



HAL
open science

The challenge of silanol species characterization in zeolites

Florent Dubray, Eddy Dib, Izabel Medeiros-Costa, Cindy Aquino, Delphine Minoux, Stijn van Daele, Nikolai Nesterenko, Jean-Pierre Gilson, Svetlana Mintova

► **To cite this version:**

Florent Dubray, Eddy Dib, Izabel Medeiros-Costa, Cindy Aquino, Delphine Minoux, et al.. The challenge of silanol species characterization in zeolites. *Inorganic Chemistry Frontiers*, 2022, 9 (6), pp.1125-1133. 10.1039/D1QI01483H . hal-04295903

HAL Id: hal-04295903

<https://hal.science/hal-04295903>

Submitted on 20 Nov 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

The challenge of silanol species characterization in zeolites

Florent Dubray,^a Eddy Dib^a, Izabel Medeiros-Costa,^{a,b} Cindy Aquino,^b Delphine Minoux,^b Stijn van Daele,^b Nikolai Nesterenko,^b Jean-Pierre Gilson^a and Svetlana Mintova^{a,*}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

The chemistry of silica-based materials, including zeolites, is strongly influenced by the nature and amount of their silanols. In zeolites, they are either isolated (non H-bonded) silanol species, or silanol (H-bonded) nests corresponding to hydrolyzed Si-O-Si bonds; their hydrophilic nature will in turn impact the overall properties of the corresponding material. It is therefore important to assess the nature and to quantify silanol species. This work pools spectroscopic techniques to that effect. The zeolites with a very relevant MFI type structure were prepared as (i) pure siliceous silicalite-1, (ii) aluminium-containing ZSM-5 (Si/Al=110), and (iii) molybdenum-containing silicalite-1 providing a rich spectrum of chemical compositions. The occurrence of both silanol types in silicalite-1 is confirmed as well as their removal by isomorphous substitution with molybdenum. On ZSM-5 is highlighted the effect of silanol species configuration in the presence of strong Brønsted acid sites. General guidelines for the evaluation of silanol species in zeolites using spectroscopic approaches (IR, Raman and NMR) is proposed.

Introduction

The extensive use of zeolite-based materials in liquid and gas separation as well as in catalysis is well known, and was a driver to their in depth characterization, so as to optimize their efficiency and better control their synthesis.¹ Zeolites are primarily composed of silicon (Si) and aluminium (Al) atoms tetrahedrally coordinated with oxygen (O) bridges forming a three-dimensional framework.² A “point defect” in the zeolite framework is an irregularity in the periodic crystalline structure, linked to the presence of Brønsted Acid sites (BAS) or silanol (Si-OH) species. These latter consists of either: (i) isolated silanols mainly located at the edges or on the surface of the crystals, or (ii) H-bonded silanols located within the periodic structure due to the absence of a framework tetrahedrally coordinated Si atom, thus generating a vacancy.^{3–5} Usually, these silanol species are described as external (isolated) or geminal silanols, and internal silanol, or silanol nests, respectively. These silanol species are considered as weakly acidic.⁶

In the case of aluminium containing zeolites, other hydroxyl groups are present in the zeolite structure: the so-called BAS. They emerge in zeolites due to the presence of some hetero-

elements such as Al, Ge, Fe, etc. in the framework.^{6,7} These hetero-elements in the zeolite framework are tetrahedrally coordinated, and thus bring a negative charge to the framework due to their valence, located on one of the bridging oxygen atoms linking the hetero-element to the zeolite framework; the negative charge is therefore compensated by a neighbour cation. A Brønsted acid site is generated when the corresponding cation is a hydrogen atom. BAS are not far away from being silanols or aluminium hydroxides, and thus are often being referred to as “bridging hydroxyl groups”. Their structure can be summarized as follows: (SiO)₃-Si-O(H)-Al-(OSi)₃. These hydroxylated sites are however very different in nature and properties from usual silanols, and are therefore not considered as silanol species, especially due to their strong acidity in comparison to silanols.

The nature and amount of silanols that can be found in a zeolite framework is directly linked to the synthesis procedures or post-synthesis modifications applied toward the preparation of zeolites. By variation of the synthesis conditions, zeolites with variable properties such as crystal size, crystal morphology, aggregation degree, chemical composition and elemental homogeneity can be designed. All these properties are in turn, influencing the nature and amount of silanol species present in the corresponding zeolites, influencing their hydrophobicity and catalytic properties.

A non-exhaustive list of silanol features in zeolites is for instance:

- They are weak points in zeolite structures that will lead to their collapse under harsh conditions.^{8,9} These weak points are for instance the base for the generation of hollow zeolite

^a Normandie Université, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie (LCS), 14000 Caen, France.

^b Total Research and Technology Feluy, B-7181 Seneffe, Belgium.

* Corresponding author, E-mail: mintova@ensicaen.fr.

Electronic Supplementary Information (ESI) available: FTIR spectra of zeolite samples dispersed in KBr (Figure S1); deconvolutions of the ¹H MAS NMR spectra (Figure S2); SEM images (Figure S3); quantification of silanol species for each samples (Table S1); and attribution of the ³¹P MAS NMR chemical shifts (Table S2). See DOI: 10.1039/x0xx00000x

materials, thanks to the fact that the centre of zeolite crystals usually contains more silanol nests, and are consequently more prone to dissolution under controlled conditions.⁸

- Silanols can be seen as reactive species that are able to stabilize metals into zeolite tetrahedral positions through a process called isomorphous substitution.^{10,11}

- Silanol species are affecting the surface properties of zeolites, such as their hydrophobicity,^{12–15} in turn modifying their sorption properties depending on the polarity and nature of the guest molecules.^{13,16}

- Silanol sites can act (synergistically or on their own) as active site in catalysis, influencing the selectivity,^{17,18} or the formation of coke, and coke retention in other cases.^{19–22}

The characterization of silanol species is therefore of major interest, since their presence, amount, location, and nature play a significant role in the design of fit-for-purpose zeolitic materials.

Fourier transform infrared spectroscopy (FT-IR) is one of the most widely used techniques to characterize silanols in zeolites. The IR spectral region of 3000 - 4000 cm^{-1} (O-H stretching vibrations) is commonly used to distinguish bridging hydroxyl groups (Brønsted acid sites, linked to the presence of Al-OH, around 3608 cm^{-1}) from isolated silanols (3745 cm^{-1}), or silanol nests (3500 - 3600 cm^{-1}).^{10,11,23–26} While the O-H stretching vibrations provide valuable information on the nature of the silanols (internal, external, ...), they cannot be quantified since both band positions and extinction coefficients are affected by the environment of the different hydroxyl groups and H-bonding (depending whether the silanols are geminal, vicinal, isolated, ...).^{9,27,28}

To quantify the total amount of silanols in zeolites, the combination ($\nu+\delta$) OH bands (corresponding to the combination of hydroxyl stretching and bending modes) in the 4800 - 4200 cm^{-1} range is more valuable. The silanol and water contents of various porous silicas were quantified and reported by Gallas et al.²⁷, by combining a simultaneous in-situ recording of IR spectroscopy with thermogravimetric analysis (TG-IR, thermo gravimetric-IR); the extinction coefficient of the ($\nu+\delta$) OH combination band was determined. In addition, deuterium isotopic exchange was carried out on the silanols using deuterated water. Back-exchange with alcohols of different sizes was subsequently performed, allowing the quantification of silanols and the drawing of a silanol accessibility map: silanols were consumed by alcohols based on their accessibility as a function of alcohols sizes, since the ($\nu+\delta$) OD combination band is shifted with regards to the corresponding ($\nu+\delta$) OH combination band. In a similar study, Ide et al.²⁹ treated the silanols with silanes of different sizes to derive their accessibility.

Alternatively, silanol quantification was also attempted using pyridine as a probe molecule.³⁰ However, the variation of extinction coefficient and significant overlapping between the coordinated and physisorbed pyridine bands make this approach of little use.³¹ The relative acidity of silanols was

assessed using CO as a probe molecule monitored by FTIR; some silanols displayed strong acidity related to the nature of the material under consideration (crystalline vs. amorphous, hydrophobic vs. hydrophilic).³²

In addition to IR spectroscopy, a commonly used technique for silanol evaluation is solid-state ^1H MAS NMR (magic angle spinning nuclear magnetic resonance) as ^1H possesses a spin $\frac{1}{2}$ and quantification is more straightforward than with IR due to the molar response of NMR signal. ^1H MAS NMR can therefore quantify and distinguish silanols based on their chemical shifts (non-H-bonded isolated silanols: ~ 1.4 ppm, weakly H-bonded silanols: ~ 2.2 ppm, Brønsted acid sites: ~ 4.0 ppm and strongly H-bonded silanols and BAS above 4 ppm) although the chemical shift range is rather narrow and overlapping occurs frequently due to dipolar couplings.^{33–35} By comparing the relative quantities of different silanols in as synthesized zeolites, after template removal by calcination, and ion exchange procedures, the formation mechanism of internal silanols as a function of the template location could be elucidated.^{36–38} Deuterium exchange of ZSM-5 zeolite studied by both ^1H and ^2H NMR spectroscopy was used to reveal silanol species based on their geometry.³⁹ While ^{29}Si NMR could estimate the total amount of silanols by quantifying the Q^2 (-91 ppm) and Q^3 (-103 ppm) species as presented by Zhang et al.³³, this approach remains of limited precision especially in the case where other heteroelements such as Al are present in the zeolite framework, since the corresponding Al-induced Q^3 species ($(\text{SiO})_3\text{-Si-O-Al}$ species) will also be displayed as Q^3 species (in addition to H-induced Q^3 species: $(\text{SiO})_3\text{-Si-O-H}$), appearing at a similar chemical shift.

In this paper, spectroscopic techniques are used to determine the nature and to quantify silanols in three zeolite samples, all MFI framework types, namely: (i) silicalite-1 (Si-MFI), (ii) ZSM-5 (Al-MFI), and (iii) molybdenum containing silicalite-1 (Mo-MFI). Their silanols are thoroughly characterized by FTIR, Raman, ^{29}Si MAS NMR, $\{^1\text{H}\}$ ^{29}Si CP-MAS NMR (CP: Cross Polarization), ^1H MAS NMR, and ^{31}P MAS NMR of adsorbed trimethylphosphine oxide (TMPO).^{40,41}

Experimental

Synthetic procedures

Different zeolites of MFI (Mobil five) topology: Si-MFI, Al-MFI and Mo-MFI zeolites were prepared using the following chemicals without further purification: tetraethyl orthosilicate (TEOS, 98%, Aldrich), tetra n-propylammonium hydroxide (TPAOH, 20 wt. % in water solution, Alfa Aesar), aluminium nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 97%, Prolabo), and sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, Alfa Aesar, 98%). Double distilled water was systematically used in all synthesis steps requiring the use of water. Syntheses were carried out in closed 125 mL polypropylene (PP) bottles under autogenous pressure and quiescent conditions (Si-MFI and Mo-MFI), or in Teflon-lined autoclaves under autogenous pressure and quiescent

conditions (Al-MFI). All harvested sample have approximately the same particle size (around 150 nm), as measured using SEM (Figure S3).

Synthesis of Si-MFI

The chemical composition of the precursor mixture was: 1 SiO₂ : 0.28 TPAOH : 40 H₂O. The resulting clear suspension was stirred 1h at room temperature, before hydrolysis for 18 h on an orbital shaker. Then, hydrothermal synthesis was carried out at 90 °C for 48 h. The crystalline product was recovered and purified by high speed centrifugation (20,000 rpm) until a pH of 7 was reached; the product was then dried at 80 °C and calcined in a muffle furnace (550 °C, 5 h); this sample was abbreviated as Si-MFI.

Synthesis of Al-MFI

The chemical composition of the precursor mixture was: 1 SiO₂ : 0.357 TPAOH : 0.004 Al₂O₃ : 16.189 H₂O. The resulting clear suspension was stirred 1h at room temperature, before hydrolysis for 18h on an orbital shaker. The precursor mixture was then transferred into Teflon-lined autoclaves, and hydrothermal synthesis was carried out at 180 °C for 72 h. The crystalline product was recovered and purified following the procedure described above. The sample with a Si/Al ratio of 110 according to ICP was abbreviated as Al-MFI.

Synthesis of Mo-MFI

To an aqueous and homogeneous solution of sodium molybdate (0.107 m, 8 mL) was added 300 mg of sample Si-MFI *vide-supra*; the resulting suspension was stirred for 1 h and further heated at 90 °C for 96 h in quiescent conditions. The crystalline product was recovered following the procedure described above so as to prevent any unreacted Mo species from staying in the microporous volume of the zeolite sample. The H-form of the Mo-MFI zeolite was prepared by ion exchange treatment: the calcined powder is dispersed in an ammonium chloride solution (NH₄Cl, 0.2 M, solid/liquid weight ratio = 0.1), and stirred for 1 h, prior being subjected to calcination (550 °C; 5 h). The sample was abbreviated as Mo-MFI.

Characterization

The silanols in the zeolite were characterized by FTIR spectroscopy using a Nicolet Magna 550-FT-IR spectrometer (4 cm⁻¹ optical resolution). Self-supported zeolite wafers (1 cm², av. 20 mg, hydraulic press at 1 t.cm⁻²) were first activated at 480 °C for 3 h under vacuum (av. 2.5 x 10⁻⁶ Torr) prior to the measurements. Additionally, the zeolites were mixed with KBr and directly measured; the wafer mass was 100 mg with approximately 0.5 wt. % of zeolite in this case.

Raman spectra were collected on a Jobin Yvon Labram 300 confocal Raman spectrometer coupled with a microscope (objective: 50x) and a CCD detector. A 532 nm laser was used, and the spectra were accumulated three times for 60 s each.

²⁹Si, ¹H, and ³¹P NMR spectra were all collected on a Bruker Avance III-HD (11.7 T) spectrometer operating at 99.3, 500, and 202.4 MHz, respectively; a 4 mm outer diameter zirconia

rotor spun at 12, and 14 KHz for ²⁹Si NMR, a 3.2 mm outer diameter zirconia rotor spun at 22 KHz for ³¹P NMR and a 1.9 mm outer diameter zirconia rotor spun at 40 kHz for ¹H NMR were respectively used. Single pulse excitations were used, with a flip angle of 30° for ²⁹Si, and 90° for ¹H and ³¹P spectra, corresponding to radio frequency fields of 21, 114, and 41 KHz for ²⁹Si, ¹H, and ³¹P respectively. {¹H} ²⁹Si CP-MAS NMR cross-polarization experiments were performed with a contact time of 5 ms, and a recycle delay of 2 s. Chemical shifts were referenced to tetramethyl silane (TMS) for ¹H and ²⁹Si, and to phosphoric acid (H₃PO₄, 1M) for ³¹P.

Prior the ¹H MAS NMR experiments, the samples were activated under dynamic vacuum at 350 °C for 10h, followed by packing in the NMR rotor under protective atmosphere (Ar) so as to avoid water re-adsorption. Prior to the ³¹P MAS NMR experiments, trimethylphosphine oxide (TMPO) was impregnated on the dehydrated zeolitic sample according to the following procedure. All steps were conducted under an inert Argon (Ar) atmosphere to prevent any reaction of the TMPO with moisture in the air and zeolitic water. The zeolite samples were first dehydrated at 400 °C under vacuum (4.0 x10⁻⁵ Torr) while a solution of TMPO dissolved in dichloromethane (CH₂Cl₂) was prepared in parallel. The solution was then mixed with the dehydrated zeolite powder followed by sonication for 15 min. The obtained suspensions were then evaporated for 2 h at room temperature and under vacuum. The harvested TMPO loaded samples were then transferred into 3.2 mm outer diameter zirconia rotors, still under Ar atmosphere, so as to record ³¹P MAS NMR spectra. The (excess) precise TMPO loading was chosen so as to not have too much non-chemisorbed species (crystalline and/or physisorbed TMPO) that might “hide” the NMR signals of interest.

Results and discussion

The FTIR spectra of Si-MFI, Al-MFI, and Mo-MFI samples are depicted in Figure 1. The Si-MFI spectrum displays one intense narrow band at 3746 cm⁻¹, attributed to the presence of isolated silanols, and a band located at 3520 cm⁻¹, attributed to the presence of silanol nests. Another band at 4550 cm⁻¹ related with all silanols (combination of hydroxyls stretching and bending modes: (ν+δ) OH bands) is observed as well, but its low intensity prevents a reliable quantification. In sample Al-MFI, a new band appears at 3615 cm⁻¹, and is the usual signature of bridged hydroxyls, the so-called Brønsted acid sites. The bands at 3746 and 3520 cm⁻¹ are still observed, indicating that both isolated silanols and silanol nests species are also present in the Al-MFI sample. However, sample Mo-MFI does not show bands at 3520 cm⁻¹ (silanol nests) or at 3615 cm⁻¹ (bridged hydroxyls) as this zeolite sample is Al-free. Furthermore, the band at 3746 cm⁻¹ (isolated silanols) is still present albeit with a much lower intensity, while the band at 4550 cm⁻¹ is absent, attributable to a very low amount of

silanols being present in the Mo-MFI zeolite sample. In Figure 2, a schematic representation of different types of silanols identified in the three samples studied are presented. It is important to note that the amount of OH defects in zeolites is mediated by the synthesis procedures applied. More general, the silanols amount in zeolites depend on the alkalinity of the synthesis media, conditions of crystallization and ultimate size of the crystallites.

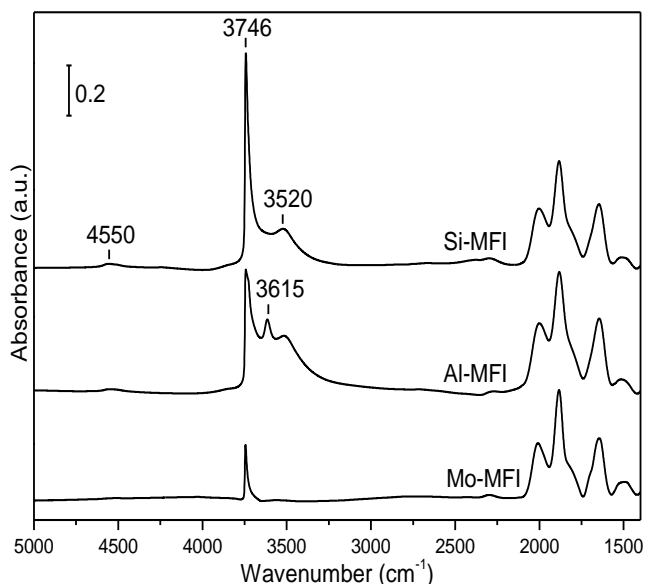


Figure 1. FTIR spectra of (dehydrated) zeolite samples: Si-MFI, Al-MFI, and Mo-MFI.

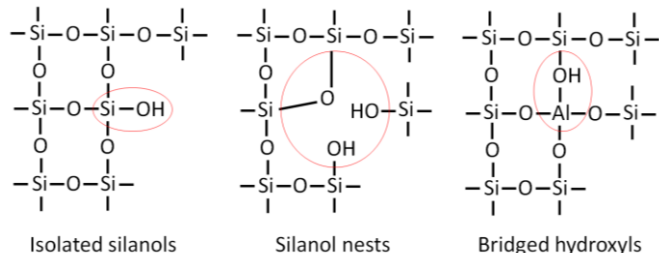


Figure 2. Visual representation of isolated silanols, silanol nests, and bridged hydroxyls (Brønsted acid sites).

Silanols were also observed by Raman spectroscopy (Figure 3) where the 980 cm^{-1} band is attributed to Si-O stretching vibrations linked to the presence of silanol species.^{42,43} This band is intense on both samples Si-MFI and Al-MFI, indicating the presence of silanol species, but seemingly slightly red-shifted in Al-MFI sample due to the presence of bridged hydroxyls (Si-O-Al stretching in addition to Si-O-H stretching).⁴⁴ However, on the Mo-MFI sample, almost no signal is observable at 980 cm^{-1} in agreement with the very low concentration of silanols as observed by IR, while new bands (332 , 416 , 803 , and 820 cm^{-1}) witness the presence of framework Mo.^{40,45} The bands at 332 and 416 cm^{-1} are attributed to Si-O-Mo framework vibrations, highlighting the framework nature of the inserted Mo species, thus, explaining why the majority of silanols species are removed.

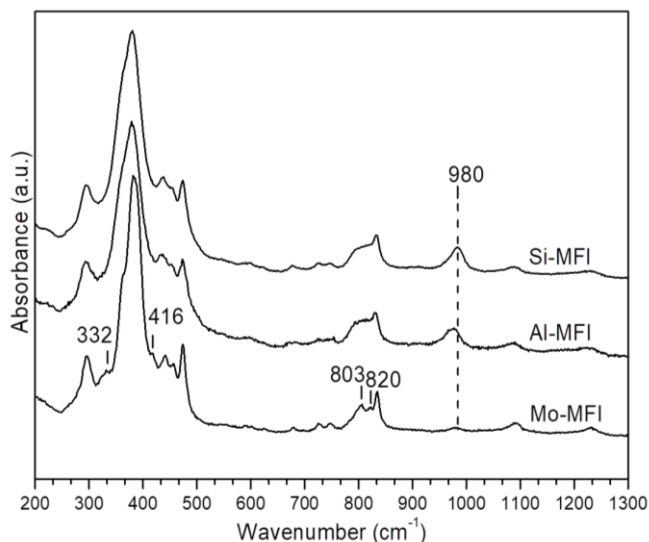


Figure 3. Raman spectra of zeolite samples Si-MFI, Al-MFI, and Mo-MFI.

The Raman results are in a good agreement with IR as shown in Figure S1. The band attributed to silanols Si-O(-H) stretching at 980 cm^{-1} is clearly observed in the IR spectrum of Si-MFI sample, and seemingly slightly red-shifted towards 965 cm^{-1} for the Al-MFI sample (as previously observed in Raman spectroscopy) due to the additional presence of framework Al species (Si-O-Al stretching vibration mode).^{42–44} While, Mo-MFI sample does not display any band in this region, due to the very low amount of silanol that are present in this sample.

The local environment of Si atoms in the zeolite samples was further investigated by ^{29}Si MAS NMR (Figure 4). Both Si-MFI and Al-MFI samples contain Q^3 ($(\text{SiO})_3\text{-OH}$) and unresolved Q^4 (SiO_4) species, indicating the presence of silanol species. In addition, Q^3 species in Al-MFI should present contribution of both $(\text{SiO})_3\text{-Al}$ and $(\text{SiO})_3\text{-OH}$. In the case of sample Mo-MFI, no Q^3 species are observed, and well-resolved Q^4 species are present instead, pointing out the extremely low amount of silanol species and the exceptionally high local homogeneity of the Mo-MFI sample due to the absence of silanol nests.⁴⁰ Indeed, the relative homogeneity between T-sites of the crystalline structure is linked to the presence of silanol species: by removing silanols, the local structure homogeneity is improved (lower distribution of chemical shift for each T-site signal), thus, improving the resolution of the Q^4 ^{29}Si MAS NMR signal. This clearly demonstrates that Mo introduced in the MFI framework by isomorphous substitution reacts with silanol species, leading to a crystalline structure free of any silanol nests, and only containing a greatly reduced amount of isolated silanols.

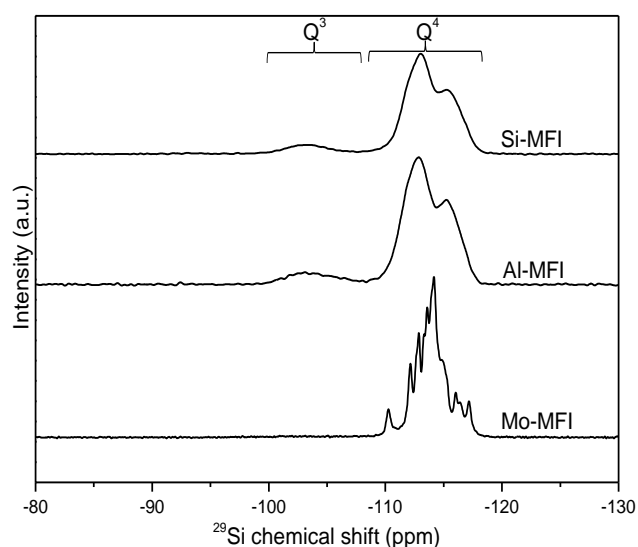


Figure 4. ^{29}Si MAS NMR spectra of Si-MFI, Al-MFI, and Mo-MFI samples.

The samples were also characterized by Cross-Polarization $\{^1\text{H}\}^{29}\text{Si}$ CP MAS NMR spectroscopy (Figure 5). The presence of Q^2 ($(\text{SiO})_2\text{-}(\text{OH})_2$), Q^3 and Q^4 species is observed in both Si-MFI and Al-MFI samples while no signal is present in the spectrum of sample Mo-MFI. This indicates that almost no hydrogen atoms are spatially in close proximity to any Si atoms in Mo-MFI, in line with its very low silanol content, in contrast to samples Si-MFI and Al-MFI. In Al-MFI, however, almost no Q^2 species are observed even though silanol species are still present. Despite quite close intensity of Q^3 signal in the ^{29}Si MAS NMR spectra of samples Si-MFI and Al-MFI (Figure 4), the latter presents less abundant silanols as seen from the $\{^1\text{H}\}^{29}\text{Si}$ CP MAS NMR spectra. This is related to the fact that Q^3 signal in the ^{29}Si MAS NMR of Al-MFI corresponds to both $(\text{SiO})_3\text{-Al}$ and $(\text{SiO})_3\text{-OH}$. Unfortunately, such a spectroscopic study using cross polarization does not provide any quantitative information due to the distances and dynamics distributions and further NMR studies are necessary, as ^1H MAS NMR, *vide infra*.

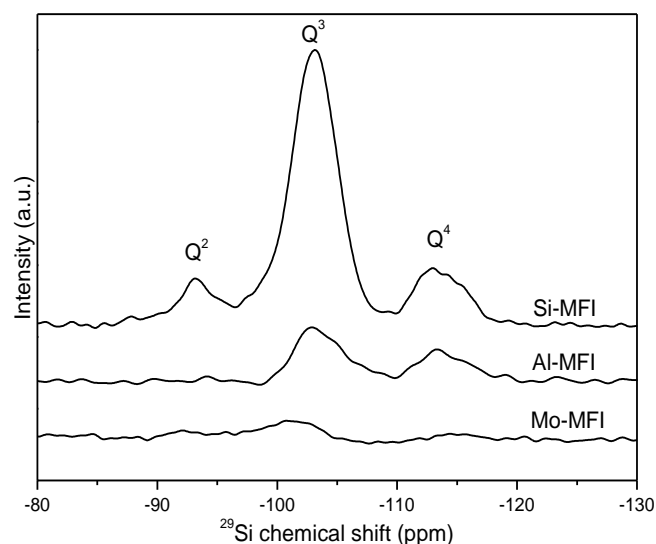


Figure 5. $\{^1\text{H}\}^{29}\text{Si}$ CP MAS NMR spectra of samples Si-MFI, Al-MFI, and Mo-MFI.

^1H MAS NMR spectroscopic study was performed to quantify the hydroxyl groups in the zeolite samples. A complete dehydration of the samples under treatment at 350°C was performed to prevent an unwanted contribution of water in the spectra (Figure 6). In the ^1H MAS NMR spectrum of Si-MFI sample, two types of peaks at 1.8, 1.9, 2.1, and 3.3, 3.9, 4.6 ppm attributed to isolated silanols, isolated vicinal and/or geminal silanols, and silanol nests, respectively are observed.^{46–48} The same kind of peaks is observed for the Al-MFI sample, but the peak at 3.9 ppm is more intense due to the presence of Brønsted acid sites (av. 4 ppm) and H-bonded Brønsted acid sites and H-bonded silanols (av. 5.2 ppm). Due to the overlapping of these two contributions the precise quantification of the Brønsted acid sites is not straightforward. While, in the ^1H MAS NMR spectrum of sample Mo-MFI, only a low-intensity signal at 1.8 ppm (isolated silanols) is observed; no peak corresponding to the presence of silanol nests (above 3 ppm) are observed, which is in an agreement with the IR spectroscopy *vide supra*. To quantify the silanol species by means of ^1H MAS NMR, all samples were measured under identical conditions. A rotor containing a known amount of adamantane was used as a reference for the quantification of OH. Since samples are dehydrated, all ^1H nucleus measured are solely due to the presence of silanols, and also to the presence of bridged hydroxyl groups. As a result, the content of silanol species as isolated, vicinal and geminal, and nests can be evaluated precisely by deconvolution of the ^1H MAS NMR spectra. The deconvolution of spectra (Figure S2) allows the quantification of different silanol species for Si-MFI, Al-MFI, and Mo-MFI samples (Table S1). The total amount of silanol species of samples Si-MFI, Al-MFI, and Mo-MFI is 4.9, 11.3, and 0.24 mmol.g^{-1} , respectively (all OH sites without distinction were taken into account).

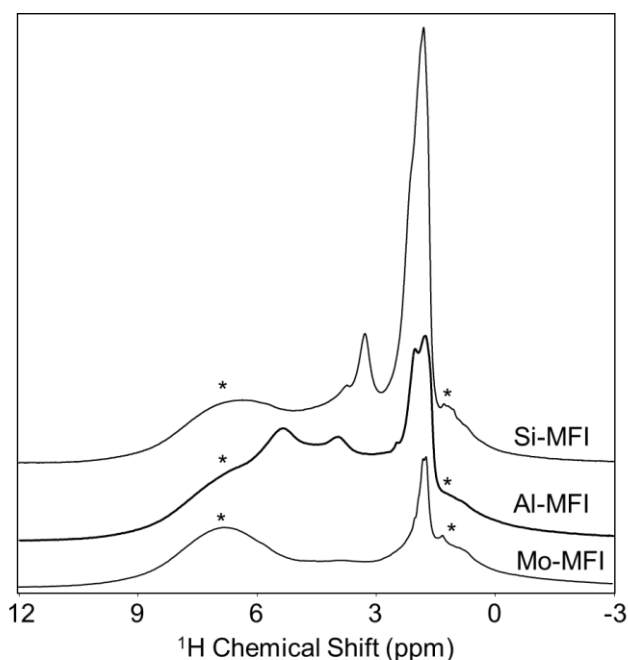


Figure 6. ^1H MAS NMR spectra of samples Si-MFI, Al-MFI, and Mo-MFI dehydrated at 350 °C for 12h. The stars (*) correspond to the rotor signal (see SI for more details).

Additionally, the hydroxyl groups of the three samples were investigated by impregnation of the dehydrated samples with trimethyl phosphine oxide (TMPO) and monitored by ^{31}P MAS NMR, so as to evaluate their acidity (Figure 7). The peak at 30 ppm correspond to physisorbed TMPO that does not provide any relevant information on the zeolite surface (Table S2). On Si-MFI sample, the peak at 50 ppm is attributed to the presence of TMPO interacting with silanols. On Al-MFI, two additional peaks appearing at 64 and 75 ppm can be assigned to bridged BAS at different locations.^{49,50} While Mo-MFI displays only one peak at 45 ppm, attributed to TMPO interacting with framework molybdenum Lewis acidity, and no peak attributable to silanol species (50 ppm) is observed.⁴⁰ This result clearly highlights the removal of most of the Si-OH species (complete removal of silanol nests, and partial removal of isolated silanol species, as shown in the ^1H MAS NMR) upon introduction of Mo by isomorphous substitution in the MFI

framework. By controlling the amount of TMPO adsorbed on the Mo-MFI sample, it was possible to quantify the Mo species due to the fact that one TMPO interacts with one Mo atom⁴⁰. This quantification was possible since the presence of the peak corresponding to the physisorbed TMPO at 30 ppm ensures complete coverage of the Mo species (Figure 7). The Mo content in sample Mo-MFI is 1.59 wt. % that corresponds to 0.166 mmol.g⁻¹ ('mmol' of Mo per 'g' of zeolite). By comparing this result with the ^1H MAS NMR data of Si-MFI 4.9 mmol.g⁻¹ ('mmol' of Mo per 'g' of zeolite), we can conclude that an excess of silanols is healed in relation to the amount of Mo introduced into the zeolite framework. This means that a part of the silanols is accessible to the Mo atoms, while the rest of the silanols must be annealed during partial recrystallization of the zeolite structure.

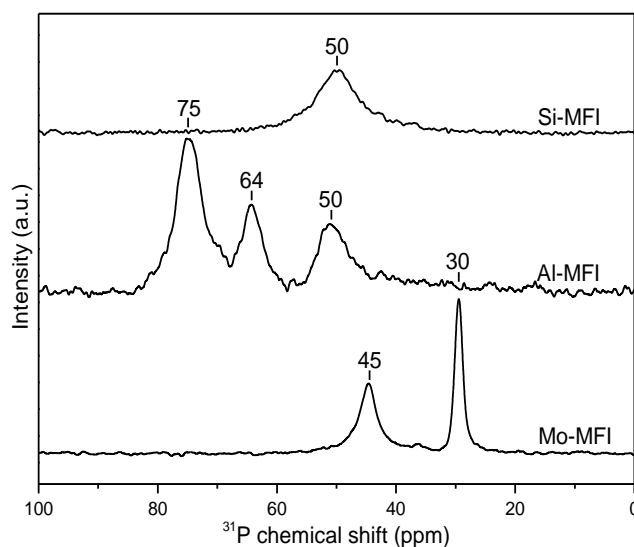


Figure 7. ^{31}P MAS NMR spectra of TMPO adsorbed on Si-MFI, Al-MFI, and Mo-MFI samples.

The summary of the characterization techniques used in this work, together with the information revealed for evaluation of silanols in zeolites is provided in Table 1.

Table 1. Comparison of different techniques applied to characterize (nature and quantity) of zeolitic hydroxyls.

Technique	Quantification	Comments
FTIR	Yes, low precision	Identification of silanols using the 4000-3000 cm ⁻¹ bands; no precise quantification. ^[6b,13] Total silanol content is determined using the 5000-4000 cm ⁻¹ bands; low sensitivity due to weak intensity of IR bands. No quantification and poor identification in the framework vibration region (500-1500 cm ⁻¹), observed by dilution of samples in KBr.
^1H MAS NMR	Yes	Identification of the nature of silanol species based on their chemical shifts. Quantification of silanols on dehydrated samples.

^{29}Si MAS NMR	Relative	Identification of silanols but very poor quantification (only relative comparison between samples). Silanols mostly visible as Q^3 , and undistinguishable from aluminium-induced Q^3 .
$\{^1\text{H}\}^{29}\text{Si}$ CP-MAS NMR	Relative	Identification of silanols depending on their coordination to the framework Q^2 and Q^3 species is possible. No quantification is possible.
TMPO/ ^{31}P MAS NMR	Yes, low precision	Identification of silanol as a function of their relative acidity is possible as long as they are accessible for TMPO, but with poor precision and resolution. Approximative quantification of TMPO accessible sites possible when the peak attributed to silanol is relatively isolated, and all sites are covered as ensured by the presence of physisorbed TMPO.
Raman	No	Poor identification of silanols, quantification is impossible unless a probe molecule is used; the results have a low accuracy.

Conclusions

Hydroxyl groups, silanols in particular, in three nanosized MFI type zeolites (Si-MFI, Al-MFI, and Mo-MFI) with identical particle size, have been characterized by IR, Raman, and NMR spectroscopies. The nature and amount of the various silanols were determined unambiguously by cross-checking the results of different techniques. The almost complete removal of silanols from the pure silica sample (Si-MFI) upon post-synthesis introduction of molybdenum (Mo-MFI) leads to a full isomorphous substitution of Mo in framework positions. Based on this study, a summary evaluation of the used characterization techniques towards identification and quantification of silanol species is provided (Table 1). Accordingly, the most efficient way to identify and quantify silanols simultaneously was the use of ^1H MAS NMR of dehydrated zeolites. However, the use of other techniques and especially of IR was complementary, in particular for the identification of silanols. The characterization of silanols in zeolite samples is challenging and therefore several spectroscopic techniques are required.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was supported by TOTAL and Industrial Chair ANR-TOTAL "Nanoclean energy" and the Label of Excellence for the Centre of Zeolites and Related Nanoporous Materials supported by the Region of Normandy.

References

- 1 C. J. Rhodes, Properties and applications of zeolites. *Sci. Prog.*, 2010, **93**, 223–284.
- 2 J. Weitkamp, Zeolites and catalysis. *Solid state ionics*, 2000, **131**, 175–188.
- 3 B. Bonelli, L. Forni, A. Aloise, J. B. Nagy, G. Fornasari, E. Garrone, A. Gedeon, G. Giordano and F. Trifirò, Beckmann rearrangement reaction: About the role of defect groups in high silica zeolite catalysts. *Microporous Mesoporous Mater.*, 2007, **101**, 153–160.
- 4 T. Karbowiak, M. A. Saada, S. Rigolet, A. Ballandras, G. Weber, I. Bezverkhyy, M. Soulard, J. Patarin and J. P. Bellat, New insights in the formation of silanol defects in silicalite-1 by water intrusion under high pressure. *Phys. Chem. Chem. Phys.*, 2010, **12**, 11454–11466.
- 5 S. Bordiga, I. Roggero, P. Ugliengo, A. Zecchina, V. Bolis, G. Artioli, R. Buzzoni, G. Marra, F. Rivetti, G. Spano and C. Lamberti, Characterisation of defective silicalites, *J. Chem. Soc. Dalt. Trans.*, 2000, 3921–3929.
- 6 M. Boronat and A. Corma, Factors Controlling the Acidity of Zeolites. *Catal. Letters*, 2015, 162–172.
- 7 G. L. Woolery and G. H. Kuehl, On the nature of framework Brønsted and Lewis acid sites in ZSM-5. *Zeolites*, 1997, **19**, 288–296.
- 8 Y. Wang and A. Tuel, Nanoporous zeolite single crystals: ZSM-5 nanoboxes with uniform intracrystalline hollow structures. *Microporous Mesoporous Mater.*, 2008, **113**, 286–295.
- 9 L. Zhang, K. Chen, B. Chen, J. L. White and D. E. Resasco, Factors that Determine Zeolite Stability in Hot Liquid Water. *J. Am. Chem. Soc.*, 2015, **137**, 11810–11819.
- 10 S. Dzwigaj, P. Massiani, A. Davidson and M. Che, Role of silanol groups in the incorporation of V in β zeolite. *J. Mol. Catal. A Chem.*, 2000, **155**, 169–182.
- 11 P. Wolf, C. Hammond, S. Conrad and I. Hermans, Post-synthetic preparation of Sn-, Ti- and Zr-beta: A facile route to water tolerant, highly active Lewis acidic zeolites. *Dalt. Trans.*, 2014, **43**, 4514–4519.
- 12 E. E. Mallon, M. Y. Jeon, M. Navarro, A. Bhan and M. Tsapatsis, Probing the relationship between silicalite-1 defects and polyol adsorption properties. *Langmuir*, 2013, **29**, 6546–6555.
- 13 J. Grand, S. N. Talapaneni, A. Vicente, C. Fernandez, E. Dib, H. A. Aleksandrov, G. N. Vayssilov, R. Retoux, P. Boullay, J. Gilson, V. Valtchev and S. Mintova, One-pot synthesis of silanol-free nanosized MFI zeolite. *Nature*, 2017, **16**, 1010–1015.
- 14 H. Zhou, J. Mouzon, A. Farzaneh, O. N. Antzutkin, M. Grahn and J. Hedlund, olloidal Defect-Free Silicalite-1 Single Crystals: Preparation, Structure Characterization,

- Adsorption, and Separation Properties for Alcohol/Water Mixtures. *Langmuir*, 2015, **31**, 8488–8494.
- 15 C. H. Wang, P. Bai, J. I. Siepmann and A. E. Clark, Deconstructing hydrogen-bond networks in confined nanoporous materials: Implications for alcohol-water separation. *J. Phys. Chem. C*, 2014, **118**, 19723–19732.
- 16 J. W. Harris, M. J. Cordon, J. R. Di Iorio, J. C. Vega-Vila, F. H. Ribeiro and R. Gounder, Titration and quantification of open and closed Lewis acid sites in Sn-Beta zeolites that catalyze glucose isomerization. *J. Catal.*, 2016, **335**, 141–154.
- 17 X. Meng, Q. Yu, Y. Gao, Q. Zhang, C. Li and Q. Cui, Enhanced propene/ethene selectivity for methanol conversion over pure silica zeolite: Role of hydrogen-bonded silanol groups. *Catal. Commun.*, 2015, **61**, 67–71.
- 18 N. Rai, S. Caratzoulas and D. G. Vlachos, Role of Silanol Group in Sn-Beta Zeolite for Glucose Isomerization and Epimerization Reactions. 2013, **3**, 10, 2294–2298.
- 19 K. Lee, S. Lee, Y. Jun and M. Choi, Cooperative effects of zeolite mesoporosity and defect sites on the amount and location of coke formation and its consequence in deactivation. *J. Catal.*, 2017, **347**, 222–230.
- 20 L. Lakiss, F. Ngoye, C. Canaff, S. Laforge, Y. Pouilloux, Z. Qin, M. Tarighi, K. Thomas, V. Valtchev, A. Vicente, L. Pinard, J.-P. Gilson and C. Fernandez, On the remarkable resistance to coke formation of nanometer-sized and hierarchical MFI zeolites during ethanol to hydrocarbons transformation. *J. Catal.*, 2015, **328**, 165–172.
- 21 F. Thibault-starzyk, A. Vimont and J. Gilson, 2D-COS IR study of coking in xylene isomerisation on H-MFI zeolite. *Catal. Today*, 2001, **70**, 227–241.
- 22 C. Fernandez, I. Stan, J.-P. Gilson, K. Thomas, A. Vicente, A. Bonilla and J. Pérez-Ramirez, Hierarchical ZSM-5 zeolites in shape-selective xylene isomerization: role of mesoporosity and acid site speciation. *Chem. Eur. J.*, 2010, **16**, 6224–6233.
- 23 J. N. Kondo, E. Yoda, H. Ishikawa, F. Wakabayashi and K. Domen, Acid Property of Silanol Groups on Zeolites Assessed by Reaction Probe IR Study. *J. Catal.*, 2000, **281**, 275–281.
- 24 G. L. Woolery, L. B. Alemany, R. M. Dessau and A. W. Chester, Spectroscopic evidence for the presence of internal silanols in highly siliceous ZSM-5. *Zeolites*, 1986, **6**, 14–16.
- 25 P. Hoffmann and J. A. Lobo, Identification of diverse silanols on protonated ZSM-5 zeolites by means of FTIR spectroscopy. *Microporous Mesoporous Mater.*, 2007, **106**, 122–128.
- 26 J. Chen, Q. Li, R. Xu and F. Xiao, Distinguishing the silanol groups in the mesoporous molecular sieve MCM-41. *Angew. Chemie (International Ed. English)*, 1996, **34**, 2694–2696.
- 27 J. P. Gallas, 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**, 5825–5834.
- 28 J. M. Chezeau, L. Delmotte, J. L. Guth and Z. Gabelica, Influence of synthesis conditions and postsynthesis treatments on the nature and quantity of structural defects in highly siliceous MFI zeolites: A high-resolution solid-state ²⁹Si n.m.r. study. *Zeolites*, 1991, **11**, 598–606.
- 29 M. Ide, M. El-Roz, E. De Canck, A. Vicente, T. Planckaert, T. Bogaerts, I. Van Driessche, F. Lynen, V. Van Speybroeck, F. Thybault-Starzyk and P. Van Der Voort, Quantification of silanol sites for the most common mesoporous ordered silicas and organosilicas: Total versus accessible silanols. *Phys. Chem. Chem. Phys.*, 2013, **15**, 642–650.
- 30 S. Ashtekarl, J. J. Hastingsz, P. J. Barriol and L. F. Gladden, Quantification of the Number of Silanol Groups in Silicalite and Mesoporous MCM-41: Use of Ft-Raman Spectroscopy. *Spectroscopy Letters*, 2000, **33**, 569–584.
- 31 V. Zholobenko, C. Freitas, M. Jendrlin, P. Bazin, A. Travert and F. Thibault-Starzyk, Probing the acid sites of zeolites with pyridine: Quantitative AGIR measurements of the molar absorption coefficients. *J. Catal.*, 2020, **385**, 52–60.
- 32 A. A. Gabrienko, I. G. Danilova, S. S. Arzumanov, A. V. Toktarev, D. Freude and A. G. Stepanov, Strong acidity of silanol groups of zeolite beta: Evidence from the studies by IR spectroscopy of adsorbed CO and ¹H MAS NMR. *Microporous Mesoporous Mater.*, 2010, **131**, 210–216.
- 33 W. Zhang, X. Bao, X. Guo and X. Wang, A high-resolution solid-state NMR study on nano-structured HZSM-5 zeolite. *Catal. Letters*, 1999, **60**, 89–94.
- 34 L. Treps, C. Demaret, D. Wisser, B. Harbuzaru, A. Méthivier, E. Guillon, D. V. 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*, DOI:10.1021/acs.jpcc.0c10200.
- 35 C. Schroeder, V. Siozios, M. Hunger, M. R. Hansen and H. Koller, Disentangling Brønsted Acid Sites and Hydrogen-Bonded Silanol Groups in High-Silica Zeolite H-ZSM-5. *J. Phys. Chem. C*, 2020, **124**, 23380–23386.
- 36 E. Dib, J. Grand, S. Mintova and C. Fernandez, Structure-Directing Agent Governs the Location of Silanol Defects in Zeolites. *Chem. Mater.*, 2015, **27**, 7577–7579.
- 37 M. Hunger, D. Freude, H. Pfeifer and W. Schwieger, Mas NMR studies of silanol groups in zeolites ZSM-5 synthesized with an ionic template. *Chem. Phys. Lett.*, 1990, **167**, 21–26.
- 38 M. Hunger, J. Kärger, H. Pfeifer, J. Caro, B. Zibrowius, M. Bülow and R. Mostowicz, Investigation of internal silanol groups as structural defects in ZSM-5-type zeolites. *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases*, 1987, **83**, 3459–3468.
- 39 J. M. Kobe, T. J. Gluszak, J. A. Dumesic and T. W. Root, Deuterium NMR characterization of bronsted acid sites and silanol species in zeolites. *J. Phys. Chem.*, 1995, **99**, 5485–5491.
- 40 F. Dubray, S. Moldovan, C. Kouvatas, J. Grand, C. Aquino, N. Barrier, J. Gilson, N. Nesterenko, D. Minoux and S. Mintova, Direct Evidence for Single Molybdenum Atoms Incorporated in the Framework of MFI Zeolite Nanocrystals. *J. Am. Chem. Soc.*, 2019, **141**, 8689–8693.

- 41 A. Zheng, S. Bin Liu and F. Deng, 31P NMR Chemical Shifts of Phosphorus Probes as Reliable and Practical Acidity Scales for Solid and Liquid Catalysts. *Chem. Rev.*, 2017, **117**, 12475–12531.
- 42 B. A. Morrow and A. J. McFarlan, Surface vibrational modes of silanol groups on silica. *J. Phys. Chem.*, 1992, **96**, 1395–1400.
- 43 J. L. Koenig, P. T. K. Shih and P. Lagally, Raman and infrared spectroscopic studies of the reactions of silica and glass surfaces. *Mater. Sci. Eng.*, 1975, **20**, 127–135.
- 44 M. A. Cambor, A. Corma and J. Perez-Pariente, Infrared spectroscopic investigation of titanium in zeolites. A new assignment of the 960 cm⁻¹ band. *J. Chem. Soc. Chem. Commun.*, 1993, 557–559.
- 45 M. Dieterle and G. Mestl, Raman spectroscopy of molybdenum oxides: Part II. Resonance Raman spectroscopic characterization of the molybdenum oxides Mo₄O₁₁ and MoO₂. *Phys. Chem. Chem. Phys.*, 2002, **4**, 822–826.
- 46 A. A. Gabrienko, I. G. Danilova, S. S. Arzumanov, L. V. Pirutko, D. Freude and A. G. Stepanov, Direct Measurement of Zeolite Brønsted Acidity by FTIR Spectroscopy: Solid-State 1H MAS NMR Approach for Reliable Determination of the Integrated Molar Absorption Coefficients. *J. Phys. Chem. C*, 2018, **122**, 25386–25395.
- 47 A. Erigoni, S. H. Newland, G. Paul, L. Marchese, R. Raja and E. Gianotti, Creating Accessible Active Sites in Hierarchical MFI Zeolites for Low-Temperature Acid Catalysis. *ChemCatChem*, 2016, **8**, 3161–3169.
- 48 S. S. Arzumanov and A. G. Stepanov, Which Activation Energy Do We Measure? Analysis of the Kinetics of Propene-3-¹³C Double-Bond-Shift Reaction on Silicalite-1 by 1H MAS NMR in Situ. *J. Phys. Chem. C*, 2018, **122**, 23432–23440.
- 49 C. Freitas, N. S. Barrow and V. Zholobenko, Accessibility and Location of Acid Sites in Zeolites as Probed by Fourier Transform Infrared Spectroscopy and Magic Angle Spinning Nuclear Magnetic Resonance, Johnson Matthey Technology Review, 2018, **62**, 279–290.
- 50 C. Bornes, M. Fischer, A. Amelse, C. F. G. C. Geraldés, J. Rocha and L. Mafra, What Is Being Measured with P - Bearing NMR Probe Molecules Adsorbed on Zeolites? *J. Am. Chem. Soc.*, 2021, **143**, 13616–13623.