

--- Supporting information---

**Hydroxyl environments in zeolites probed by deuterium solid-state MAS NMR
combined with IR spectroscopy**

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Materials and methods

Ammonium chloride (99.5%), ammonium hydroxide (28%), deuterium oxide (99.9% atom D), sodium nitrate (ACS reagent, $\geq 99.0\%$) were all used as received from Sigma Aldrich. Zeolite X (Na-X, Alfa Aesar), ultra-stable zeolite Y (USY, CBV760, Zeolyst), oxalic acid (99.8%, PROLABO) and double distilled water were used.

The preparation of proton form of zeolite X (H-X) was adapted from the literature.^{1,2} The as-received Na-X zeolite powder (400 mg) was mixed with 40 mL of 0.5 M NH_4Cl and 0.5 M NH_4OH in ratio of 1:1 and stirred at 353 K for 24 h. The material was recovered by centrifugation and the procedure was repeated another two times. The thrice exchanged material was washed three times with water (20 mL), recovered by centrifugation, and dried at 353 K for 1 h. The material was then calcined at 573 K for 20 h with a ramp of 1 K/min under air flow (50 mL/min). Preparation of Na-form of Y zeolite (Na-Y) sample was performed according to the procedure reported earlier.³ Zeolite Y powder (H-USY, CBV760, 1.00 g) was mixed with 15 mL of 0.2 M NaNO_3 at 353 K for 16 h. The obtained material in sodium form (Na-Y) was recovered by centrifugation and exchanged another two times. The thrice exchanged zeolite sample was washed three times with water (20 mL), recovered by centrifugation, and dried at 363 K for 4 h. Deuteration of the zeolite samples was performed by mixing 200 mg of zeolite with 400 mg of D_2O in a 4 mL open glass vial. The vial was placed inside a 50 mL polypropylene bottle containing 1 mL of D_2O . The polypropylene bottle was sealed and heated in an oven at 333 K for 14 h. The glass vial containing the zeolite/ D_2O mixture was then heated at 363 K for 2 h to remove excess liquid. Deuterated oxalic acid was prepared by dissolving oxalic acid (1.00 g) in deuterium oxide (10 mL) in a 60 mL sealed polypropylene vial and stirred for 24 h. The solution was then transferred to a round bottom flask and the deuterium oxide was removed by rotary evaporation.

Powder X-ray diffraction (XRD) patterns were collected with a PANalytical X'Pert Pro diffractometer using $\text{Cu-K}\alpha 1$ radiation ($\lambda = 1.5406 \text{ \AA}$, 45 kV, 40 mA).

Nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics 3Flex Surface Characterisation unit. Samples were degassed at 623 K under vacuum for 8 h prior to analysis.

FTIR spectra were obtained by using a Nicolet Magna 550-FT-IR spectrometer (4 cm^{-1} optical resolution). Zeolite wafers with an average area of 1 cm^2 using 20 mg powder samples were hydraulically pressed (1.5 t.cm^{-2}). The self-supported wafers were pretreated in the IR cell under vacuum (10^{-6} Torr): first at 423 K for 2 hours followed by a ramp to 573 K (3 K/min) and held at 573 K for 4 h. The adsorption temperature of Pyridine (1 torr at equilibrium) at 373 K was applied. After equilibration at 1 torr with pyridine, the cell was outgassed to remove the physisorbed species. All spectra were normalized to the same mass (20 mg wafers). For infrared H/D isotopic exchange experiments, samples were firstly activated in an in-situ IR cell at 573 K as described above. 1 torr of D_2O at equilibrium was then introduced. The exchange was performed at 423 K and IR spectra were recorded after evacuation under vacuum. This step was repeated three times to reach saturation level where no further changes were observed on the infrared spectra recorded.

^{29}Si and ^{27}Al NMR spectroscopic analyzes were performed on a 11.7 T Bruker Avance 500 spectrometer operating at a frequency of 99.35 and 130.32 MHz, respectively. ^2H NMR spectra were recorded on a 9.4 T Bruker Avance 400 spectrometer operating at a frequency of 61.42 MHz. The samples were packed into 4 mm zirconia rotors that spun at 10 kHz, 30° pulses were used and recycle delay was set to 2 seconds, 10240 scans were recorded for each spectrum. The number of scans for single-pulse ^{29}Si , and ^{27}Al NMR spectra were 1536 and 512, respectively. Tetramethyl silane (TMS) and aluminum nitrate ($\text{Al}(\text{NO}_3)_3$) were used as references for the chemical shifts of ^{29}Si and ^{27}Al NMR, respectively and the deuterated water (D_2O) for ^2D NMR experiments. Prior to NMR analysis, the deuterated samples were packed inside a 4 mm rotor and heated at 623 K for 6 hours with a ramp of 5 K/min.

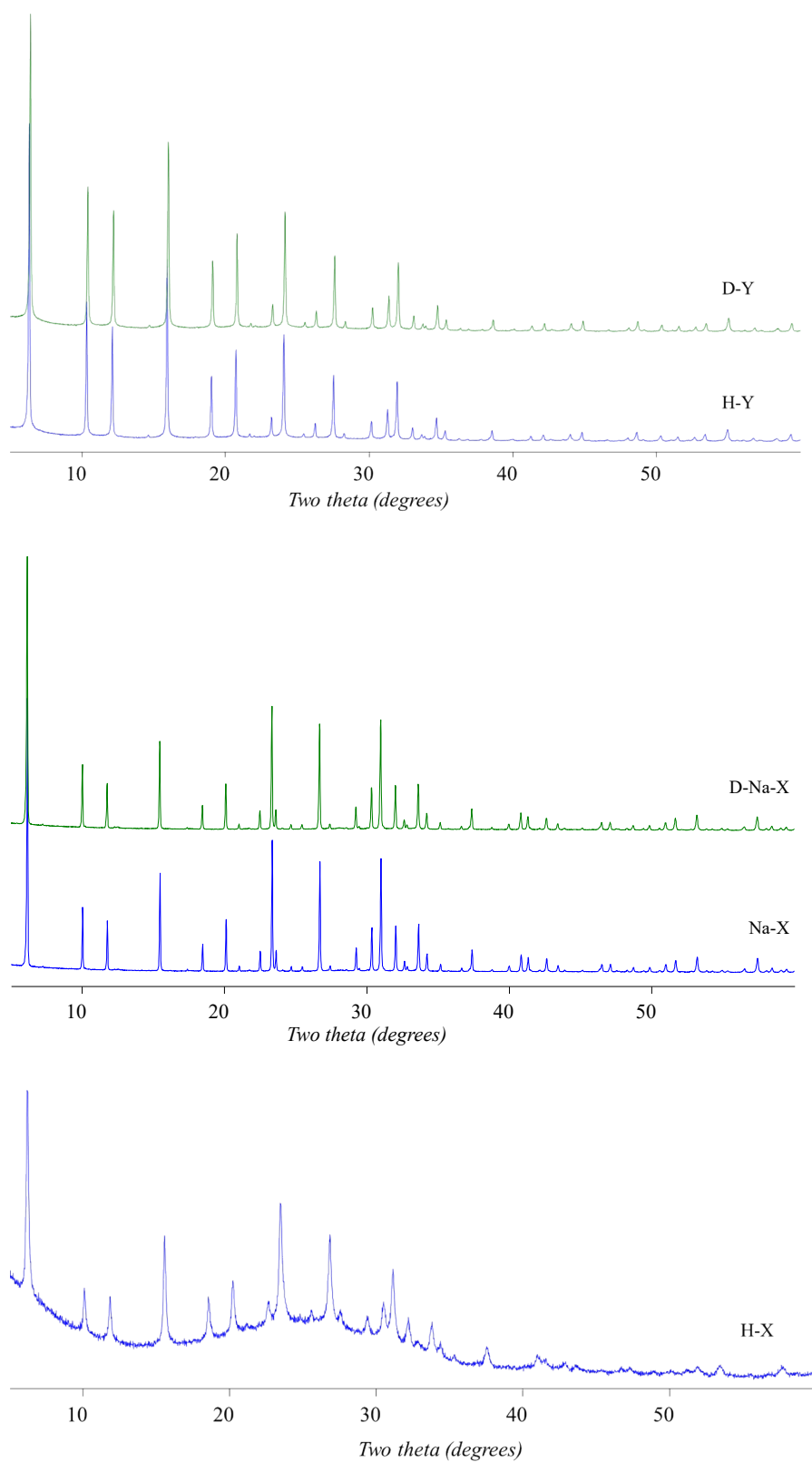


Figure S1. XRD patterns of H-Y and Na-X before and after treatment with D₂O (samples D-Na-X and D-Y), and H-X. D₂O treatment does not affect the crystallinity of the samples.

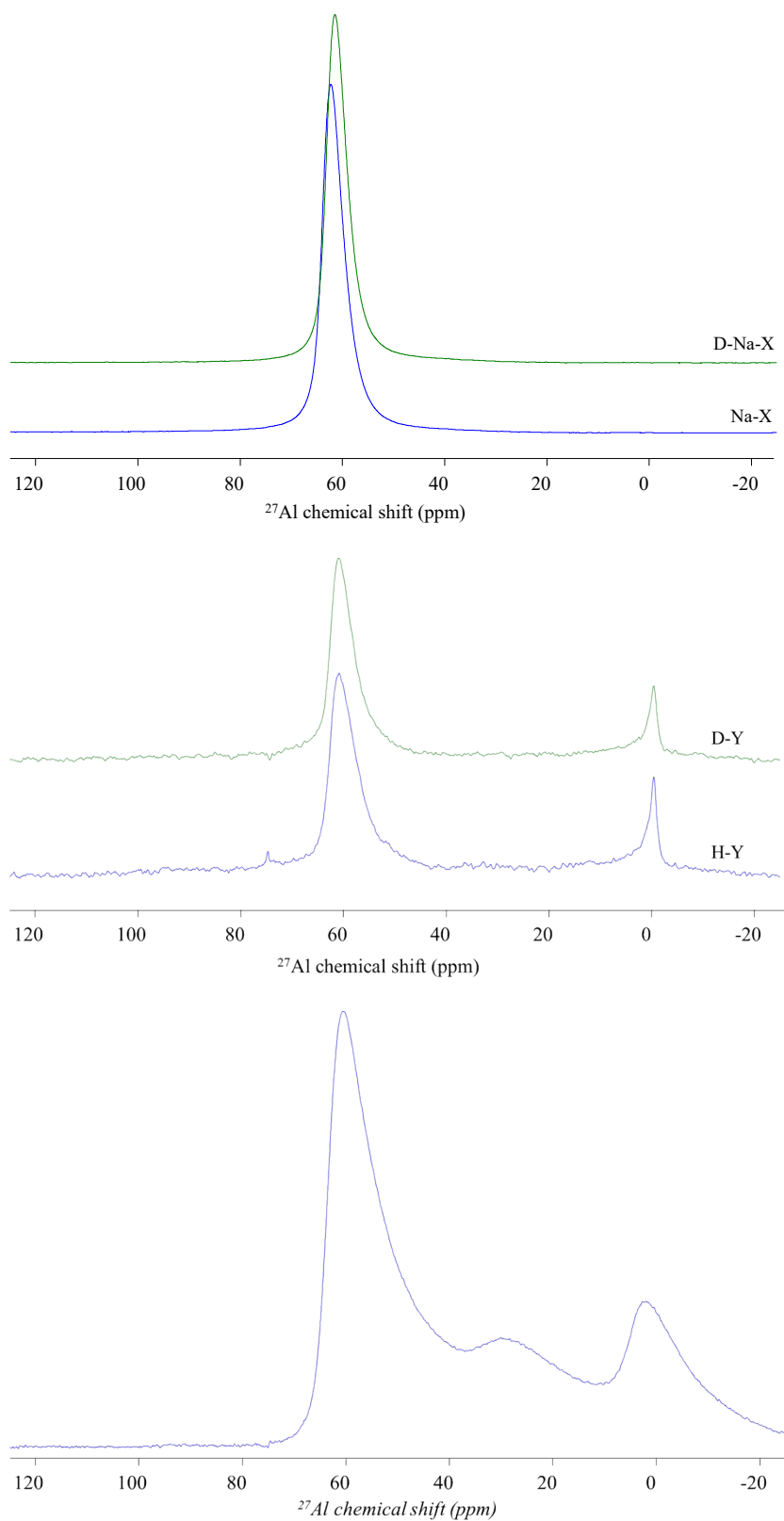


Figure S2. ^{27}Al NMR spectra of H-Y and Na-X before and after treatment with D_2O (samples D-Y and D-Na-X) and H-X. D_2O treatment does not affect the Al environments in the samples.

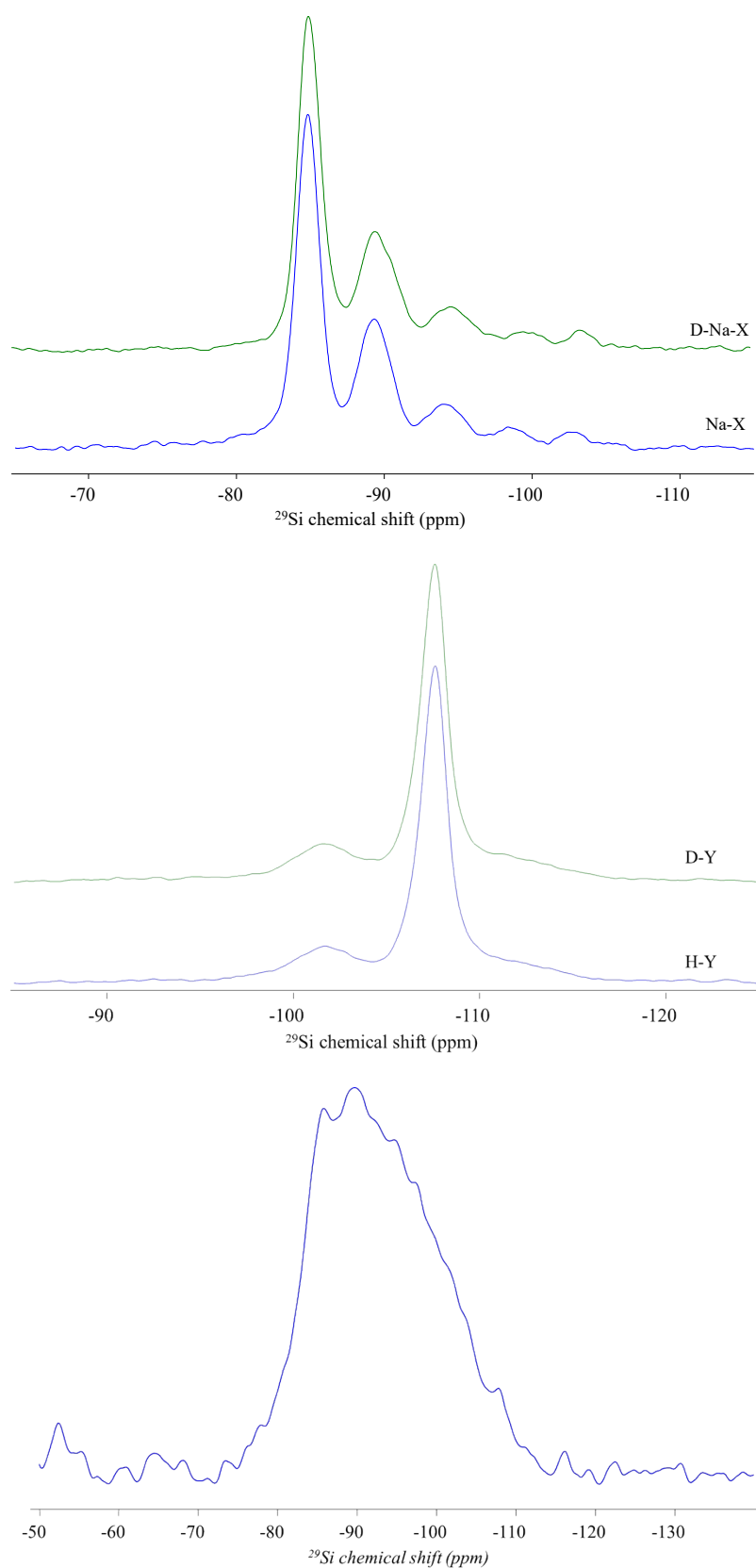


Figure S3. ^{29}Si NMR spectra of H-Y and Na-X before and after treatment with D_2O (D-Na-X and D-Y). D_2O treatment does not affect the crystallinity of the samples.

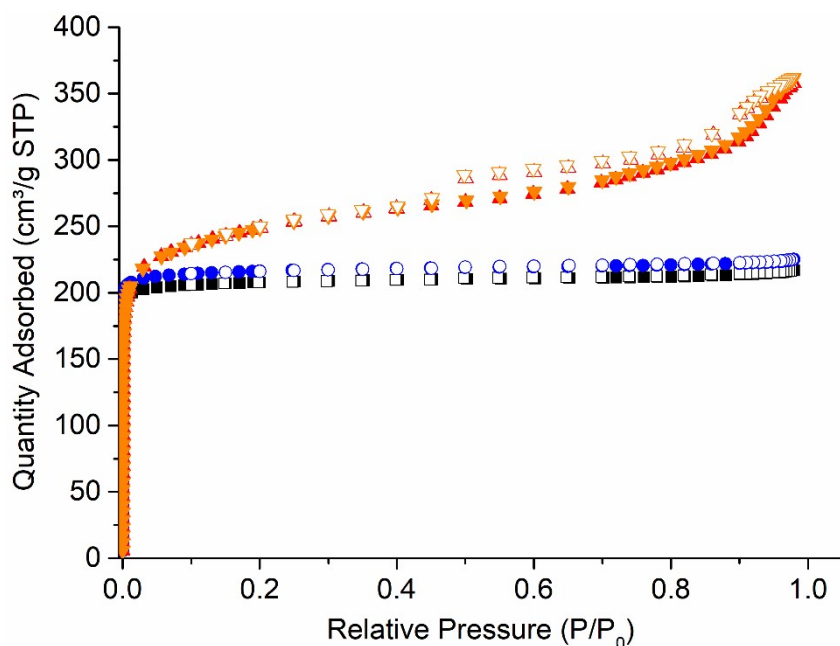


Figure S4. Nitrogen sorption and desorption isotherms of H-Y and Na-X before (red and black) and after (orange and blue) treatment with D₂O. D₂O treatment does not affect the crystallinity of the samples.

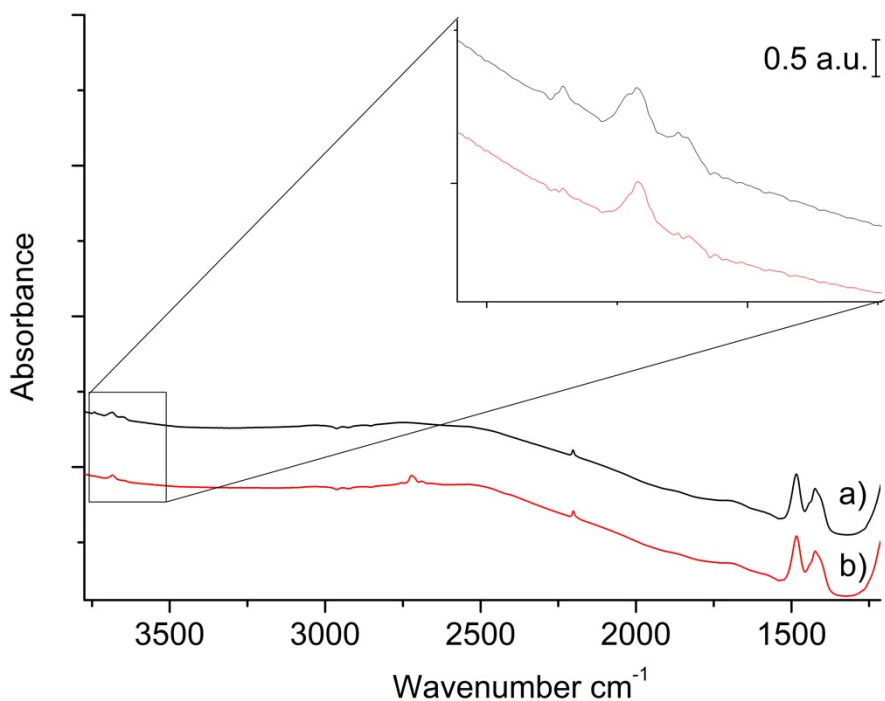


Figure S5. IR spectra of Na-X after activation at 573 K under secondary vacuum (a) and after H/D isotopic exchange (3 doses of D₂O, 1 torr) and evacuation under vacuum at 573 K (b).

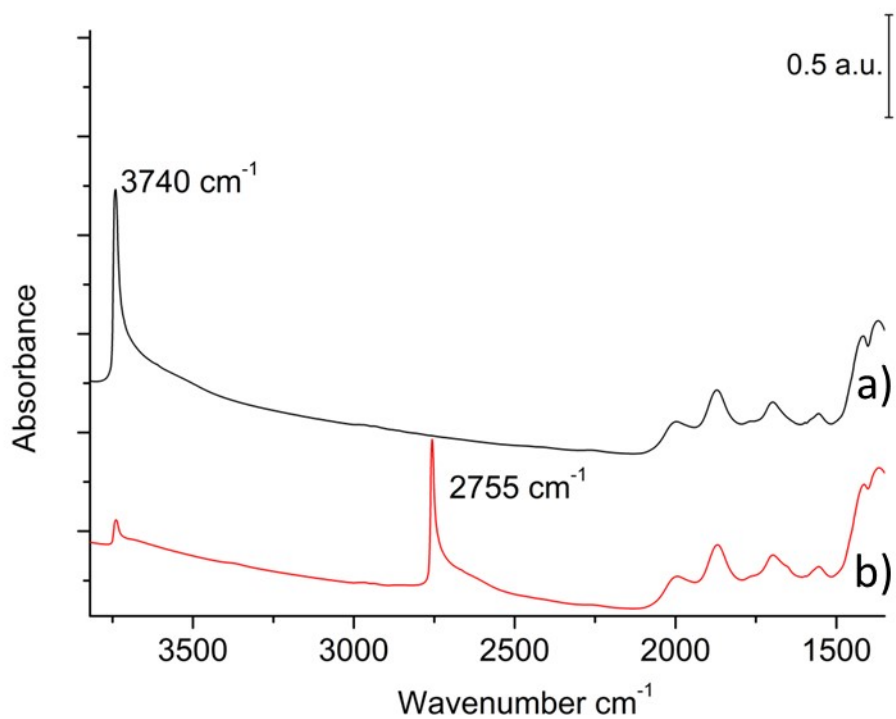
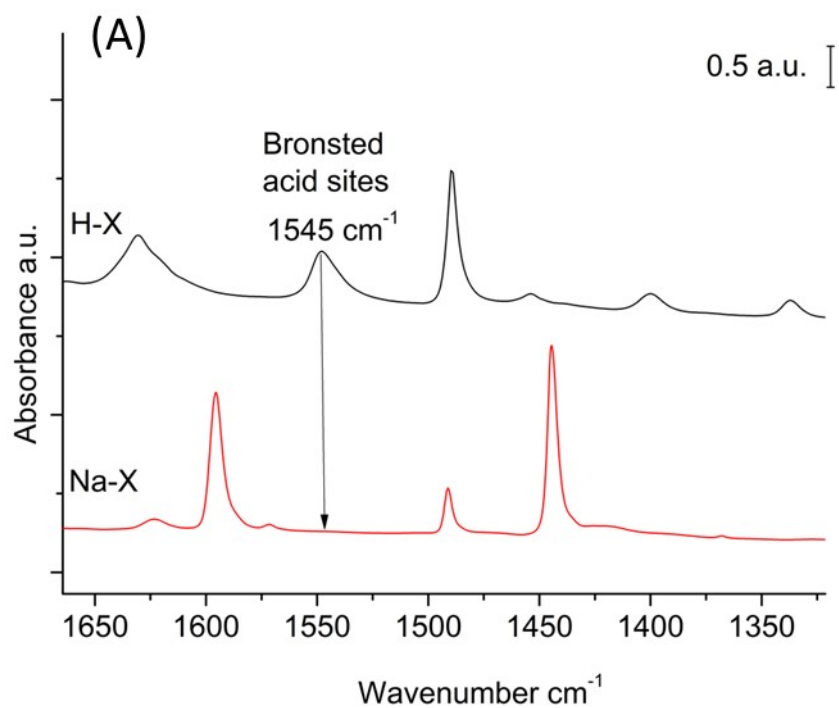


Figure S6. IR spectra of Na-Y after activation at 573 K under secondary vacuum (a) and after H/D isotopic exchange (3 doses of D₂O, 1 torr) and evacuation under vacuum at 573 K (b).



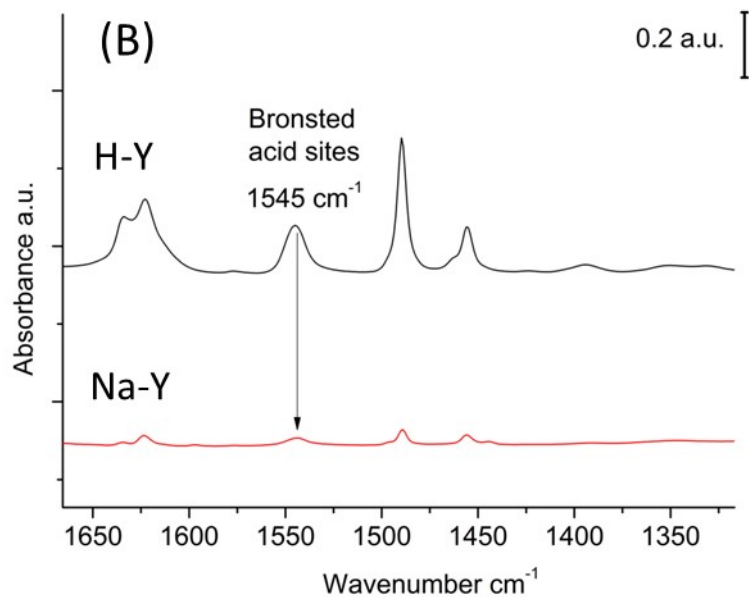


Figure S7. IR spectra after pyridine adsorption and evacuation under vacuum at 473 K for zeolites Na-X and H-X (A) and Na-Y and H-Y (B) in sodium and acidic forms.

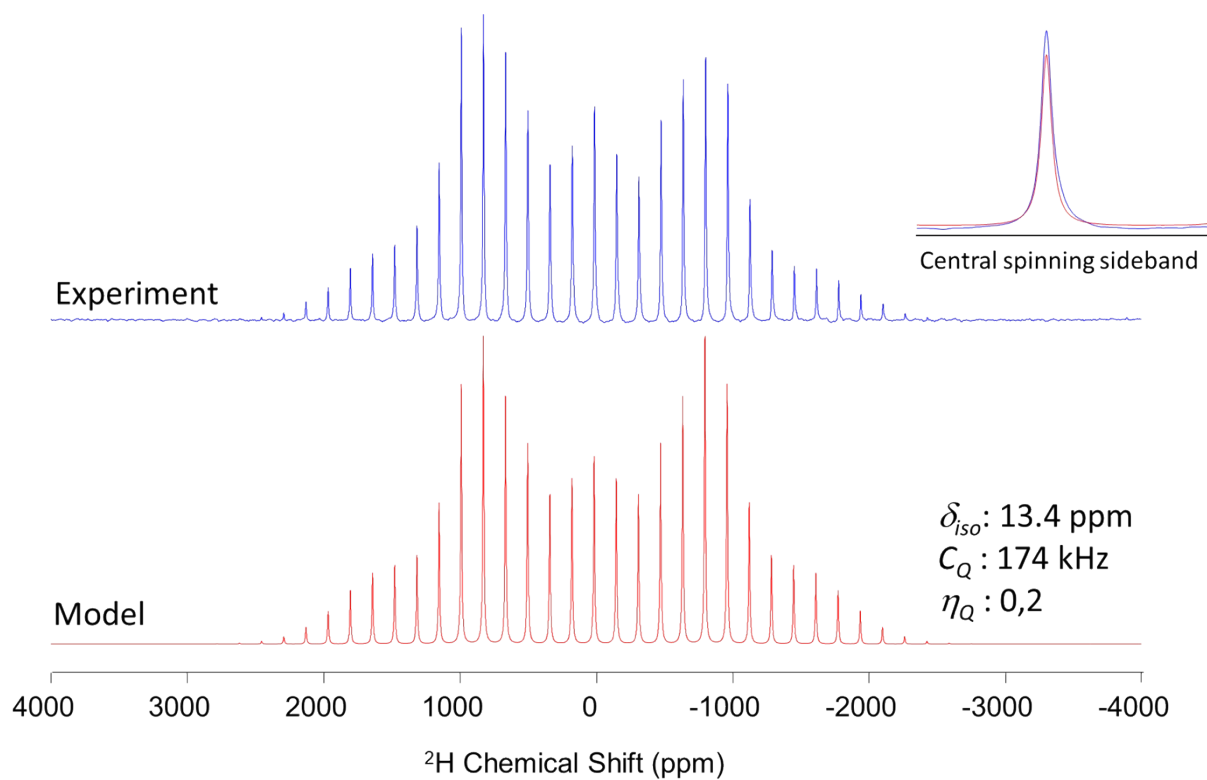


Figure S8. Experimental ^2H NMR spectrum of oxalic acid and the corresponding fit using Quad 1st model.

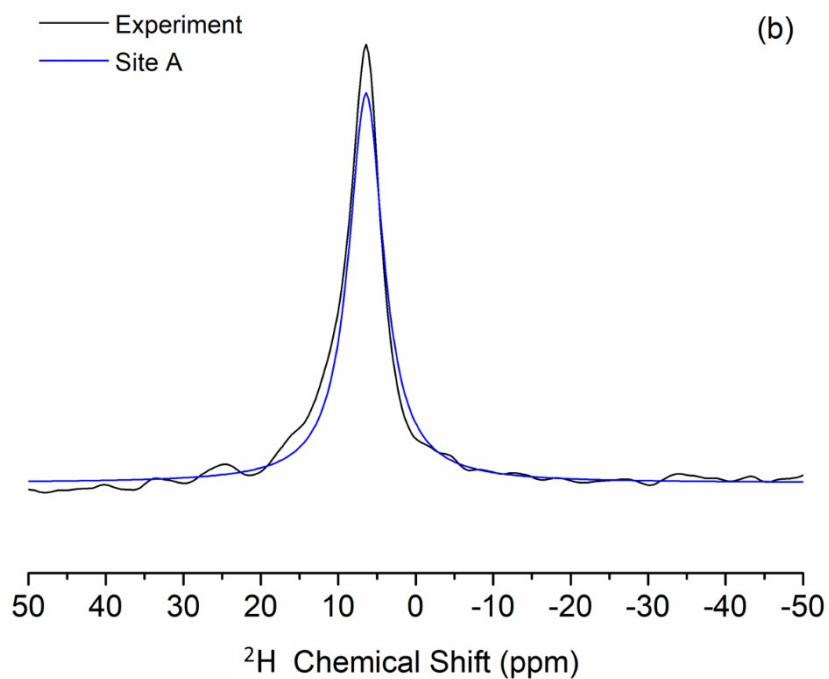
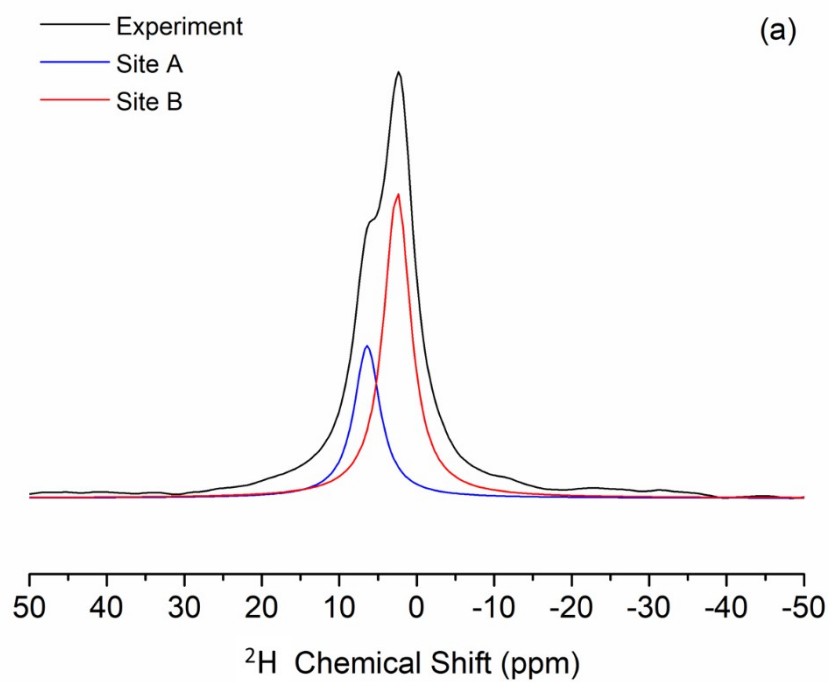


Figure S9. Deconvolution of the central spinning sideband of deuterated H-Y (a) and Na-Y (b).

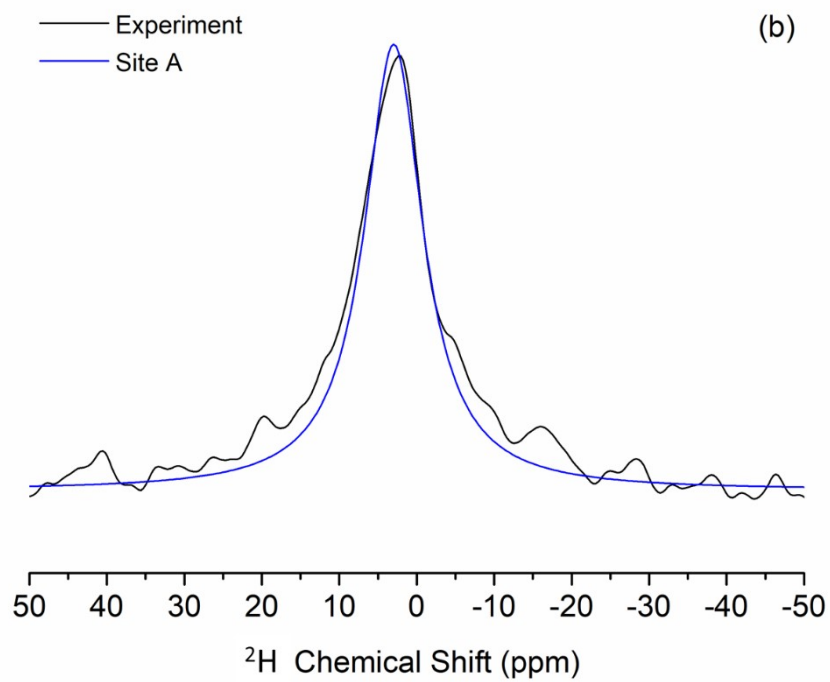
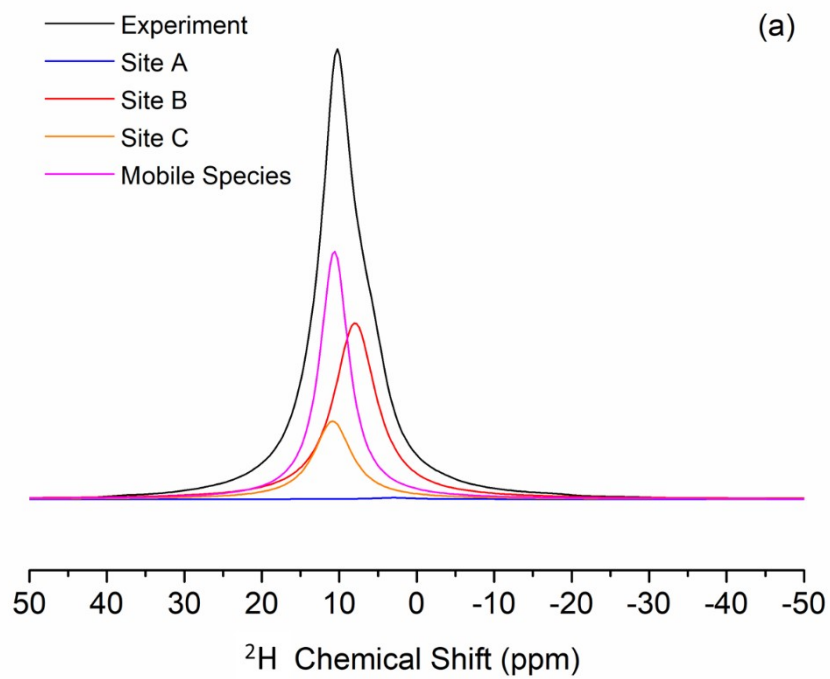


Figure S10. Deconvolution of the central spinning sideband of deuterated H-X (a) and Na-X (b)

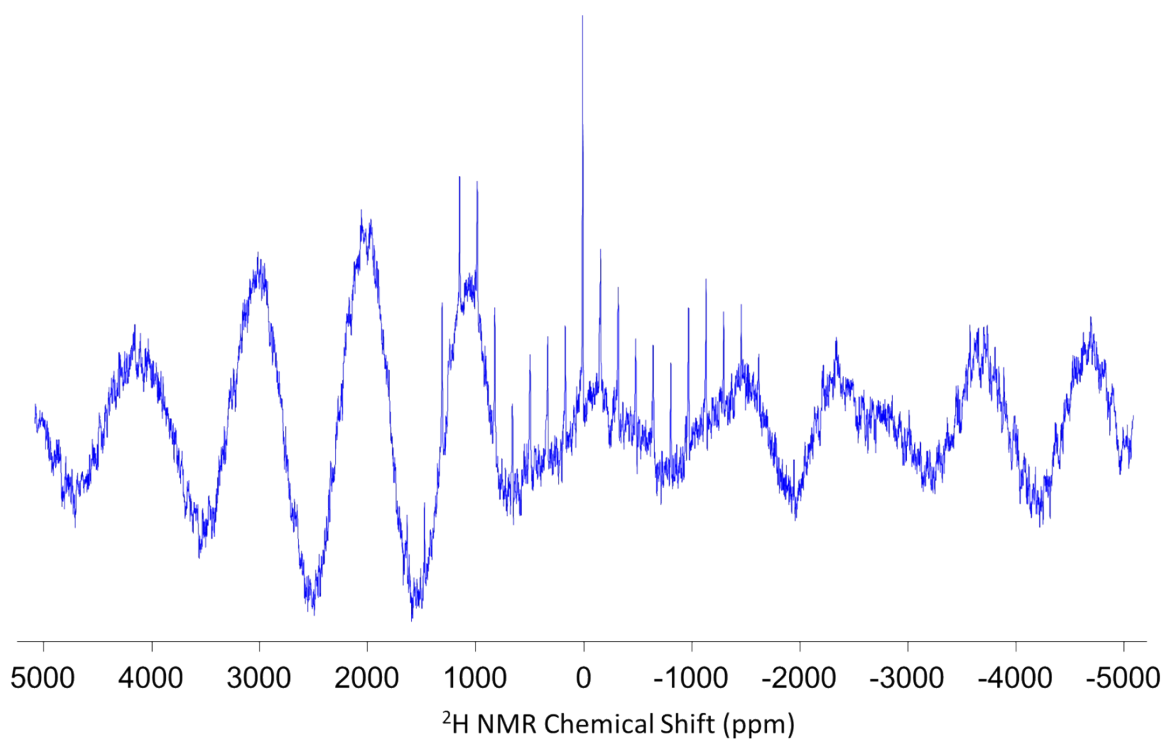


Figure S11. Deuterium NMR spectrum of deuterated H-X before baseline correction

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- 1 Chu and Dwyer, *Journal of Catalysis*, 1980, 61, 454.
 - 2 M. Huang, A. Auroux, S. Kaliaguine, *Microp. Mesop. Mater.*, 1995, 5, 17.
 - 3 M. Salzinger and J. A. Lercher, *Green Chemistry*, 2011, 13, 149.