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COMMUNICATION

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

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Deuterium (²H) solid-state MAS NMR spectroscopy is used for identifying both silanols and Brønsted acid sites in zeolites. The environments of hydroxyl groups in faujasite-type zeolites (FAU) with different aluminum contents and porosities in both acid- and sodium-forms were investigated. The results revealed a clear spectroscopic difference between zeolites possessing either silanols or both silanols and Brønsted acid sites compared to classical static ²H NMR spectroscopic studies. This study reinforces the versatility of solid-state MAS NMR spectroscopy and its synergy with IR spectroscopy to provide critical information on zeolite properties, adding a new tool to the set of characterizations available for silanols and Brønsted acid sites.

The activity of zeolites, microporous crystalline aluminosilicate materials widely employed in industrial-scale catalysis and adsorption, resides in special hydroxyl groups present within their frameworks: Brønsted acid sites located near the oxygen bridge between Si and Al atoms ($\equiv\text{Si}-\text{OH}-\text{Al}\equiv$). In addition, other less acidic hydroxyl groups also exist in zeolites: silanols, adjacent to Si atoms ($\equiv\text{Si}-\text{OH}$) within the channels or at the zeolite external surface. Brønsted acid sites remain a topic of intense investigation with recent efforts at tempting to achieve their localization.^{1,2} In comparison, silanols are gaining increased attention lately because they permit the engineering and functionalization of well-known zeolites in order to improve their catalytic performances. They are also identified as sites of catalytic deactivation due to their sensitive nature to moisture and ability to trap coke leading to reduced catalyst stability and lifetime.³ Both hydroxyl groups (Brønsted acid sites and silanols) have been the subject of several spectroscopic investigations to identify, localize or quantify them.^{4,5,6,7} ²⁷Al, ²⁹Si, ¹H solid-state NMR and IR spectroscopy were the most frequently employed techniques.^{8,9,10} However, the overlapping of the corresponding signals in both NMR and IR spectra hinders precise interpretations.¹¹ The limitations encountered are intrinsic to each technique; both spectroscopies suffer from a low resolution because of the

occurrence of strong couplings. Either the isotropic chemical shift of protons in NMR spectra (varying between 1 and 10 ppm) or the wavenumber frequency of the O–¹H bond in IR (varying between 3200 and 3750 cm⁻¹) are reaching the limit to deliver new insights on the environments of hydrogen in zeolites.¹² In order to overcome these drawbacks, hydrogen (¹H) - deuterium (²H) isotopic exchange monitored by IR spectroscopy is often used to analyze the O¹H and remove ambiguity in the assignment of the bands in the O¹H region. The O–²H bonds present a shift of the IR bands when compared to the O–¹H bonds as a result of the corresponding isotope mass difference.¹³ Earlier studies of deuterium-exchanged materials were performed with IR and NMR spectroscopy in static conditions to characterize the Brønsted acid sites in zeolites.¹⁴ The use of deuterium is insightful when characterizing hydroxyl groups in zeolites due to it possessing a quadrupolar nucleus, thus being sensitive to the surrounding electric field gradient through the quadrupolar interaction in solid state NMR spectroscopy.¹⁵ Despite the low natural abundance of deuterium (0.011%), the advantage of ²H NMR spectroscopy ($I = 1$) is the presence of the quadrupolar interaction that is absent in ¹H NMR spectroscopy ($I = \frac{1}{2}$). This concerns all of the nuclei having a spin $I > \frac{1}{2}$ that interact through their electric quadrupolar moment with their surrounding electric field gradient. In addition to the anisotropic chemical shift tensor parameters (Δ_{CSA} , η_{CSA} and δ_{iso}) arising from the interaction between the nuclear magnetic dipole and the surrounding magnetic fields, the quadrupolar interaction parameters (C_Q and η_Q) contribute to the width and the shape of the observed spectrum in powders.¹⁶ Precious information about the geometry and the dynamics of organic molecules may be gained by exploring the quadrupolar interaction of ²H NMR spectroscopy.¹⁷

Zeolites with different framework structures such as faujasite (FAU) and zeolite rho (RHO) were the subject of earlier studies using ²H NMR spectroscopy. The environment of hydroxyl groups, coke, and adsorbed water molecules in the zeolites were reported using static ²H NMR spectroscopy.^{18,19,20} A recent theoretical study showed the high sensitivity of deuterium quadrupolar coupling parameters towards the O–²H distance in FAU zeolites.²¹ However, the assignment of the static signals is still unclear, because of their low chemical shift

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resolution in presence of strong quadrupolar couplings in addition to the presence of 'hydrogen' bonds.^{22,23} The isotope effect of deuteration in a hydrogen-bonded host-guest crystal geometry has also been shown recently.²⁴ Herein, we will consider two zeolite samples with FAU type framework structure but with different chemical compositions: ultra-stable zeolite Y (USY, Si/Al=30) and zeolite X (Na-X, Si/Al= 1) in sodium (samples Na-Y and Na-X) and proton (samples ¹H-Y and ¹H-X) forms in order to probe the hydroxyl environments using magic angle spinning NMR spectroscopy aiming to obtain high resolution spectra by reducing the effect of dipolar couplings.

Select samples were characterized by XRD before and after the ²H₂O exchange. As shown in Figures S1-S3 (Supporting Information, SI), ²H₂O exchange did not alter neither crystallinity (XRD) nor local order (²⁹Si and ²⁷Al NMR spectroscopy) of the samples. The nitrogen sorption analyses performed on both zeolites before and after ²H₂O exchange also revealed no change in their micro or mesoporosity due to the ²H₂O exchange, Figure S4.

The samples were characterized by infrared spectroscopy and the results were correlated with the NMR spectroscopic data; the assignment of different hydroxyl ²H NMR signals will be presented below. Figure 1(A) shows infrared spectra of ¹H-X and Na-X zeolite samples in acidic and sodium forms after activation. While the ¹H-X shows in addition to the silanol bands, two distinct absorption bands at 3650 cm⁻¹ and 3570 cm⁻¹ that correspond to the bridging hydroxyl sites present in the supercages and sodalite cages of the FAU type structure, respectively. The same results have been observed for the Y zeolite samples as acidic (¹H-Y) and sodium (Na-Y) form. As shown in Figure 1(B), the infrared spectrum of Na-Y, displays an intense band at 3740 cm⁻¹ with a tail that covers the range of 3700–3500 cm⁻¹. This band is attributed to the native external silanol sites already present in the Na-Y in addition to the silanol sites resulting from the dealumination and hierarchization processes during ultra-stabilization of the zeolite. Similar to the ¹H-X zeolite, the ¹H-Y sample shows two more distinct bands at 3630 cm⁻¹ and 3560 cm⁻¹. These two bands are assigned to the bridging hydroxyl sites present in the supercages and sodalite cages, respectively. In order to confirm the absence of Brønsted acid sites in the Na-X and Na-Y zeolite samples, they have been subjected to pyridine adsorption monitored by infrared spectroscopy. The infrared spectra recorded after adsorption and evacuation at 473 K under secondary vacuum (Figure S7) did not reveal any traces of Brønsted acid sites in the Na-X, while Na-Y displays a weak infrared band at 1545 cm⁻¹, the fingerprint of pyridine adsorbed on bridging hydroxyl sites. This might be related to a small amount of acid sites that are still present in the sample after sodium exchange. The IR spectra of both zeolites (H-X and H-Y) show clearly a pronounced band at 1545 cm⁻¹.

The samples were further subjected to in-situ ¹H/²H isotopic exchange monitored by infrared spectroscopy to identify the different types of O¹H/O²H sites present on the two zeolites.

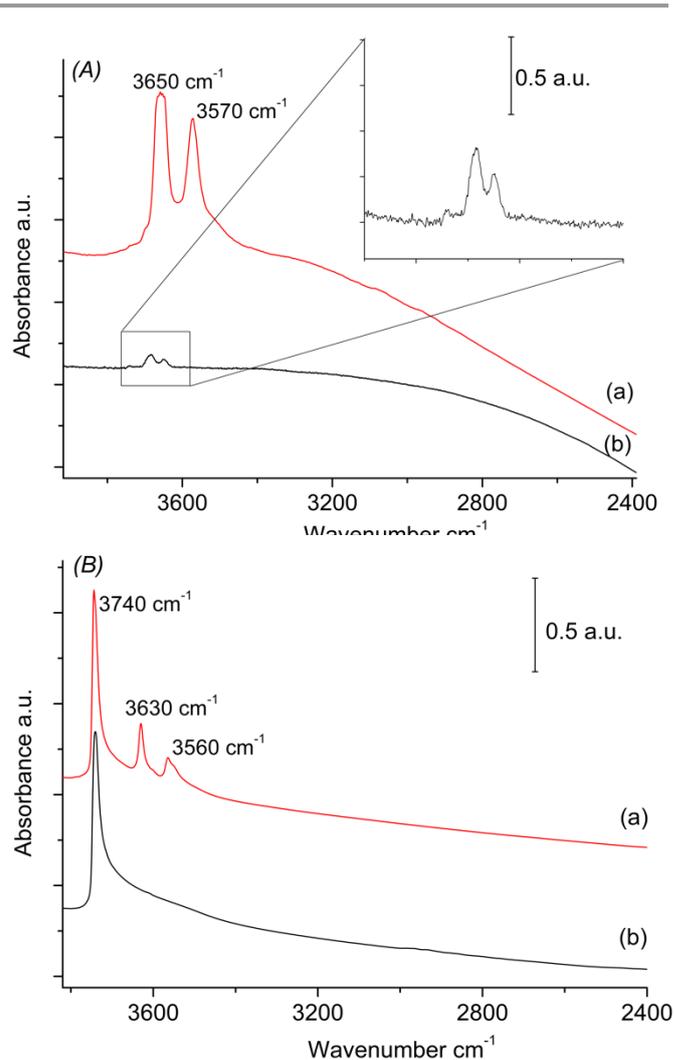


Figure 1. IR spectra after activation at 623 K and evacuation under secondary vacuum of zeolites X (A) and Y (B) in acidic (a) and sodium (b) forms.

Figure 2 (A) shows the IR spectra of H-X after activation, before and after ¹H/²H exchange. The infrared O¹H bands assigned to SiO¹H (3740 cm⁻¹) and bridging hydroxyl sites (3630 cm⁻¹ for supercages and 3570 cm⁻¹ for sodalite cages) shifted to low wavenumber values after exchange confirming the presence of three types of hydroxyl sites as observed in the O¹H region before deuteration. Similar results have been observed for ²H-Y; the three O²H bands are shifted to lower wavenumber values due to the O¹H/O²H exchange. The Na-X and Na-Y zeolite samples were also subjected to ¹H/²H exchange. For both samples, a shift of the SiO¹H band is observed confirming the presence of a single type of hydroxyl site *i.e.* silanols (see Figures S5 and S6, SI).

In addition to IR characterization of the Brønsted acid sites and silanol sites in both the sodium and acid forms of the zeolite samples, the ²H NMR spectra were acquired. The acquisitions were performed at 10 kHz; this spinning rate was chosen as a compromise aiming to (i) keep the shape of the spectrum with numerous spinning sidebands and (ii) increase the signal to noise ratio and the resolution by averaging other

anisotropic interactions that are smaller than the quadrupolar contribution. The spectra were modeled using appropriate models in the Dmfit software.²⁵ The experimental ^2H spectra for Na-Y and ^2H -Y zeolite samples with the corresponding fits are depicted in Figure 3. The spectra are not typical of a unique electric field gradient in the deuterium surroundings, as observed for deuterated oxalic acid ($\text{C}_2^2\text{H}_2\text{O}_4$) (Figure S8). A unique electric field gradient model 'Quad 1st' was used to fit the spectrum; the spectroscopic parameters were determined as a quadrupolar coupling constant $C_Q = 174$ kHz, an asymmetry

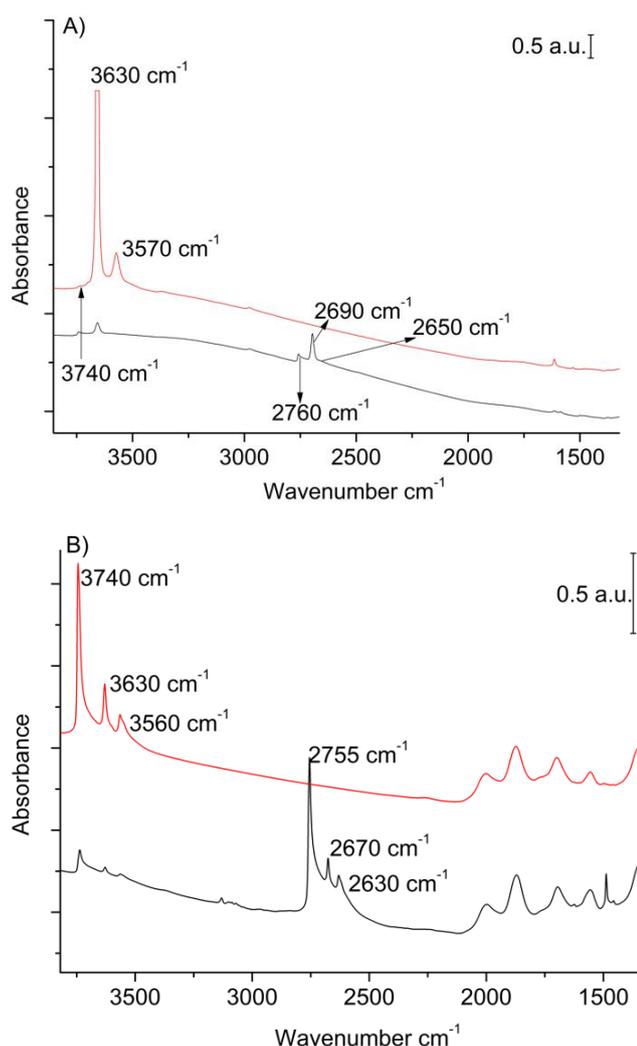


Figure 2. IR spectra after H/D isotopic exchange (black) and evacuation under secondary vacuum (red) at 573 K of zeolite X (A) and Y (B) in acidic forms.

parameter $\eta_Q = 0.2$ and an isotropic chemical shift $\delta_{iso} = 13.4$ ppm, as presented in the supporting information (Figure S7). The spectra corresponding to both zeolite samples Na-Y and H-Y were fitted using 'Czjzek all' and a Gaussian isotropic model using the Dmfit software. The result represents a distribution in deuterium surroundings reflecting a short-range local disorder.²⁶ The ^2H -Y (Figure 3(a)) presents two sites: A ($\langle C_Q \rangle = 50$ kHz; $\delta_{iso} = 6.4$ ppm, 80% contribution) and B ($\langle C_Q \rangle = 100$ kHz; $\delta_{iso} = 2.4$ ppm, 20% contribution) while only the A site

($\langle C_Q \rangle = 50$ kHz; $\delta_{iso} = 6.4$ ppm) is present in Na-Y, (Figure 3(b)). From these results, supported by the IR spectroscopic characterization, sites A and B were assigned to silanols and Brønsted acid sites, respectively. Interestingly, in opposite to usual observations in ^1H NMR spectroscopy, the isotropic chemical shift of the acid sites is lower than that of the silanols in ^2H NMR spectra. One possible interpretation for that is a different 'hydrogen' bonding network in this sample as recently reported for organic compounds,²⁴ however, the average quadrupolar coupling constant is always larger for Brønsted acid sites compared to SiOH.

The ^2H spectra of both the H-X and Na-X are shown in Figure 4. The signal corresponding to the silanols was identified in the spectrum of the Na-X zeolite sample (Figure 4 (b)); it corresponds to site A having a C_Q of 147 kHz, an η_Q of 0.8 and δ_{iso} of 2.4 ppm with a unique peak in the central spinning sideband. The shape of this

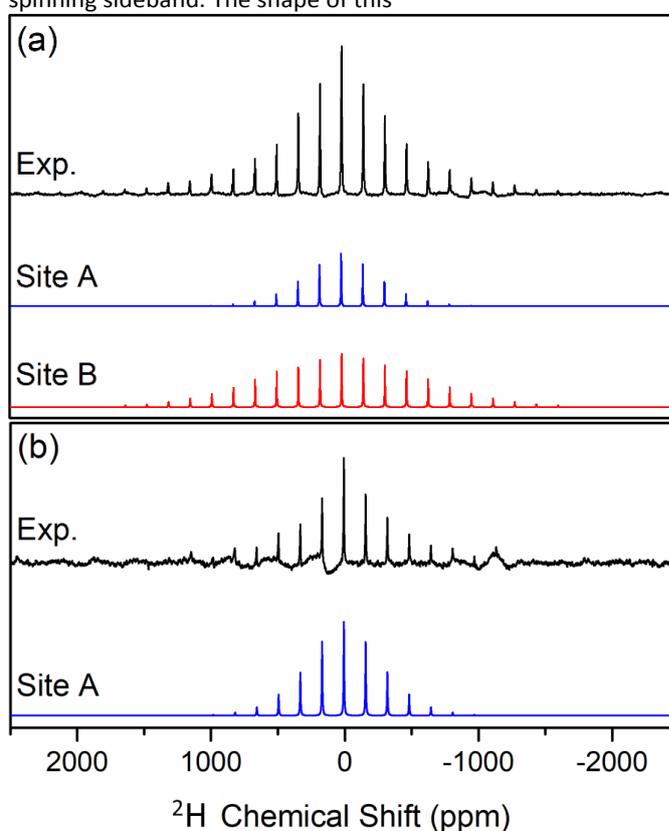


Figure 3. Experimental and corresponding fits of ^2H NMR spectra of deuterated H-Y (a) and Na-Y (b). 'Czjzek all' model was used from Dmfit software. The deconvoluted central spinning sidebands are presented in the SI (Figure S9).

spectrum is deeply insightful and reflects the different electric environments of the silanols in zeolites X and Y. Despite their unique spectroscopic signature in the IR spectra at 3740 cm^{-1} , the electric environments around silanols are not the same in both zeolites. A different shape is observed for the ^2H -X and the central spinning sideband contains several peaks (Figure 4 (a)). To fit this spectrum, three main sites were used based on the results obtained from the corresponding IR spectra before and after deuteration (Figure 2 (A)), one for silanols (already observed in the Na-X and Na-Y) and two for Brønsted acid sites

present in sodalite cages and supercages simultaneously. An unexpected sharp peak for a spin equal to 1 was observed in the spectrum, thus an additional sharp Lorentzian peak at 10.8 ppm with no quadrupolar parameters was added to the fit. This does not correspond to any bonded O^2H group and may represent some highly mobile extra-framework species present in the sample as a consequence of calcination and amorphization (Figure S1). Due to the negligible population of these species ($\sim 3\%$), they will not be considered in the discussion. The three main sites, A ($C_Q = 147$ kHz, $\eta_Q = 0.8$; $\delta_{iso} = 2.4$ ppm), less than 1%, B ($C_Q = 139$ kHz, $\eta_Q = 0.7$; $\delta_{iso} = 8.0$ ppm), 52% and C ($C_Q = 217$ kHz, $\eta_Q = 0.2$; $\delta_{iso} = 10.9$ ppm), 44% are assigned to silanols and two different Brønsted acid sites at 2690 and 2650 cm^{-1} respectively (see IR spectrum in Figure 2(A)). Brønsted acid sites (B and C) have different C_Q values reflecting two different environments for these sites in the

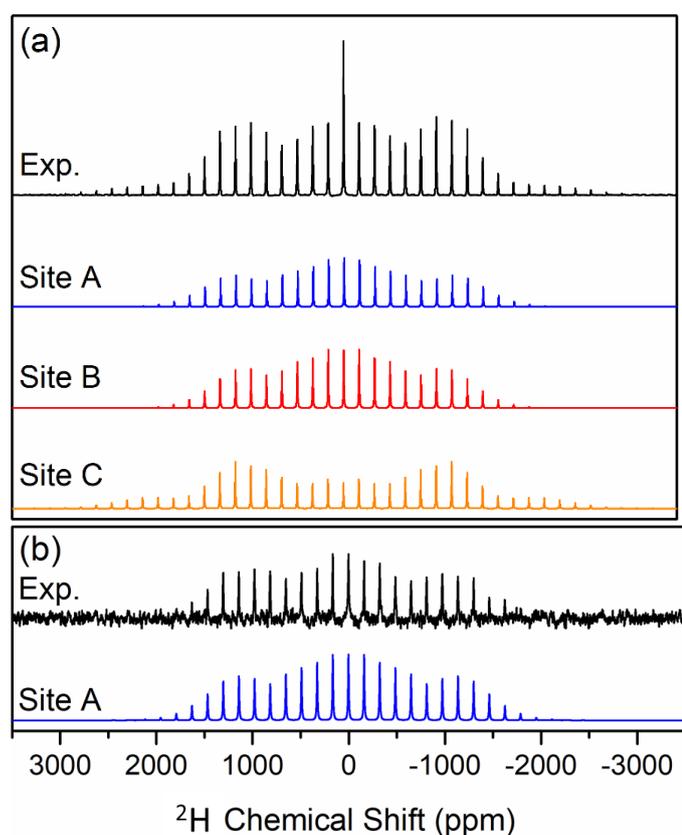


Figure 4. Experimental and corresponding fits of 2H NMR spectra of deuterated 2H -X (a) and Na-X (b). QUAD 1st model was used from Dmfit software. For clarity, the intensity of sites A, B and C for deuterated 2H -X zeolite sample are multiplied by 2, 2 and 200, respectively. The deconvoluted central spinning sidebands are presented in the SI (Figure S10).

supercages and sodalite cages, respectively. The deuterons in supercages being less confined than the ones in the sodalite cages, their quadrupolar coupling constant is smaller and seems to be closer to that of silanols typically attributed to surface groups. A similar behaviour was recently observed for several O^2H groups in clay minerals.²⁷ This distinction is impossible to be made for Brønsted acid sites in zeolite Y appearing at 2670 and 2630 cm^{-1} (see IR spectra, Figure 2(B))

because of the short-range electric distribution. Thus, the combination of IR and 2H NMR spectroscopy presents a novel approach for peak assignment.

It is also interesting to note that either silanols or Brønsted acid sites present different spectral shapes for each of the different zeolites. Ordered O^2H groups are observed in Na-X with a unique electric field gradient while electrically disordered ones (distributed) are observed in ultra-stable zeolite Y. Then, a homogeneous (unique) and large electric field gradient (~ 200 kHz) is observed in Na-X (Si/Al = 1) while a heterogeneous (distributed) and narrow (~ 100 kHz) electric field gradient is observed in the ultra-stable Y (Si/Al = 30). The same trend is found for the deuterated silanols, 147 kHz of width for Na-X versus 50 kHz for Na-Y. The main difference between both zeolites is the density (proximity) of acid sites (Si/Al ratio is multiplied by 30) and type of porosity (microporous vs. hierarchical). Despite the significant amount of Al^V and Al^VI species in sample H-X (Figure S2), they did not give rise to a distribution in the deuterium environments, as in the Y zeolite samples containing a lesser amount of Al^VI . These results shown how 2H NMR spectroscopy may offer a way for a direct measurement of Brønsted acid sites and silanol site densities that is related to the width of the spectrum and site ordering giving an overall unique shape to the spectrum, although the quantitative aspect of this spectroscopy is not straightforward because of the ease of $^1H/^2H$ exchange. In addition, 2H is an excellent probe of temperature-dependent dynamics, a critical parameter necessary to understand the diffusion of molecules through porous materials. Due to length of time required for such an experiment (3 days) this is not reported in the present work. In conclusion, this approach may lead to improved understanding of the electric environments in zeolites in the future, a key-factor determining acid site strength and adsorption behaviour.

Conflicts of interest

There is no conflict to declare

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Notes and references

- 1 J. Dědeček, E. Tabor and S. Sklenak, Tuning the Aluminum Distribution in Zeolites to Increase their Performance in Acid-Catalyzed Reactions, *ChemSusChem*, 2019, 12, 556.
- 2 M. Guisnet and J-P. Gilson, Zeolites for Cleaner Technologies, Imperial College Press, 2005.
- 3 I. C. Medeiros-Costa, E. Dib, N. Nesterenko, J-P. Dath, J-P. Gilson and S. Mintova, Silanol defect engineering and healing in zeolites: opportunities to fine-tune their properties and performances, *Chemical Society Reviews*, 2021, 50, 11156.
- 4 E. Dib, T. Mineva, E. Veron, V. Sarou-Kanian, F. Fayon and Bruno Alonso, ZSM-5 Zeolite: Complete Al Bond Connectivity and Implications on Structure Formation from Solid-State NMR and Quantum Chemistry Calculations, *J. Phys. Chem. Lett.* 2018, 9, 19.

- 5 C. Schroeder, V. Siozios, M. Hunger, M. Ryan Hansen and H. Koller, Hydrogen Bond Formation of Brønsted Acid Sites in Zeolites, *J. Phys. Chem. C*, 2020, 124, 23380.
- 6 L. Lakiss, A. Vicente, J-P. Gilson, V. Valtchev, S. Mintova, A. Vimont, R. Bedard, S. Abdo, J. Bricker, Probing the Brønsted acidity of the external surface of Faujasite type zeolites, *Chemphyschem*, 2020, 21, 1873.
- 7 L. Treps, C. Demaret, D. Wisser, B. Harbuzaru, A. Méthivier, E. Guillon, D. Viktorovych Benedis, A. Gomez, T. de Bruin, M. Rivallan, L. Catita, A. Lesage and C. Chizallet, Spectroscopic Expression of the External Surface Sites of H-ZSM-5, *J. Phys. Chem. C*, 2021, 125, 2163.
- 8 H. G. Karge, M. Hunger and H. K. Beyer, *Catalysis and Zeolites*, Springer-Verlag Berlin Heidelberg, 1999.
- 9 M. Hunger, Brønsted Acid Sites in Zeolites Characterized by Multinuclear Solid-State NMR Spectroscopy, *Catal. Rev. Sci. Eng.*, 1997, 39, 345.
- 10 V. M. Mastikhin, I. L. Mudrakovsky, A. V. Nosov, ¹H NMR magic angle spinning (MAS) studies of heterogeneous catalysis, *Prog. in NMR Spec.*, 1991, 23, 259.
- 11 H. Koller and M. Weiss, Solid state NMR of porous materials: Zeolites and related materials, *Top Curr Chem.*, 2012, 306, 189.
- 12 G. Paul, C. Bisio, I. Braschi, M. Cossi, G. Gatti, E. Gianotti and L. Marchese, Combined solid-state NMR, FT-IR and computational studies on layered and porous materials *Chem. Soc. Rev.*, 2018, 47, 5684.
- 13 J-P. Galla, J-M. Goupil, A. Vimont, J-C. Lavalley, B. Gil, J-P. Gilson and O. Miserque, Quantification of water and silanol species on various silicas by coupling IR spectroscopy and in-situ thermogravimetry, *Langmuir*, 2009, 25, 5825.
- 14 T. J. Gluszak, D. T. Chen, S. B. Sharma, J. A. Dumesic and T. W. Root, Observation of Brønsted acid sites of D-Y zeolite with deuterium NMR *Chem. Phys. Letters*, 1992, 190, 36.
- 15 J.L. Ackerman, R. Eckman and A. Pines, Experimental results on deuterium NMR in the solid state by magic angle sample spinning, *Chemical Physics*, 1979, 42, 423.
- 16 A. Hauch, H. Bildsøe, H. J. Jakobsen, and J. Skibsted, ²H chemical shift anisotropies from high-field ²H MAS NMR spectroscopy *Journal of Magnetic Resonance*, 2003, 165, 282.
- 17 M. Chan-Huot, S. Wimperis, Christel Gervais, G. Bodenhausen and L. Duma, Deuterium MAS NMR Studies of Dynamics on Multiple Timescales: Histidine and Oxalic Acid *ChemPhysChem*, 2015, 16, 204.
- 18 A. J. Vega and Z. Luz, Characterization of NH₄-rho and vacuum-calcined H-rho zeolites by multinuclear NMR spectroscopy *J. Phys. Chem.* 1987, 91, 365.
- 19 J. M. Kobe, T. J. Gluszak, J. A. Dumesic, and T. W. Root, Deuterium NMR Characterization of Brønsted Acid Sites and Silanol Species in Zeolites, *J. Phys. Chem.* 1995, 99, 5485.
- 20 K. Yoo Cheah, P. Alexander and L. F. Gladden, Investigation of coking phenomena in zeolite HY using deuterium NMR *Applied Catalysis A*, 1997, 148, 387.
- 21 P. Błoński, A. Birczyński, Z. T. Lalowicz and J. Datka, Z. Łodziana, Structure of the Hydroxyl Groups and Adsorbed D₂O Sites in the DX Zeolite: DFT and Experimental NMR Data *J. Phys. Chem. C*, 2015, 119, 19548.
- 22 B. Berglund and R. W. Vaughan, Correlations between proton chemical shift tensors, deuterium quadrupole couplings, and bond distances for hydrogen bonds in solids, *J. Chem. Phys.*, 1980, 73, 2037.
- 23 U. Sternberg and E. Brunner, The Influence of Short-Range Geometry on the Chemical Shift of Protons in Hydrogen Bonds, *J. Magn. Reson. series A*, 1994, 108, 142.
- 24 C. Shi, X. Zhang, C. Yu, Y-F. Yao and W. Zhang, Geometric isotope effect of deuteration in a hydrogen-bonded host-guest crystal, *Nat Commun*, 2019, 9, 481.
- 25 D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J-O. Durand, B. Bujoli, Z. Gan, G. Hoatson, Modelling one and two-dimensional solid-state NMR spectra, *Magn. Reson. Chem.*, 2002, 40, 70.
- 26 E. Dib, T. Mineva, P. Gaveau and B. Alonso, ¹⁴N solid-state NMR: a sensitive probe of the local order in zeolites, *Phys. Chem. Chem. Phys.*, 2013, 15, 18349.
- 27 M. Avramovska, D. Freude, W. Schwieger, C. Song, J. Kärger and J. Haase, NMR Studies of the Dehydroxylation and Rehydroxylation (RHx) of Clays with Respect to the RHx Dating of Ceramic Materials, *J. Phys. Chem. C*, 2021, 125, 26274.