Study of the nature and density of Broensted acid sites by ¹H MAS NMR

Spectroscopic background: ¹H nuclei have a spin of I = 1/2 and, therefore, no quadrupole moment. The ¹H isotope has a natural abundance of 100 % and the highest sensitivity (1.0) of all existing nuclei, making this isotope a very suitable candidate for NMR studies of solids. For basic principles of solid-state NMR, see lectures "Solid-State NMR Spectroscopy" for Bachelor students or PhD seminars, accessible via the link "Lectures for Students".

¹H MAS NMR signals of hydroxyl groups on calcined or dehydrated solid catalysts cover a chemical shift range of $\delta_{1H} = -0.5$ to 16 ppm (see **Table 1** and Table 2 in Ref. [1] as well as Tables 1 in Refs. [2] and [3]).

At $\delta_{1H} = -0.5$ to 0.7 ppm, ¹H MAS NMR signals of non-interacting metal OH groups, such as AIOH groups at the outer surface of Al₂O₃ [4] and metal hydroxyl groups in large cages of zeolites [5], occur. Signals at $\delta_{1H} = 1.2$ to 2.2 ppm indicate the presence of SiOH groups, e.g., at the outer surface of silicate and aluminosilicate particles or at framework defects of zeolites [6-9]. In the case of hydrogen bonds of hydroxyl groups with neighbouring framework atoms, low-field shifts (larger δ_{1H} values) are observed for the signals of SiOH groups (Scheme 1a). Therefore, also





$\delta_{ m 1H}$ / ppm	OH type	Description of hydroxyl groups	Refs.
-0.5 to 0.7	AIOH CaOH MgOH	terminal metal OH groups in large cages or on the external particle surface	[4], [5]
1.2 to 2.2	SiOH	terminal silanol groups on the external particle surface or at lattice defects	[6] to [9]
1.7 to 2.7	AI(OH)AI	bridging OH groups in metal-organic frameworks, such as MIL-53(AI), MIL-118(AI)	
2.4 to 6.5	CaOH*, MgOH*, AIOH* BOH* LaOH*	hydrogen bonded metal OH groups inside small structural units, such as sodalite cages of FAU-type zeolites, zeolite channels or framework defects	[4], [5], [7], [9] to [16], [17]
3.3 to 6.7	MoOH VOH TiOH	MOH (M = Mo, V, Ti) groups of pure metal oxides and bridging M(OH)AI groups on AI_2O_3 support materials	[18], [19], [20]
3.6 to 4.3	Si(OH)AI	bridging OH groups in large cages and channels of aluminosilicate- and silicoaluminophosphate-type zeolites	[6], [7]
4.6 to 5.2	Si(OH*)Al	bridging OH groups in small cages of zeolites interacting with neighbouring framework oxygen	[6], [7]
5.0 to 8.5	SO₃H	sulfonic acid sites on perfluorosulfonic acid ionomers (such as NAFION) and functionalized mesoporous materials	[21], [22]
5.2 to 8.0	Si(OH*)Al	bridging OH groups in zeolites H-ZSM-5, H- Beta, and H-MCM-22 interacting with neighbouring framework oxygen	[23], [24], [25], [26]
7.4 to 9.1	Mo(OH)Mo W(OH)W	acidic hydroxyl protons of heteropoly acids, such as $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, and other ion exchanged forms	[27], [28], [29]
10 to 16	SiOH*	hydrogen bonded internal SiOH groups, such as in as-synthesized zeolites of structure types NON, DDR, MTW, AFI, and MFI and in layered-silica RUB-18	[30], [31]

*) hydroxyl protons involved in hydrogen bonds with neighbouring oxygen atoms

Table 1

the ¹H MAS NMR signals of metal OH groups in small cages of zeolites or inside metal oxide clusters (e.g. CaOH, MgOH, AIOH, LaOH, MoOH, VOH, TiOH) may occur at chemical shifts of up to $\delta_{1H} = 6.5$ ppm (**Scheme 1b**). Examples are different structure types of Al₂O₃ and amorphous aluminosilicates with internal AIOH groups

occurring at $\delta_{1H} \approx 3$ ppm [4, 10, 11]. In the ¹H MAS NMR spectra of dealuminated zeolites, signals of hydroxyl protons bound to extra-framework aluminum species cause similar signals at $\delta_{1H} = 2.4$ to 3.6 ppm [7, 12-14]. The low-field resonance shift of these AIOH groups indicates hydrogen bonds of the hydroxyl protons to neighbouring framework oxygen atoms in small structural units, such as in internal cages. In a similar manner, **AIOH**, **MgOH**, **CaOH**, **and LaOH groups introduced into small cages** of zeolites by cation exchange cause ¹H MAS NMR signals, which are low-field shifted up to $\delta_{1H} = 6.5$ ppm [5, 15, 16]. As an example, **Fig. 1** shows ¹H MAS NMR spectra of a lanthanum-exchanged zeolite Y (La,Na-Y/74), recorded upon dehydration at *T* = 473 to 673 K (see Fig. 1 in Ref. [15]). The ¹H MAS NMR signal at $\delta_{1H} = 5.8$ ppm is due to LaOH groups formed by dissociation of water in the electrostatic field of lanthanum cations and located in small structural units (sodalite cages). In result of the water dissociation, hydroxyl groups near negatively charged framework aluminum atoms, i.e. **bridging OH groups (Si(OH)AI)**, are formed and cause the signals at $\delta_{1H} = 3.9$ and 5.0 ppm in **Fig. 1** [15].



Fig. 1

Bridging OH groups in zeolites, also denoted structural OH groups, are catalytically active Broensted acid sites. These bridging OH groups are formed at Si-O-Al bridges in the local structure of negatively charged, tetrahedrally coordinated framework aluminum atoms. Depending on the structure type of zeolites and their cation exchange degree, the ¹H MAS NMR signals of Si(OH)Al groups are observed at δ_{1H} = 3.6 to 4.0 ppm and δ_{1H} = 4.8 to 5.2 ppm due to bridging OH groups located in large cages and inside of small structural units, respectively (see Table 1). The larger chemical shift of Si(OH)Al groups in small structural units is caused by weak hydrogen bonds with neighbouring framework oxygen atoms (Scheme 1c). This effect was recent investigated in detail by combination of ¹H MAS NMR and quantum chemical methods [32].

Generally, Si(OH)AI groups are formed in crystalline aluminosilicates and also in crystalline silicoaluminophosphates. In the latter case, phosphorus atoms in an aluminophosphate framework (e.g. AIPO-5, AIPO-11 etc.) are replaced by silicon atoms, which cause negatively charged framework aluminum atoms being not compensated by the replaced positively charged phosphorus atoms. At these framework positions, therefore, **Si(OH)AI groups** are formed, causing ¹H MAS NMR signals at $\delta_{1H} = 3.6$ and 4.6 ppm, e.g., in the spectra of dehydrated **SAPO-5 zeolites** ($n_{Si}/(n_{AI} + n_P + n_{Si}) = 0.11$), synthesized via different procedures (**Fig. 2**) [33].



For the assignment of signals occurring in the ¹H MAS NMR spectra of water-free solid catalysts, the correlation of the chemical shift, δ_{1H} , and the FTIR wavenumber, $\tilde{v}_{OH\nu}$ of hydroxyl groups is useful. By comparing OH stretching vibrations and ¹H MAS NMR chemical shifts of OH groups in various dehydrated zeolites, the following relationship was found [34]:

$$\delta_{1\rm H}$$
 / ppm = 57.1 - 0.0147 $\tilde{\nu}_{\rm OH}$ / cm⁻¹ (1)

for non-interacting (no hydrogen bonds) hydroxyl groups. Hydroxyl groups involved in hydrogen bonds gave the relationship [34]:

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$$\delta_{1\rm H}$$
 / ppm = 37.9 - 0.0092 $\tilde{\nu}_{\rm OH}$ / cm⁻¹ (2)

According to **Eq. (2)**, the FTIR band observed by Zholobenko et al. [35] in the spectra of dehydrated zeolites H-ZSM-5 at $\tilde{\nu}_{OH} = 3250 \text{ cm}^{-1}$ hint to a ¹H MAS NMR signal at $\delta_{1H} \approx 8.0 \text{ ppm}$. In the ¹H MAS NMR spectra of zeolites H-ZSM-5, a corresponding broad low-field signal was experimentally observed at $\delta_{1H} = 6$ to 7 ppm [36, 37].

An important advantage of solid-state NMR spectroscopy is the linear correlation between the NMR signal intensity and the concentration of spin $I = \frac{1}{2}$ nuclei and for spin $I > \frac{1}{2}$ nuclei in the case of a non-selective excitation with very short radio frequency pulses. A suitable way to quantify, e.g., the concentration of hydroxyl protons of solid catalysts by ¹H MAS NMR spectroscopy is the comparison of the signal intensities of the water-free samples under study with the intensity of an external intensity standard with similar spectroscopic parameters. Often, a well characterized and stable catalyst, such as dehydrated zeolite H,Na-Y with a low cation exchange degree (e.g. 35 %) and well-known OH density is used as an external intensity standard [15, 16, 38, 39]. For quantitative studies, the repetition time of the ¹H MAS NMR experiments has to be large in comparison with the spin-lattice relaxation times of the different OH species, which are of the order of $T_1 = 1$ to 30 s. The total concentration c_i of the hydroxyl groups in a water-free catalyst sample (denoted "i") is calculated by [3, 40]:

$$c_{i} = c_{st} m_{st} A_{i} / (m_{i} A_{st})$$
(3)

with the concentration, c_{st} , the weight, m_{st} , and the total integral, A_{st} , of the ¹H MAS NMR signal of the standard sample (denoted "st"), and the weight, m_i , and the total integral, A_i , of the ¹H MAS NMR signal of the catalyst sample "i". The determination of the concentration of different OH types in the sample under study is performed by decomposition of the different signals in the ¹H MAS NMR spectra. The obtained relative intensities and the total concentration, c_i , give the concentrations of the different OH types.

At room temperature, the ¹H MAS NMR spectra of dehydrated H-form zeolites are dominated by the narrow central line of bridging OH groups (Si(OH)AI) with sharp spinning sidebands in a distance of $\pm n v_{rot}$. (v_{rot} : MAS rate). In this case, the correlation time τ_c of the hydroxyl protons is large in comparison with the MAS period https://michael-hunger.de

($\tau_c > \tau_{rot} = 1/\nu_{rot}$). The dominating solid-state interaction of the hydroxyl protons in a Si(OH)AI groups is the dipolar H-AI interaction. The strength of this interaction is described by the second moment M_2^{H-AI} [1, 2]. For increasing temperature, the correlation time τ_c decreases, which results in a broadening of the corresponding ¹H MAS NMR signals. According to Refs. [1], [2], and [42], the envelope of the free-induction decay $G^{MAS}(t)$ of the ¹H MAS NMR signal of Si(OH)AI groups as a function of the correlation time τ_c is given by:

$$G^{\text{MAS}}(t) = \exp\left[-\left\{M_2^{\text{H-AI}/3}\right\} \cdot \left\{2\tau_c/(1+(2\pi\nu_{\text{rot}}\tau_c)^2) + \tau_c/(1+(4\pi\nu_{\text{rot}}\tau_c)^2)\right\}\right]$$
(4)

The Fourier transformation of $G^{MAS}(t)$ in **Eq. (4)** describes the shape of the central line. **Fig. 3** shows ¹H MAS NMR spectra of hydroxyl protons of Si(OH)Al groups with $M_2^{H-Al} = 4.5 \times 10^8 \text{ s}^{-2}$, $v_{rot} = 3 \text{ kHz}$, and $\tau_c = 10 \text{ µs}$ to 10 ms, calculated via Eq. (3) in Ref. [1] or Eq. (11) in Ref. [2]. For $\tau_c = 10 \text{ ms}$ (rigid case), the MAS sideband pattern consists of narrow lines. In contrast, the signals of sideband patterns become significantly broader for correlation times in the order of $\tau_c \cong \tau_{rot} = 1/v_{rot}$ and the sidebands disappear stepwise. For $\tau_c < \tau_{rot} = 1/v_{rot}$ (mobile case), motional narrowing occurs, because the solid-state interactions are averaged to zero by rapid isotropic reorientation.



Fig. 3

Fig. 4, bottom, shows the experimental ¹H MAS NMR spectrum of a dehydrated H-ZSM-5 ($n_{Si}/n_{AI} = 18$), recorded at T = 296 K, which consists of a MAS sideband pattern with a narrow central line at $\delta_{1H} = 4.3$ ppm, due to Si(OH)Al groups [1, 2]. Furthermore, a weak signal occurs at $\delta_{1H} = 2$ ppm, caused by SiOH groups. The increase of the temperature to T = 423 K (**Fig. 4, top**) results in a considerable broadening of the spinning sideband pattern. A simulation of the spectrum measured at T = 423 K, using a set of spectra derived by Eq. (3) in Ref. [1] or Eq. (11) in Ref. [2], yields a correlation time of the hydroxyl protons of Si(OH)Al groups of $\tau_c \approx 250$ µs [1, 2], which is less than $\tau_{rot} = 1/\nu_{rot} = 333$ µs, with $\nu_{rot} = 3$ kHz.

Finally must be added that residual water molecules on zeolite catalysts act as hydroxyl vehicles, which strongly enhance the mobility of the hydroxyl protons of Si(OH)Al groups and may cause a significant broadening of their ¹H MAS NMR signals, already at room temperature. Therefore, recording of highly resolved ¹H MAS NMR Spectra of zeolites require well-prepared samples, i.e. which were deammoniated and dehydrated at least at T = 673 K, and a transfer of the calcined samples into gas-tight MAS rotors without contact to air for omitting rehydration.



Fig. 4

See Refs. [1] to [3], [40], and [41] for reviews on the above-mentioned research topics.

Catalyst preparation: Before ¹H MAS NMR studies of solid catalysts, a standard dehydration, e.g. inside a "sample tube system 1" at "vacuum line 1" (see Sections "sample tube system 1" and "vacuum line 1", accessible via link "*In Situ* Solid-State NMR Techniques") was performed. The dehydration procedure starts with an evacuation at room temperature for ca. 10 minutes followed by a temperature ramp https://michael-hunger.de

from room temperature to T = 393 K within 2 hours. At this temperature, the sample was dehydrated for 2 hours. Subsequently, the temperature was increased up to T = 723 K within 3 hours and the sample was evacuated at this temperature for 12 hours. After this treatment, the sample tube system was closed via the vacuum valve and disconnected from "vacuum line 1" (after this line was ventilated with air).

¹H MAS NMR studies: The dehydrated catalyst in the sample tube system was transferred into an MAS NMR rotor without air contact inside a mini glove box (see Section "mini glove box", accessible via link "In Situ Solid-State NMR Techniques"), purged with dry nitrogen gas and, finally, the rotor was sealed with a gas-tight rotor cap. Most of the above-mentioned ¹H MAS NMR spectra were recorded at a Bruker AVANCE III 400 WB spectrometer with a ¹H resonance frequency of $v_0 = 400.1$ MHz, using a 4 mm MAS NMR probe with a sample spinning rate of v_{rot} = 8 kHz, $\pi/2$ single pulse excitation, and a repetition time of 10 s. For very clean and siliceous catalysts, a repetition time of 30 s is suggested. For the determination of OH densities by the ¹H MAS NMR signal intensities, an external intensity reference with similar spectroscopic properties like the samples under study is suggested (e.g. activated Na,H-Y zeolite). The intensity contributions of spinning sidebands must be considered for the quantitative evaluation of the different signals intensities. Chemical shifts are referenced to small particles of silicon rubber ($\delta_{1H} = 0.07$ ppm) at low spinning rates of v_{rot} = 1 to 2 kHz. This shift reference is easier to handle in MAS NMR rotors than liquid TMS (tetramethylsilane) with a boiling point of 299 to 301 K.

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