppm or −13 – −15 ppm in ^{27}Al MAS NMR spectra [1,2]. As shown in Fig. 2, only tiny peaks at 0.9–2.6 ppm were observed in ^{1}H MAS NMR spectra. This attributes to the Si—OH, Al—OH or P—OH locating on the outer surface. Besides, no chemical shifts of skeleton defects were detected in Fig. 3 and Fig. S3. All these indicate that the proton-form SAPO-34s are less-defective.

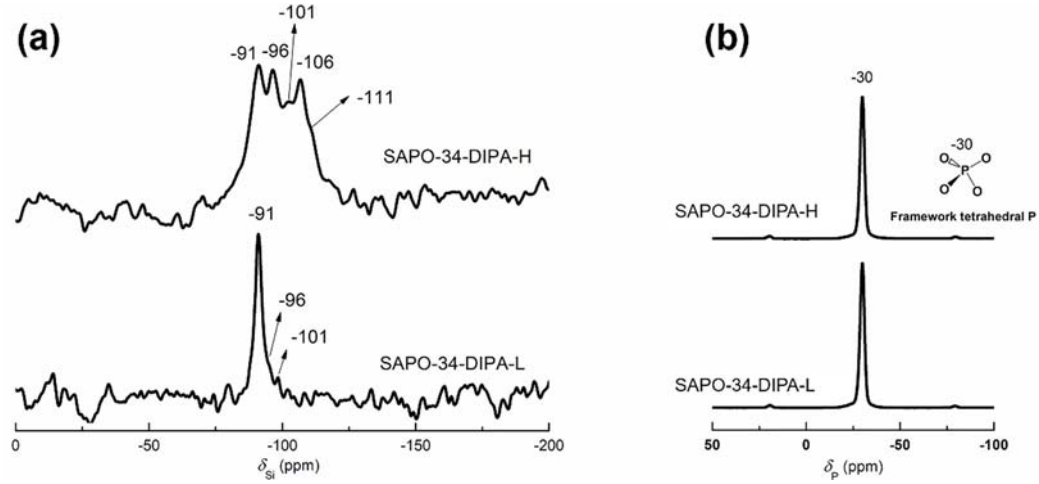

Fig. S4 (a) ^{29}Si and (b) ^{31}P MAS NMR spectra of as-made SAPO-34-DIPA-L and SAPO-34-DIPA-H (with OSDAs). Before the tests, the as made samples were dehydrated 200 °C under vacuum (< 10^{-3} Pa).

The chemical shifts of skeleton defects are present at −75 – −85 ppm in ^{29}Si MAS NMR spectra and −15 ppm in ^{31}P MAS NMR spectra. As shown in Fig. S4, no peaks are detected as mentioned above, therefore, the as-made SAPO-34-DIPA-L and SAPO-34-DIPA-H (with OSDAs) are less-defective.

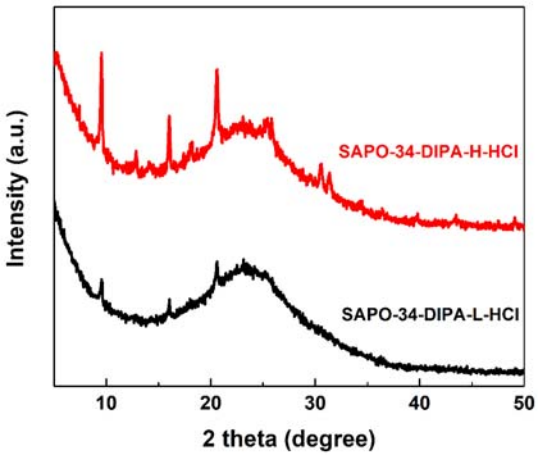

Fig. S5 PXRD patterns of hydrochloric-acid-treatment SAPO-34-DIPA-L and SAPO-34-DIPA-H.

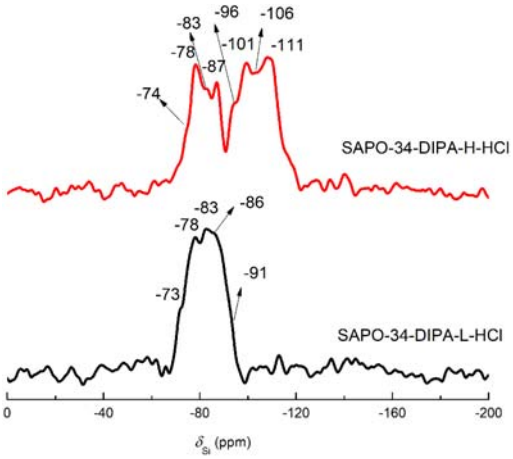

Fig. S6 ^{29}Si MAS NMR spectra of hydrochloric-acid-treatment SAPO-34-DIPA-L and SAPO-34-DIPA-H.

Peaks at −73 – −87 ppm are attributed to the skeleton defects, resulting from the severe acid etching. It is of interest to note that, under the same acid treatment conditions, SAPO-34-DIPA-L almost loses the chemical shifts of framework Si, while SAPO-34-DIPA-H maintained a certain amount of acid-resistant Si islands structures (−96 – −111 ppm).

Table S1 Crystallographic details of Rietveld refinements of SAPO-34-TEAOH-L and SAPO-34-MOR-M.

Sample	SAPO-34-TEAOH-L	SAPO-34-MOR-M
Space group	$R\ \bar{3}$	$P1$
a/Å	13.7803	13.7409
b/Å	13.7803	13.7689
c/Å	14.7499	14.9024
α/°	90	90.0221
β/°	90	89.9792
γ/°	120	120.1912
V/Å^3	2425.706	2437.035
R_p	0.0297	0.0279
R_{wp}	0.0411	0.0388
R_{exp}	0.0157	0.0203
R_{bragg}	0.0209	0.0174
GOF	2.619	1.905

1 Å = 0.1 nm.

Table S2 Detailed Si distributions of all SAPO-34s.

Samples	Si species [a]					Si atoms at the edges of Si island (%) [b]
	Si(4Al) (%)	Si(3Al) (%)	Si(2Al) (%)	Si(1Al) (%)	Si(0Al) (%)	
SAPO-34-TEAOH-L	84.1	6.1	3.2	3.2	3.4	12.5
SAPO-34-TEAOH-M	45.1	21.0	11.6	16.9	5.4	49.5
SAPO-34-TEAOH-H	28.1	19.2	20.3	25.1	7.3	64.6
SAPO-34-DIPA-L	87.2	4.1	2.7	2.9	3.1	9.7
SAPO-34-DIPA-M	40.4	22.2	10.5	13.2	13.7	45.9
SAPO-34-DIPA-H	23.1	18.2	17.3	18.5	22.9	54.0
SAPO-34-BA-M	66.8	8.6	7.5	8.5	8.6	24.6
SAPO-34-BA-H	41.5	17.8	15.1	15.4	10.2	48.3
SAPO-34-MOR-M	57.4	15.6	8.3	12.5	6.2	36.4

[a] Determined from ^{29}Si MAS NMR spectra by deconvoluting *via* Dmfit software with Gaussian-Lorentz line shapes.

[b] The sum of the values of Si(3Al), Si(2Al) and Si(1Al).

Reference

(1) Briend, M.; Vomscheid, R.; Peltre, M. J.; Man, P. P.; Barthomeuf, D. *J. Phys. Chem.* **1995,** *99*/20, 8270. doi: 10.1021/j100020a060

(2) Buchholz, A.; Wang, W.; Arnold, A.; Xu, M.; Hunger, M. *Microporous Mesoporous Mater.* **2003,** *57*/12, 157. doi: 10.1016/S1387-1811(0200562-0