

Supporting Information

Exposing active sites in zeolites with fluoropyridines as NMR probe molecules

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Experimental Procedures

Materials

γ -Alumina, Scientific Laboratory Supplies Ltd

Zeolite HZSM-5 (SAR:40, CBV 8014), Zeolyst International

Zeolite HY (SAR: 2.6, CBV300), Zeolyst International

2-Fluoropyridine, Fluorochem

3-Fluoropyridine, Fluorochem

Silicalite-1 synthesised in-house following the standard method¹

Dosing Procedure

The zeolite samples were packed into 4 mm o.d. zirconia rotors and placed inside a 100 cm³ round-bottomed flask inside open glass vials. The samples were heated to 150 °C using an oil bath under vacuum for 5 h to remove adsorbed water from the zeolites. The samples were kept in the degassed vial and, once the vacuum pump was turned off, the sealed, 0.5 cm³ of 2- or 3-fluoropyridine was added to the evacuated and sealed round-bottomed flask for the vapours to diffuse into the zeolite samples for 8 h.

Solid-State NMR

The moderate-field solid-state (ss)NMR spectra were obtained at 9.4 T using a 400 MHz (¹H Larmor frequency) spectrometer with a Bruker Avance III console and a 4 mm HFX Bruker MAS probe using 4 mm ZrO₂ rotors with Kel-F rotor caps under ambient conditions as well as with cooling to 260 K and with variable MAS frequencies.

The high-field spectra were obtained at both 16.4 and 20.0 T, (700 and 850 MHz respective ¹H Larmor frequencies), on Bruker AVANCE NEO spectrometers. The spectrometers were equipped with a Phoenix 1.6 mm HFX MAS probe in ¹H, ¹⁹F, and ²⁷Al configuration for 20.0 T measurements and a Bruker 1.3 mm HX MAS probe in ¹H and ²⁷Al configuration for 16.4 T measurements. BCUs were used to cool the probes to 260 K. Zeolites and fluoropyridine-dosed zeolites were removed from the 4 mm rotors in which they were dosed in a fume cupboard and packed into 1.3 and 1.6 mm ZrO₂ rotors and were sealed with Vespel caps.

Low temperature and dynamic nuclear polarisation (DNP)-enhanced solid-state NMR spectra were recorded using a Bruker 14.1 T (600 MHz ¹H Larmor frequency) AVANCE III HD spectrometer equipped with a 3.2 mm HX LTMAS probe in ¹⁹F/²⁷Al or ¹H/¹⁵N configuration for appropriate experiments. Zeolites

and fluoropyridine-dosed zeolites were removed from the 4 mm rotors in which they were dosed in a fume cupboard and packed into 3.2 mm ZrO₂ rotors and were sealed with Vespel rotor caps. For the DNP experiments, 40 mg of the 3FP@HY sample was impregnated in a fume cupboard with 60 µL of “DNP solution” (11 mM TEKPol in 1,1,2,2-tetrachloroethane).

Chemical shifts were externally referenced to liquid ammonia for ¹⁵N, 1 M Al(NO₃)₃ aqueous solution for ²⁷Al, CFC₃ for ¹⁹F, and TMS for ¹H. Spectra were analysed in Topspin 4.1.4 using the SOLids Lineshape Analysis tool version 2.2.4 (SOLA). Further experimental details may be found in the below Tables S1-S6.

For the calibration of the Hartmann-Hahn conditions for ¹⁹F-²⁷Al CP MAS NMR experiments, AlF₃ was used to establish the matching conditions as it has a high abundance of both isotopes. ¹H-²⁷Al CP MAS NMR experiments were calibrated directly on zeolite HY as the low SAR enabled low power central-transition selective pulses to be calibrated and subsequently ¹H powers to be calculated and optimized.

Chemical shift anisotropy (CSA) is described using the Haeberlen convention, where δ_{iso} is the isotropic chemical shift (units of ppm), δ_{CSA} is the reduced anisotropy (units of ppm), and $\eta(CSA)$ is the (dimensionless) asymmetry parameter. The principal components are defined as

$$|\delta_{zz} - \delta_{iso}| \geq |\delta_{xx} - \delta_{iso}| \geq |\delta_{yy} - \delta_{iso}|$$

δ_{CSA} is defined as

$$\delta_{CSA} = \delta_{zz} - \delta_{iso}$$

and η is defined as

$$\eta = \frac{\delta_{xx} - \delta_{yy}}{\delta_{zz} - \delta_{iso}}$$

Table S1. ²⁷Al direct excitation MAS NMR experimental parameters.

Experiment	²⁷ Al one-pulse	²⁷ Al one-pulse	²⁷ Al one-pulse
Figure(s)	Fig 4, S7	Fig S3 and S9	Fig S10
B_0 (T)	14.1	9.4	20.0
MAS (kHz)	5	8	33
Recycle delay (s)	0.5	2.0	0.5 (HY), 1.0 (HZSM-5)
Number of transients	128	2048	2048 (HY), 1024 (HZSM-5)
²⁷ Al RF field strength (kHz)	~8	~70	~70
²⁷ Al RF pulse duration (µs)	1	0.5	0.5

Table S2. {X-}²⁷Al CP MAS NMR experimental parameters.

Experiment	{ ¹⁹ F-} ²⁷ Al CP MAS		¹ H– ²⁷ Al HETCOR
Figure(s)	Fig 4	Fig S6	Fig S11
<i>B</i> ₀ (T)	14.1	20.0	16.4
MAS (kHz)	5	33	50
Recycle delay (s)	9.3 (HY), 13.4 (HZSM-5)	2 (HZSM-5), 5 (AlF ₃)	0.425
Number of transients	3072	4096 (HZSM-5), 4 (AlF ₃)	512
Indirect dimension complex increments	-	-	256
¹⁹ F RF field strength (kHz)	100	74	-
¹⁹ F CP RF field strength (kHz)	29	16	-
¹ H RF field strength (kHz)	-	-	150
¹ H CP RF field strength (kHz)	-	-	84
²⁷ Al CP RF field strength (kHz)	~8	~6	11
CP spin lock duration (μs)	2000 (Square)	600 (Square)	700 (Square)

Table S3. ¹⁹F direct excitation MAS NMR experimental parameters.

Experiment	¹⁹ F Hahn-echo
Figure(s)	Fig 2, S2a, S2c
<i>B</i> ₀ (T)	9.4
MAS (kHz)	8 (HY, HZSM-5), 12 (Silicalite-1 and γ-Alumina)
Recycle delay (s)	5
Number of transients	16 (Silicalite-1), 80 (γ-Alumina), 2048 (HY, HZSM-5)
¹⁹ F RF field strength (kHz)	71

Table S4. $\{^1\text{H}\}\text{-}^{19}\text{F}$ CP MAS NMR experimental parameters.

Experiment	$\{^1\text{H}\}\text{-}^{19}\text{F}$ CP MAS	
Figure(s)	Fig 2, S1, S2	Fig 3
B_0 (T)	9.4	20.0
MAS (kHz)	8	33
Recycle delay (s)	1.5 (RT)	4.7 (HY), 2.0 (HZSM-5)
Number of transients	128 (2FP@HZSM-5, 3FP 260K spectra), 8192 (3FP RT spectra, 2FP@HY)	4096
^1H RF field strength (kHz)	100	71
^{19}F CP RF field strength (kHz)	~52	74
^1H CP RF field strength (kHz)	~66	46
CP spin lock duration (μs)	1250 (Ramp 70-100)	500 (Ramp 80-100)

Table S5. DNP-enhanced $\{^1\text{H}\}\text{-}^{15}\text{N}$ CP MAS NMR experimental parameters.

Experiment	$\{^1\text{H}\}\text{-}^{15}\text{N}$ CP MAS NMR
Figure(s)	Fig 4
B_0 (T)	14.1
MAS (kHz)	8
Recycle delay (s)	5
Number of transients	15360
^1H RF field strength (kHz)	100
^1H CP RF field strength (kHz)	76
^{15}N CP RF field strength (kHz)	~64
CP spin lock duration (μs)	800 (Ramp 90-100)

Table S6. ^1H direct excitation MAS NMR experimental parameters.

Experiment	^1H Hahn-echo	^1H - ^1H DQ-SQ dipolar correlation
Figure(s)	Fig S4	Fig S5
B_0 (T)	20.0	16.4
MAS (kHz)	33	33.3
Recycle delay (s)	10	0.425
Number of transients	16	1024
Indirect dimension complex increments	-	64
^1H RF field strength (kHz)	71	150

FT-IR

Zeolites HY and HZSM-5 and the 2- and 3-fluoropyridine dosed derivatives have been tested using a Bruker Vertex 70 benchtop FT-IR spectrometer with 64 scans between wavenumbers (ν) 4000-250 cm^{-1} with a resolution of 1.29 cm^{-1} . A background was taken and subtracted from the final spectra. Pyridine is commonly used as a probe molecule for IR studies of active sites in zeolites since the resulting spectra can be used to discriminate between protonated pyridine (Py- H^+ ; $\nu_{8a} = 1640 \text{ cm}^{-1}$, $\nu_{19b} = 1545 \text{ cm}^{-1}$), pyridine adsorbed at a weak BAS through H-bonding (Py-B; $\nu_{8a} = 1595 \text{ cm}^{-1}$, $\nu_{19b} = 1445 \text{ cm}^{-1}$), and pyridine adsorbed at a LAS (Py-L; $\nu_{8a} = 1600\text{--}1630 \text{ cm}^{-1}$, $\nu_{19b} = 1450 \text{ cm}^{-1}$).^{2,3} Since ν_{8a} and ν_{19b} modes are associated with motions of the aromatic ring⁴, it is expected that these modes would appear at very similar wavenumbers for the fluoropyridines used here.⁴

Supplementary Results

Table S7. Assigned FT-IR spectrum for the peaks shown in Figure 1.

	Wavenumber cm^{-1}	Assignment
HY	1565	3FP-H ⁺
	1547	2FP-H ⁺
	1440	2FP-L
	1434	3FP-L
ZSM-5	1571	3FP-H ⁺
	1543	2FP-H ⁺
	1439	2FP-L
	1433	3FP-L

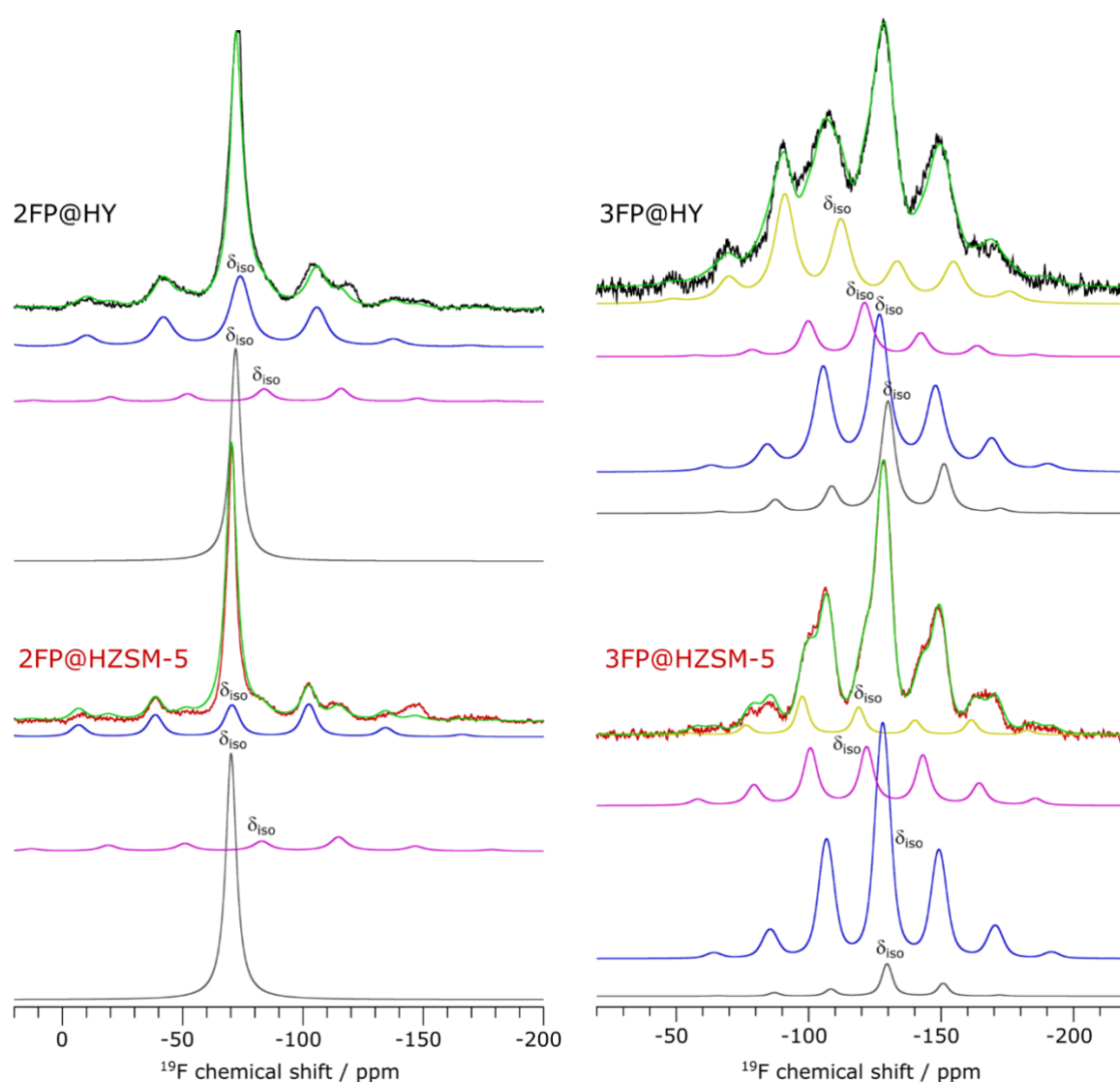


Figure S1. 9.4 T $\{^1\text{H}\}\text{-}^{19}\text{F}$ CP MAS NMR spectra of 2FP-dosed zeolites HY (black) and HZSM-5 (red) acquired under ambient temperatures (left) and 3FP-dosed zeolites HY (black) and HZSM-5 (red) at 260 K (right), recorded with a MAS frequency of 8 kHz with associated spectral deconvolutions (purple, blue, yellow and grey) and the envelope (green).

Table S8. Fitting parameters for the deconvoluted resonances from Figure S1. LB = Lorentzian broadening, GB = Gaussian broadening, and Int. = relative integral. In the Haeberlen convention of the CSA tensor, δ_{iso} is the isotropic chemical shift (units of ppm), δ_{CSA} is the reduced anisotropy (units of ppm), and $\eta(CSA)$ is the asymmetry parameter.

	Site	δ_{iso}	δ_{CSA}	$\eta(CSA)$	LB (kHz)	GB (kHz)	Int.
2FP@ HY	Physisorbed	-72	0	-	2.0	0	0.79
	2FP-B	-74	70	0.7	3.0	1.5	1
	2FP-L	-84	90	0.6	2.6	0.8	0.22
2FP@ ZSM-5	Physisorbed	-70	0	-	2.0	0	1.78
	2FP-B	-71	90	0.7	2.0	1.4	1
	2FP-L	-83	105	0.6	3.0	0.6	0.49
3FP@ HY	3FP-L	-112	-66	0.2	3.2	0.9	0.85
	3FP-B/L	-121	-50	0.6	2.0	1.2	0.26
	3FP-B	-127	-50	0.8	2.7	1.1	1
	Physisorbed	-130	43	0.0	2.0	0.8	0.38
3FP@ HZSM-5	3FP-L	-118	-68	0.3	1.5	1.0	0.17
	3FP-B	-122	-59	0.9	1.9	1.0	0.42
	3FP-B	-128	-45	0.9	1.2	1.9	1
	Physisorbed	-130	42	0.0	1.3	1.0	0.07

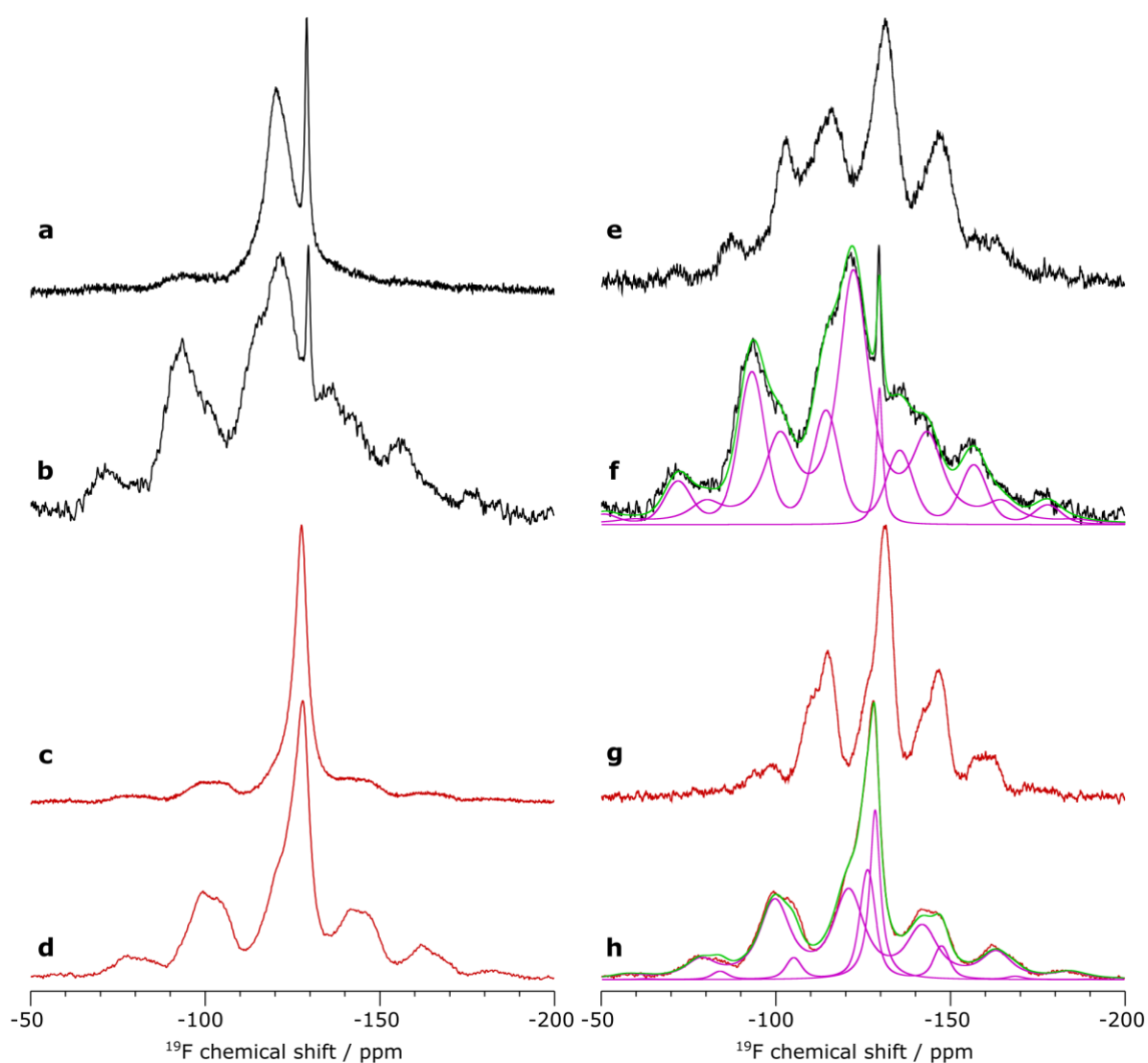


Figure S2. LHS: ^{19}F direct excitation (a, c) and $\{^1\text{H}\}\text{-}^{19}\text{F}$ CP (b, d) MAS NMR spectra recorded with ^1H decoupling at 9.4 T, under ambient conditions, and with 8 kHz MAS frequency, of 3FP@HY (a, b, black) and 3FP@HZSM-5 (c, d, red). RHS: Deconvolutions (purple) and the envelope (green) of the $\{^1\text{H}\}\text{-}^{19}\text{F}$ CP MAS NMR spectra (from b, deconvolution shown in f and from d, deconvolution shown in h). $\{^1\text{H}\}\text{-}^{19}\text{F}$ CP MAS NMR spectra of 3FP@HY (e, black) and 3FP@HZSM-5 (g, red) recorded with ^1H decoupling at 9.4 T, with cooling to 260 K are shown for comparison.

Table S9. Fitting parameters for the deconvoluted resonances from Figure S2. LB = Lorentzian broadening, GB = Gaussian broadening, and Int. = relative integral. In the Haeberlen convention of the CSA tensor, δ_{iso} is the isotropic chemical shift (units of ppm), δ_{CSA} is the reduced anisotropy (units of ppm), and $\eta(CSA)$ is the asymmetry parameter. Note that the fitted CSA parameters do not match those of Table S8 owing to the increased dynamics at the higher temperatures used to record the corresponding spectra.

	Site	δ_{iso}	δ_{CSA}	$\eta(CSA)$	LB (kHz)	GB (kHz)	Int.
3FP@ HY	3FP-L	-114	-67	0.5	1.1	2.8	0.74
	3FP-B	-122	-37	1	3.2	1.6	1
	Physisorbed	-130	0	-	0.8	0	0.07
3FP@ HZSM-5	3FP-L	-121	-56	0.7	3.2	1.6	1
	3FP-B	-126	36	0.4	1.1	1.3	0.31
	Physisorbed	-128	0	-	1.4	0	0.24

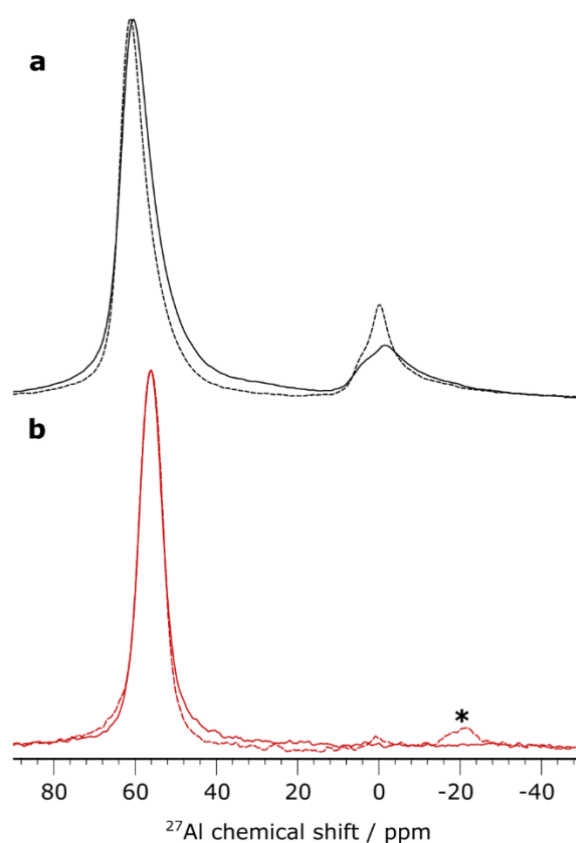


Figure S3. ^{27}Al direct excitation MAS NMR spectra of zeolites (a) HY (black) and (b) HZSM-5 (red) dosed with 3FP (solid line) and undosed (dashed lines) with ^1H decoupling recorded at 9.4 T with 8 kHz MAS frequency. Asterisks (*) denote spinning side bands.

Table S10. Fitting parameters for the deconvoluted resonances from Figure 3. LB = Lorentzian broadening, GB = Gaussian broadening, and Int. = relative integral. In the Haeberlen convention of the CSA tensor, δ_{iso} is the isotropic chemical shift (units of ppm), δ_{CSA} is the reduced anisotropy (units of ppm), and $\eta(CSA)$ is the asymmetry parameter.

	Site	δ_{iso}	LB (kHz)	GB (kHz)	Int.
3FP@HY	3FP-L	-110	5.5	0	0.6
	3FP-L	-114	5.0	0	0.2
	3FP-L	-120	5.0	0	0.2
	3FP-B/physisorbed	-123	5.0	0	0.8
	3FP-B/physisorbed	-126	5.0	0	0.9
	3FP-B/physisorbed	-130	5.0	0	1.0
3FP@HZSM-5	3FP-L	-118	2.0	3.3	0.6
	3FP-B/physisorbed	-124	2.0	1.8	0.3
	3FP-B/physisorbed	-126	2.0	1.9	0.1
	3FP-B/physisorbed	-129	2.0	1.9	1.0

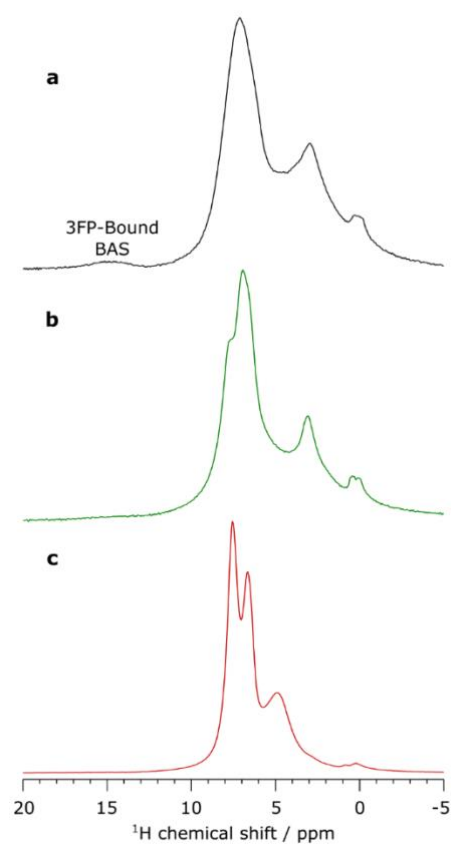


Figure S4. 20 T ^1H MAS NMR spectra recorded with and without cooling using a MAS frequency of ~ 33 kHz. Spectra shown are of 3FP-dosed zeolite HY at (a) 259 K (black) and (b) 293 K (green) and of (c) 3FP-dosed HZSM-5 at 259 K (red).

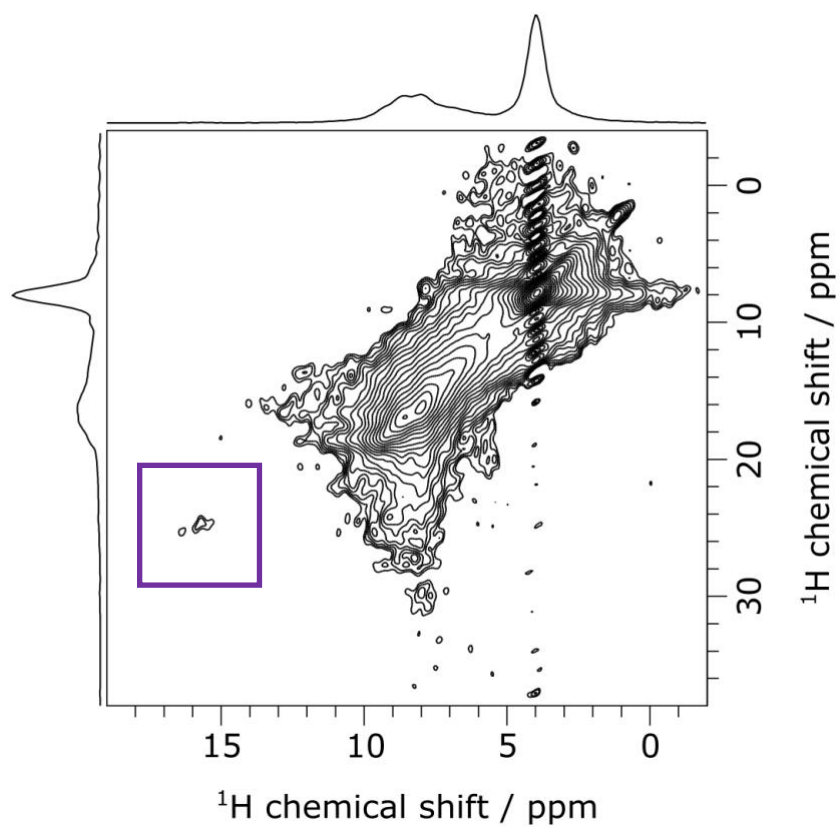


Figure S5. ^1H - ^1H 2D DQ-SQ S_2 dipolar correlation MAS NMR spectrum of 3FP@HY recorded at 260 K at 16.4 T with a MAS frequency of 33.3 kHz. Skyline projections are given on both axes. The cross-peak highlighted by the purple box at (16, 22) corresponds to 3FP- H^+ correlations with other 3FP protons.

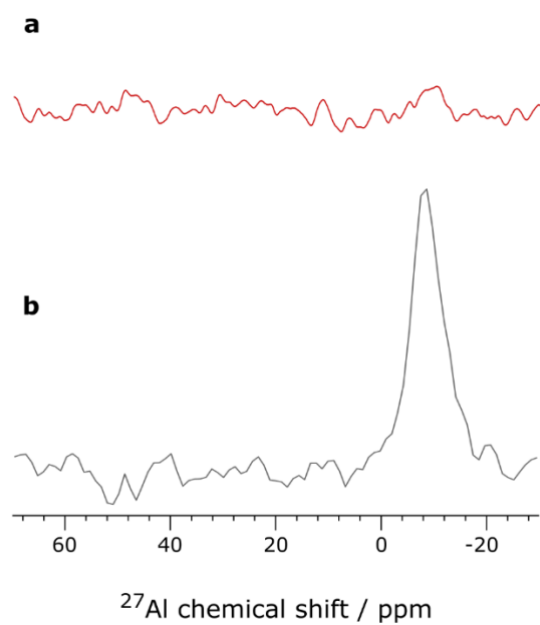


Figure S6. $\{^{19}\text{F}\}\text{-}^{27}\text{Al}$ CP MAS spectra recorded at 20 T and 260 K with ~ 33 kHz MAS frequency. Spectra shown are of (a) zeolite HZSM-5 (red) and reference sample (b) AlF_3 (grey).

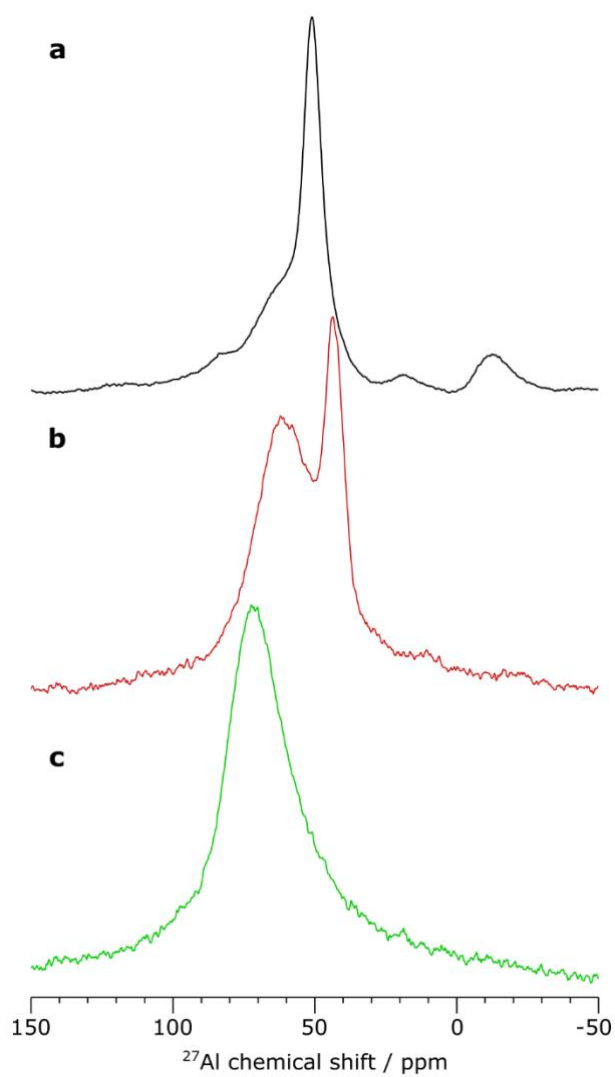


Figure S7. ^{27}Al direct excitation MAS NMR spectra of 3FP-dosed zeolites (a) HY (black) and (b) HZSM-5 (red) with (c) background signal (green) recorded at 100 K and 14.1 T with 8 kHz MAS frequency.

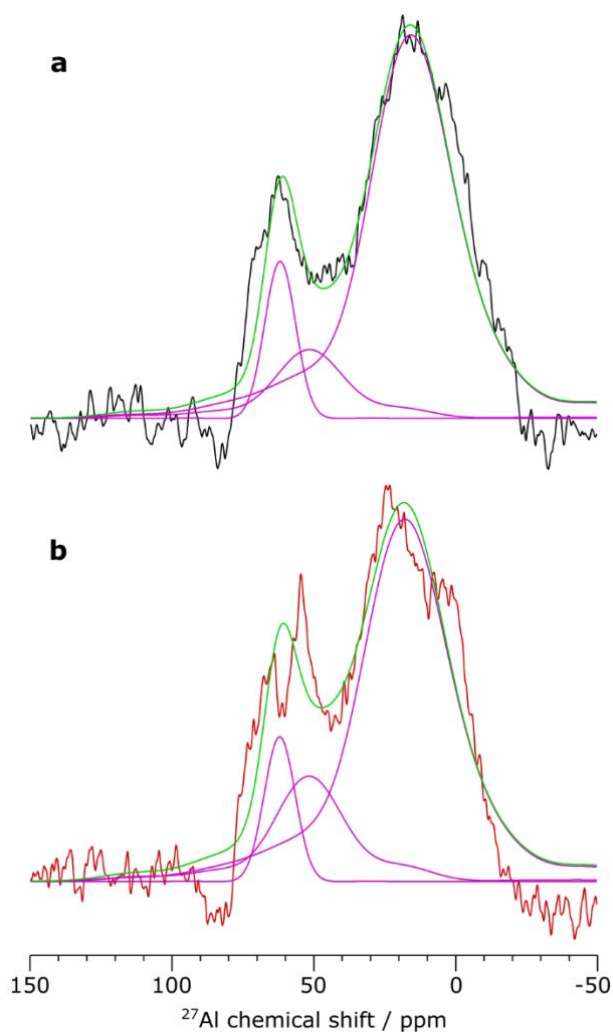


Figure S8 – $\{^{19}\text{F}\}\text{-}^{27}\text{Al}$ CP MAS NMR spectra with associated deconvolutions (purple) and the envelope (green) of the Al sites of dosed zeolites (a) 3FP@HY (black) and (b) 3FP@HZSM-5 (red) recorded at 100 K and 14.1 T with 8 kHz MAS frequency.

Table S11. Fitting parameters for the deconvoluted resonances from Figure S8. GB = Gaussian broadening, and Int. = relative integral. δ_{iso} is the isotropic chemical shift (units of ppm). C_Q is the quadrupolar coupling constant.

	Site	δ_{iso} (ppm)	C_Q (MHz)	GB (kHz)	Int.
3FP@HY	3FP@Al ^{IV} -1	64	2.9	2.0	1.0
	3FP@Al ^{IV} -2	64.5	6.4	3.5	1.2
	3FP@Al ^V	30	7.5	4.5	7.9
3FP@HZSM-5	3FP@Al ^{IV} -1	64	2.9	2.0	1.0
	3FP@Al ^{IV} -2	64.5	6.4	3.5	2.0
	3FP@Al ^V	32	7.5	4.7	8.3

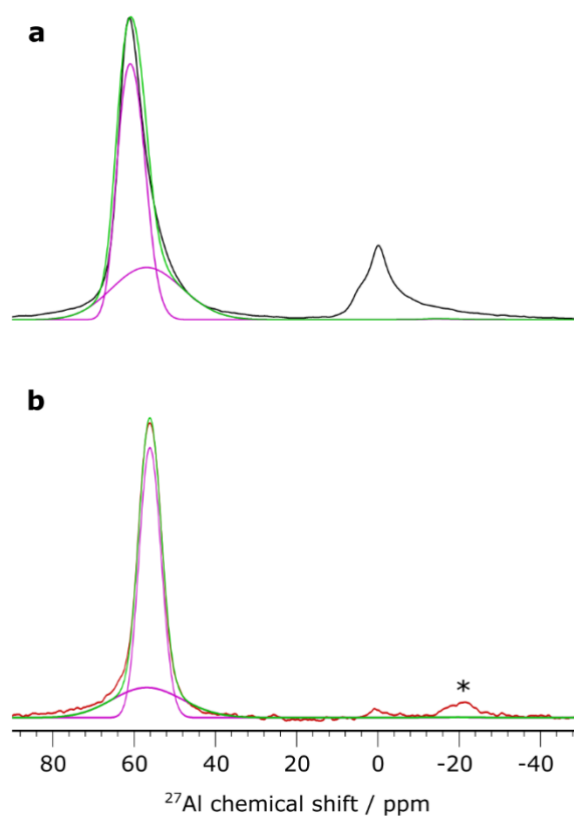


Figure S9. ^{27}Al direct excitation MAS NMR spectra with associated deconvolutions (purple) and the envelope (green) of the Al^{IV} sites of zeolites (a) HY (black) and (b) HZSM-5 (red) recorded at 9.4 T with 8 kHz MAS frequency. Asterisks (*) denote spinning side bands.

Table S12. Fitting parameters for the deconvoluted resonances from Figure S9. GB = Gaussian broadening, and Int. = relative integral. δ_{iso} is the isotropic chemical shift (units of ppm). C_Q is the quadrupolar coupling constant

	Site	δ_{iso} (ppm)	C_Q (MHz)	GB (kHz)	Int.
HY	Al ^{IV} -1	65.2	2.9	0.6	1.0
	Al ^{IV} -2	65.5	4.0	1.8	0.5
HZSM-5	Al ^{IV} -1	59.0	2.3	0.6	1.0
	Al ^{IV} -2	65.5	4.0	1.8	0.4

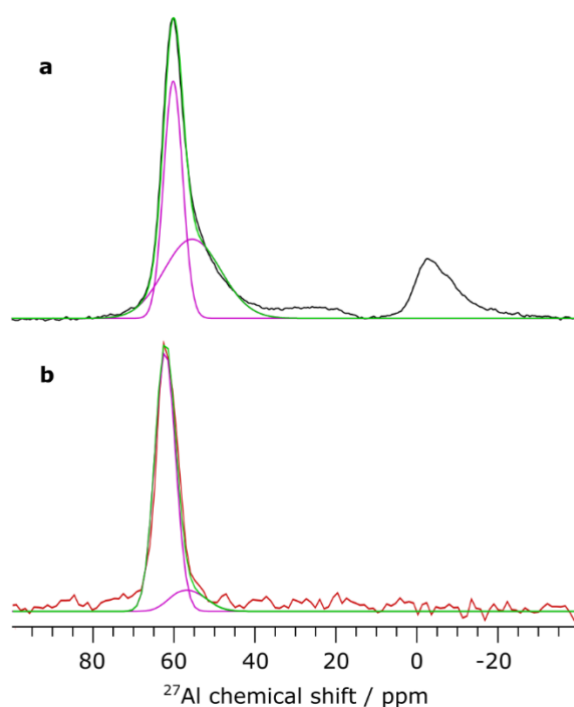


Figure S10. ^{27}Al direct excitation MAS NMR spectra with associated deconvolutions (purple) and the envelope (green) of the Al^{IV} sites of 3FP-dosed zeolites (a) HY (black) and (b) HZSM-5 (red) recorded at 20.0 T with ~33 kHz MAS frequency.

Table S13. Fitting parameters for the deconvoluted resonances from Figure S10. GB = Gaussian broadening, and Int. = relative integral. δ_{iso} is the isotropic chemical shift (units of ppm). C_Q is the quadrupolar coupling constant.

	Site	δ_{iso} (ppm)	C_Q (MHz)	GB (kHz)	Int.
HY	Al ^{IV} -1	64.2	2.9	1100	1.0
	Al ^{IV} -2	64.6	7.0	3000	1.0
HZSM-5	Al ^{IV} -1	63.0	2.9	1300	1.0
	Al ^{IV} -2	63.0	7.0	1500	0.1

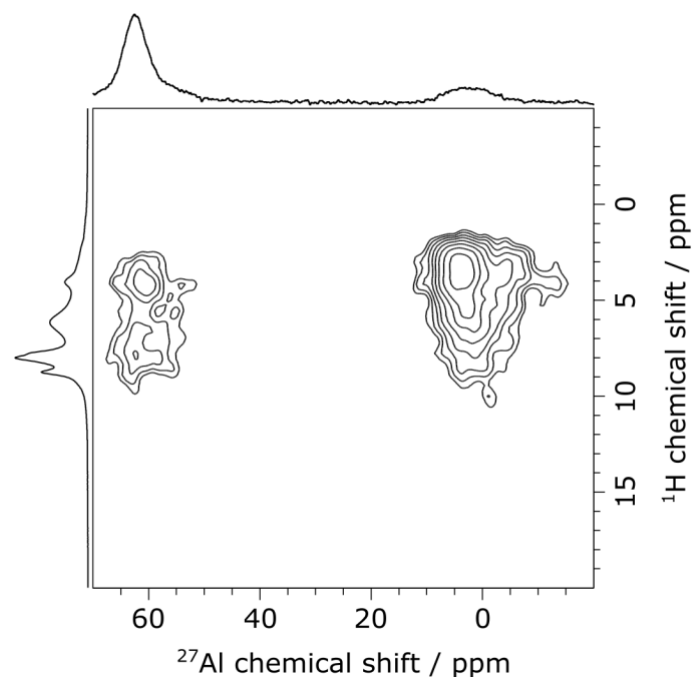


Figure S11. ^1H – ^{27}Al 2D HETCOR dipolar correlation MAS NMR spectrum of 3FP@HY recorded at ambient temperature at 16.4 T with 50 kHz MAS frequency; respective direct excitation spectra are shown on both axes for comparison.

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