Supplementary Material

Dynamic Evolution of HZSM-5 Zeolite Framework under Steam Treatment

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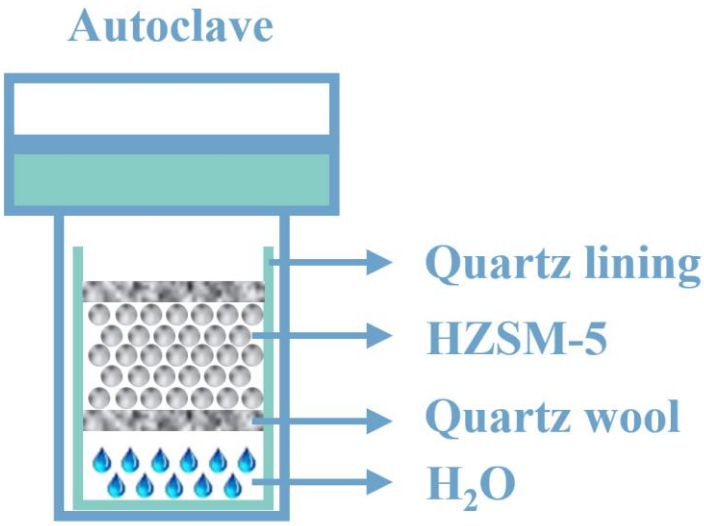
ZSM-5 zeolite preparation

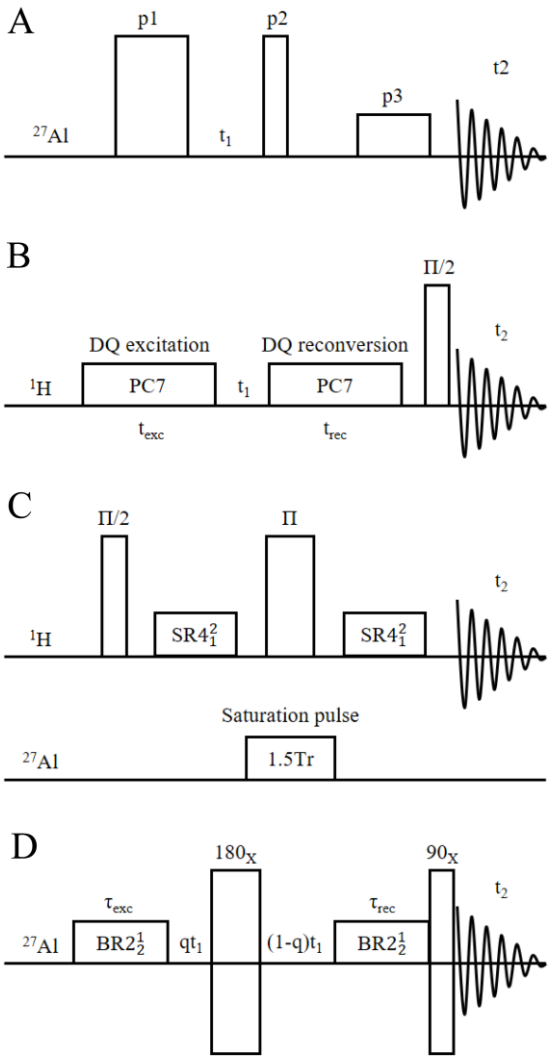
The ZSM-5 zeolite was synthesized following the procedure described in the literature[1]. The molar composition of the synthesized gel was 1 SiO_2/0.0125 Al_2O_3/0.20 TPABr/1 Ethylamine/17 H_2O. The synthesis procedure is as follows. TPABr and seeds were added into silica sol (30 wt % in H_2O) at 35 ℃ and stirred for 0.5 h to dissolve fully to obtain silica gel. Then, $AlCl_3 \cdot 6H_2O$ solution was added dropwise into the silica gel to obtain the silica-aluminum gel. Finally, ethylamine aqueous solution (65 wt % in H_2O, as alkali source) was poured into the silica-aluminum gel to obtain the mother gel, which was transferred into a Teflon-lined stainless- steel autoclave and crystallized at 170 ℃ for 72 hours. The product was collected by centrifugation, washed three times with deionized water, and dried overnight at 100 ℃. The as-synthesized sample was calcined in air at 550 ℃ for 6 hours to obtain the HZSM-5 zeolite, whose Si/Al ratio was about 36, as measured by XRF.

Ammonium ion exchange treatment

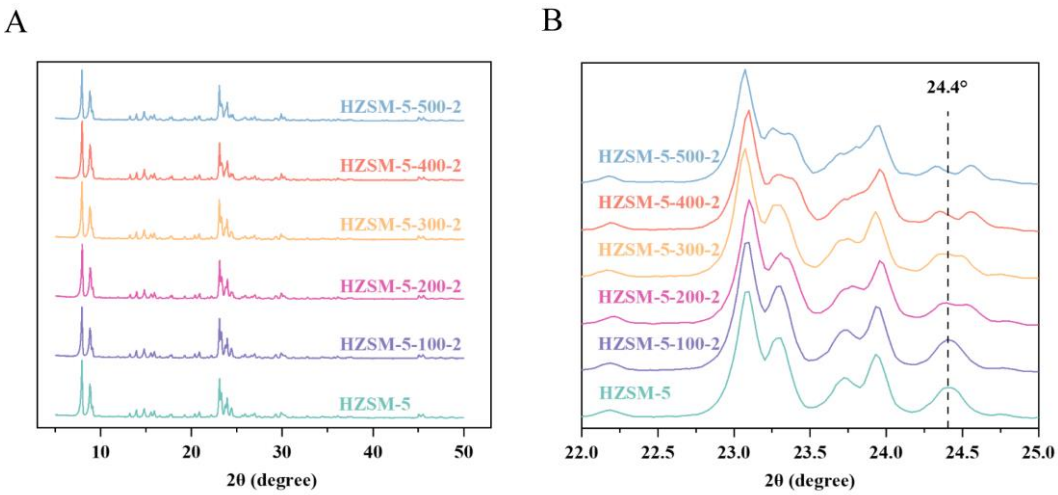
The steamed samples (HZSM-5-T-X) were dispersed in a 1 mol/L solution of ammonium nitrate at a concentration of 30 g/L and stirred at 80 ℃ for 2 hours. Subsequently, the mixtures were centrifuged and washed three times with deionized water. This procedure was repeated three times, and the final samples in ammonium form (denoted as HZSM-5-T-X-NH_4) were dried overnight at 100 ℃.



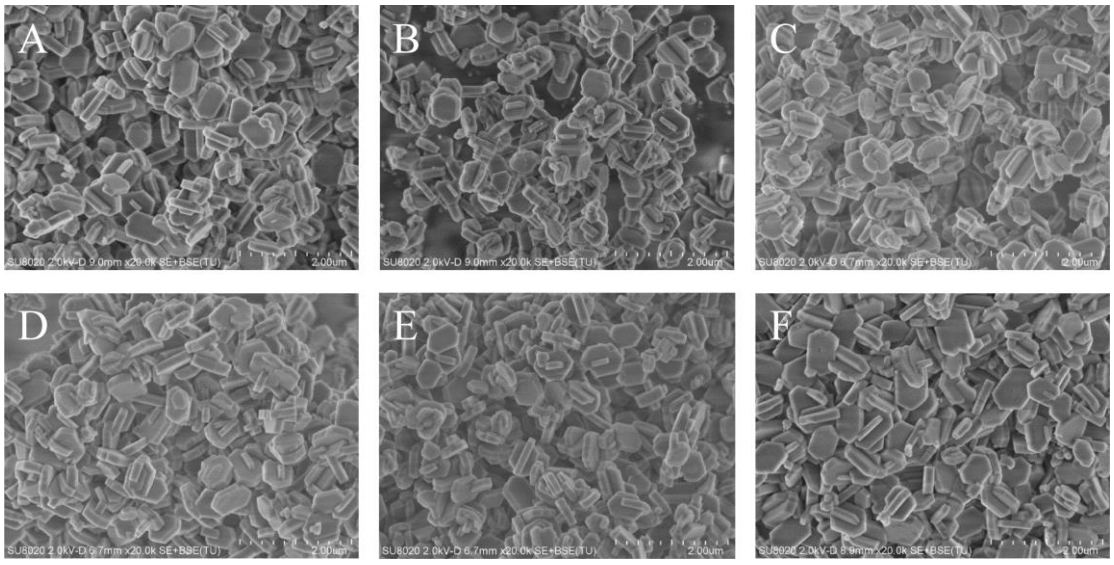
Supplementary Figure 1. Schematic diagram of high-temperature and high-pressure hydrothermal treatment of HZSM-5 zeolite.



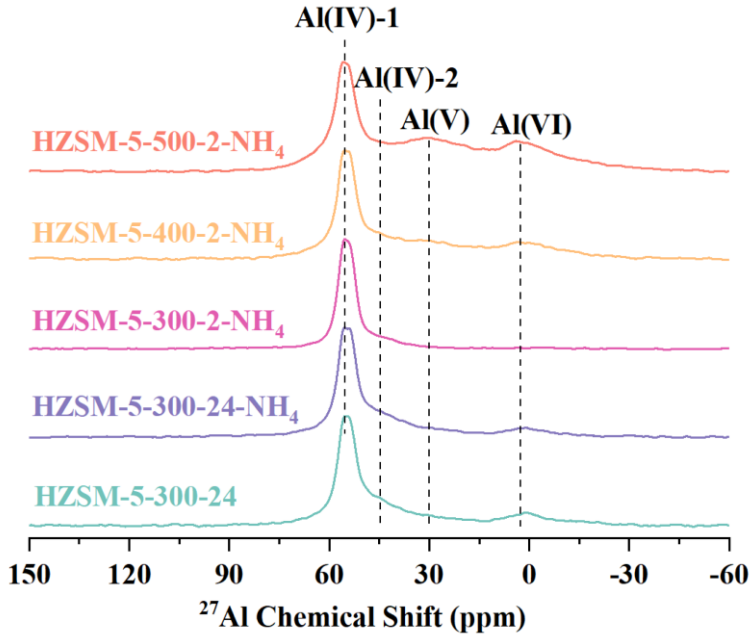
Supplementary Figure 2. Pulse-sequences of (A) ^{27}Al MQ MAS NMR[2,3]; (B) ^{1}H-^{1}H DQ-SQ MAS NMR with the POST-C7 pulse sequence[4,5]; (C) ^{1}H-^{27}Al S-RESPDOR MAS NMR[6,7] and (D) ^{27}Al-^{27}Al DQ-SQ MAS NMR with the $BR2^1_2$ dipolar recoupling[8].



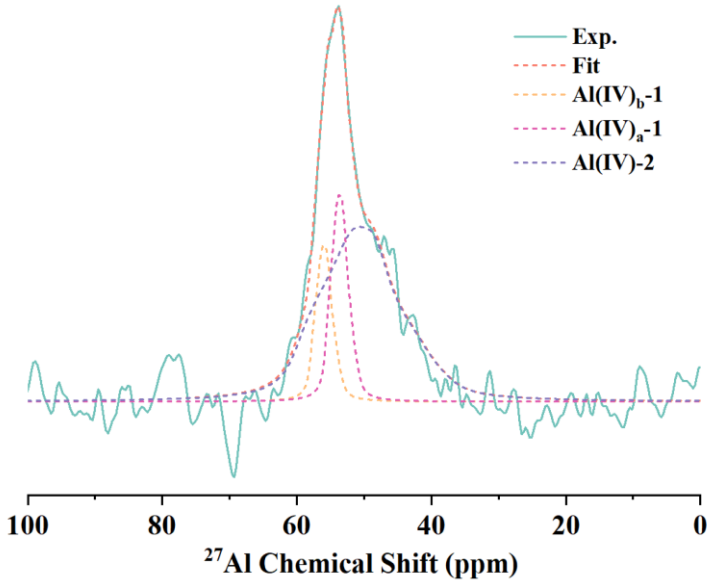
Supplementary Figure 3. (A) XRD patterns of HZSM-5 zeolite before and after steam treatment; (B) expanded XRD patterns in the range 22.0°–25.0° 2θ.



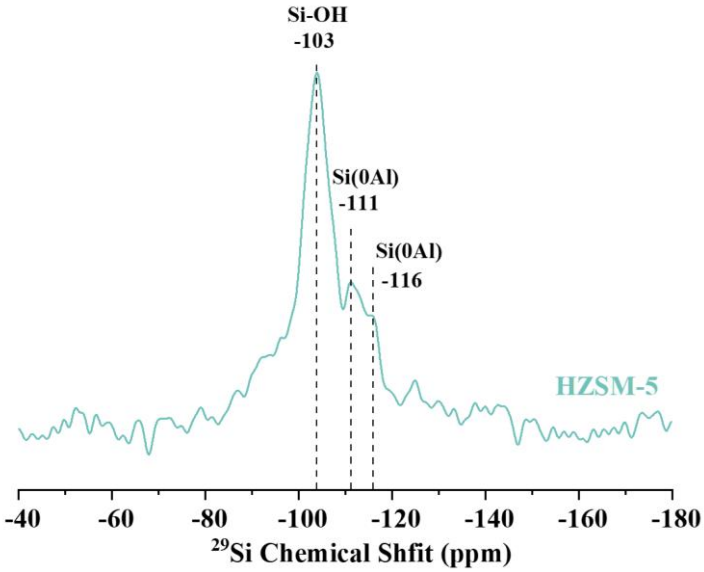
Supplementary Figure 4. SEM images of HZSM-5 (A), HZSM-5-100-2 (B), HZSM-5-200-2 (C), HZSM-5-300-2 (D), HZSM-5-400-2 (E) and HZSM-5-500-2 (F).



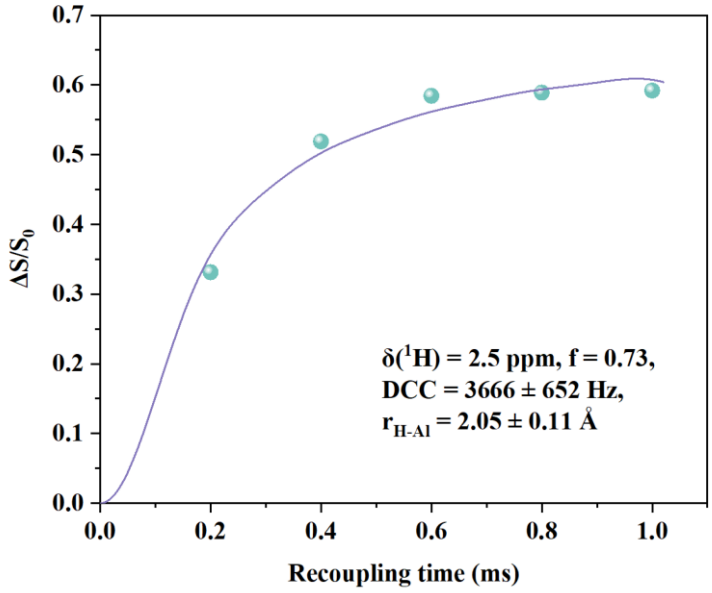
Supplementary Figure 5. ^{27}Al single-pulse MAS NMR spectra of HZSM-5 zeolite after steam and ammonium ion exchange treatment.



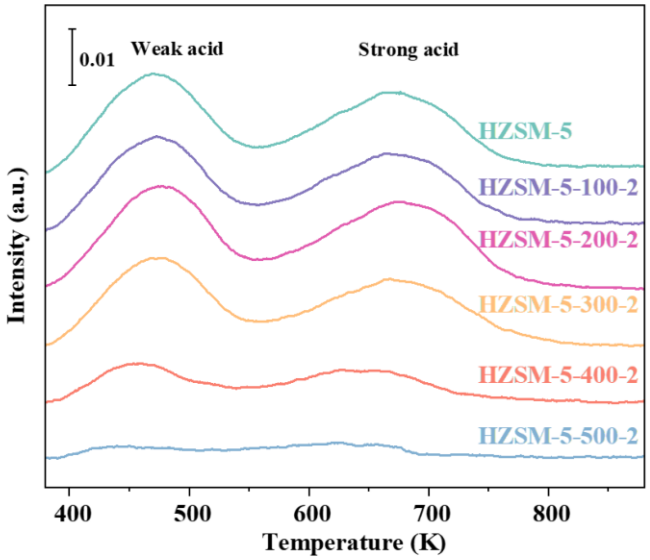
Supplementary Figure 6. Deconvolution of 1D projection at F1 = 63.5 ppm in ^{27}Al MQ MAS NMR spectra of HZSM-5-300-2.



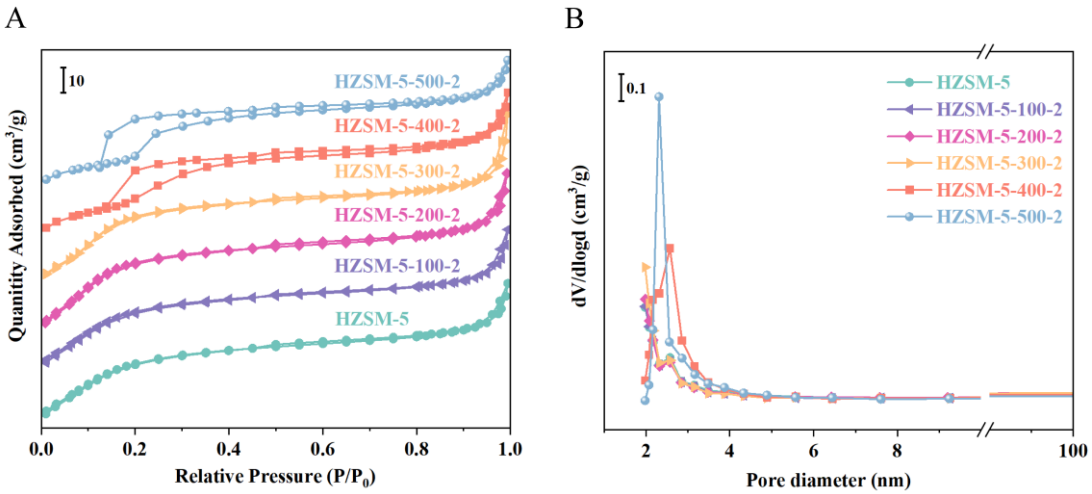
Supplementary Figure 7. ^{1}H-^{29}Si MAS NMR spectrum of HZSM-5 zeolite.



Supplementary Figure 8. ^{1}H-^{27}Al S-RESPDOR fraction curve of δ(^{1}H) = 2.5 ppm on HZSM-5-300-2 sample. The signal fraction was determined by integrating signal at 2.5 ppm. The points represent the experimental signal fraction, whereas the continuous curve is the best fit to equation $\left(\frac{\Delta S}{S_0} = \frac{f}{2I+1}\left\{2I - \frac{\Pi\sqrt{2}}{4(2I+1)}\sum_{k=1}^{2I}[4I - 2(k-1)]J_{1/4}\left(\frac{k\Pi\lambda}{4}\right)J_{-1/4}\left(\frac{k\Pi\lambda}{4}\right)\right\}\right)$[7] with DCC(^{1}H–^{27}Al) = 3666 ± 652 Hz, with the pre-factor fixed to f = 0.73.



Supplementary Figure 9. NH_3-TPD profiles of HZSM-5 zeolite before and after steam treatment.



Supplementary Figure 10. (A) The N_2-physisorption curves and (B) pore-size distributions curves of HZSM-5 zeolite before and after steam treatment.

Supplementary Table 1. NMR parameters extracted from ^{27}Al MQ MAS NMR.

Samples	Species	δ_{F1} (ppm	δ_{F2} (ppm	δ_{iso} (ppm	C_Q (MHz)	η	P_Q (MHz
HZSM-5	$Al(IV)_a$-1	54.0	53.5	55.6[a]	2.73	0.60	2.89[b]
	$Al(IV)_b$-1	56.5	55.8	57.7[a]	2.70	0.60	2.86[b]
HZSM-5-200-2	$Al(IV)_a$-1	54.0	53.6	55.6[a]	2.75	0.60	2.91[b]
	$Al(IV)_b$-1	56.8	55.7	57.7[a]	2.72	0.58	2.87[b]
HZSM-5-300-2	$Al(IV)_a$-1	54.5	53.8	55.8[a]	2.75	0.60	2.91[b]
	$Al(IV)_b$-1	56.8	56.0	57.8[a]	2.70	0.60	2.96[b]
	Al(IV)-2	63.5	47.0	60.2[a]	5.90	0.65	6.30[b]
HZSM-5-300-2-NH_4	$Al(IV)_a$-1	54.2	53.8	55.3[a]	2.63	0.58	2.77[b]
	$Al(IV)_b$-1	56.9	55.9	57.7[a]	2.63	0.58	2.77[b]
	Al(IV)-2	63.4	49.4	58.5[a]	5.60	0.65	5.98[b]
HZSM-5-500-2	$Al(IV)_a$-1	54.5	53.8	55.0[a]	2.73	0.60	2.89[b]
	$Al(IV)_b$-1	56.8	56.0	58.0[a]	2.70	0.60	2.86[b]
	Al(IV)-2	63.5	47.0	61.0[a]	5.80	0.65	6.19[b]
	Al(V)	40.0	32.0	37.0[c]	—	—	4.53[d]
	Al(VI)	7.0	3.0	5.5[c]	—	—	3.20[d]

[a]Isotropic chemical shift values (δ_{iso}) obtained by fitting sliced spectrum, as shown in Supplementary Figure 6. [b]$P_Q = C_Q\sqrt{1+\eta^2/3}$.

Due to poor signal-to-noise ratio for Al(V) and Al(VI) species, δ_{iso} and P_Q calculated by the formula: [c]$\delta_{iso} = (17\delta_{F1} + 10\delta_{F2})/27$ and [d]$P_Q = \frac{\nu_L}{25} \times \sqrt{85(\delta_{F1} - \delta_{F2})/1296}$.

Supplementary Table 2. Relative percentage of Si species in different chemical environments by deconvolution of the ^{29}Si MAS NMR spectra.

Samples	Si-OH (%)	Si(1Al) (%)	Si(0Al) (%)	Total (%)	Framework Si/Al ratio[a]
HZSM-5	0.62	10.81	88.56	100.00	37.00
HZSM-5-100-2	0.56	10.72	88.72	100.00	37.31
HZSM-5-200-2	0.46	10.73	88.82	100.00	37.28
HZSM-5-300-2	0.36	10.78	88.87	100.00	37.11
HZSM-5-400-2	0.20	5.63	94.17	100.00	71.05
HZSM-5-500-2	0.16	2.96	96.88	100.00	135.14

[a]The values of the framework Si/Al ratio were obtained from the formula: $(\mathrm{Si/Al})_{\mathrm{NMR}} = \frac{I_4+I_3+I_2+I_1+I_0}{I_4+0.75I_3+0.5I_2+0.25I_1}$, where I_n represents the area of the NMR peak corresponding to the Si(nAl) unit.[9]

Supplementary Table 3. Concentrations of different hydroxyl groups of HZSM-5 zeolite before and after steam treatment by quantifying and deconvoluting the ^{1}H MAS NMR spectra.

Samples	4.6 ppm (mmol/g)	BAS (mmol/g)	Al-OH (mmol/g)	Si-OH (mmol/g)	Total (mmol/g
HZSM-5	0.262	0.107	0.042	0.087	0.498
HZSM-5-100-2	0.221	0.101	0.033	0.071	0.440
HZSM-5-200-2	0.146	0.109	0.025	0.058	0.339
HZSM-5-300-2	0.101	0.082	0.041	0.045	0.269
HZSM-5-400-2	0.053	0.036	0.031	0.033	0.153
HZSM-5-500-2	0.026	0.024	0.025	0.030	0.105

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