Method for the study of the nature and density of Broensted acid sites by ^{1}H MAS NMR in the absence of probe molecules

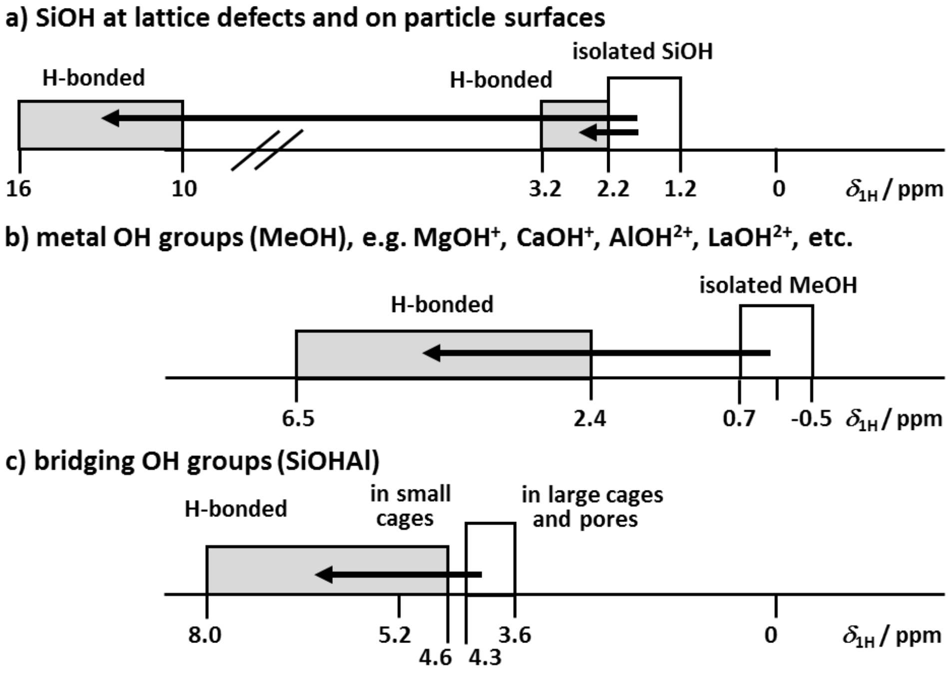
Spectroscopic background: ^{1}H MAS NMR signals of hydroxyl groups on dehydrated and calcined solid catalysts cover a range of chemical shifts of **δ_{1H} = -0.5 to 16 ppm** (see Table 1 shown below, Table 2 in [1], and Tables 1 in [2] and [3]).

δ_{1H} / ppm	OH type	Description of hydroxyl groups
-0.5 to 0.7	AlOH CaOH MgOH	terminal metal OH groups in large cages or on the external particle surface
1.2 to 2.2	SiOH	terminal silanol groups on the external particle surface or at lattice defects
1.7 to 2.7	Al(OH)Al	bridging OH groups in metal-organic frameworks, such as MIL-53(Al) and MIL-118(Al)
2.4 to 6.5	CaOH*, MgOH*, AlOH* LaOH*	hydrogen bonded metal OH groups in small structural units, such as sodalite cages of FAU-type zeolites or channels of ZSM-5
3.3 to 6.7	MoOH VOH TiOH	MOH (M = Mo, V, Ti) groups of pure metal oxides and bridging M(OH)Al groups on Al_2O_3 supports
3.6 to 4.3	Si(OH)Al	bridging OH groups in large cages and channels of silicoaluminophosphate- and aluminosilicate-type zeolites
4.6 to 5.2	Si(OH*)Al	bridging OH groups in small cages of zeolites Y interacting with neighbouring framework oxygen
5.0 to 8.5	SO_3H	sulfonic acid sites on perfluorosulfonic acid ionomers (such as NAFION) and functionalized mesoporous materials
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
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
10 to 16	SiOH*	hydrogen bonded internal SiOH groups, such as in as-synthesized zeolites of structure type NON, DDR, MTW, AFI, and MFI and in layered-silica RUB-18

* hydroxyl protons involved in hydrogen bondings with neighbouring oxygen atoms.

Table 1

At δ_{1H} = -0.5 to 0.7 ppm, ^{1}H MAS NMR signals of non-interacting metal OH groups, such as AlOH groups at the outer surface of Al_2O_3 [4] and metal hydroxyl groups in large cages of zeolites [5], occur. Signals at δ_{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 bondings 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 the ^{1}H MAS NMR signals of metal OH groups in small cages of zeolites or inside metal oxide clusters (e.g. CaOH, MgOH, AlOH, LaOH, MoOH, VOH, TiOH) may occur at chemical shifts of up to δ_{1H} = 6.5 ppm (Scheme 1b).



Scheme 1

Examples are different structure types of Al_2O_3 and amorphous aluminosilicates with internal AlOH groups occurring at $\delta_{1H} \approx 3$ ppm [4, 10, 11]. In the ^{1}H MAS NMR spectra of dealuminated zeolites, signals of hydroxyl protons bound to extra-framework aluminium species cause similar signals at δ_{1H} = 2.4 to 3.6 ppm [7, 12-14].The low-field resonance shift of these AlOH groups indicates a hydrogen bonding of the hydroxyl protons to neighbouring framework oxygen atoms in small structural units, such as internal cages. In a similar manner, AlOH, MgOH, CaOH, and LaOH groups introduced into small cages of zeolites by cation exchange cause ^{1}H MAS

NMR signals, which are low-field shifted up to δ_{1H} = 6.5 ppm [5, 15, 16]. As an example, **Fig. 1** shows ^{1}H MAS NMR spectra of a lanthanum-exchanged zeolite Y (La,Na-Y/74), recorded upon dehydration at 473 to 673 K (see Fig. 1 in Ref. [15]). The signal at δ_{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. In result of the water dissociation, hydroxyl groups near negative charged framework aluminium atoms are formed, which are assigned bridging OH groups and cause the signals at δ_{1H} = 3.9 and 5.0 ppm in **Fig. 1** [15].

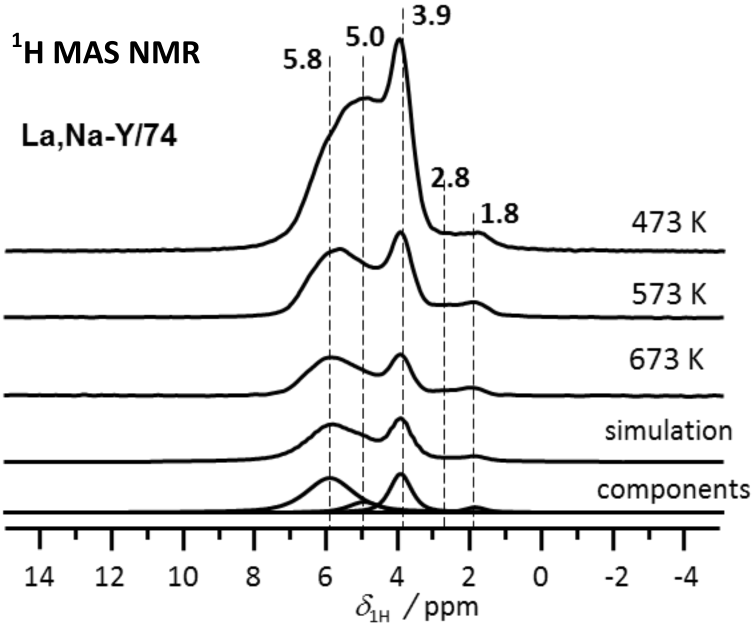


Fig. 1

The catalytically active Broensted acid sites in zeolites are bridging OH groups (Si(OH)Al), which are also denoted structural OH groups. These bridging OH groups are formed at Si-O-Al bridges in the local structure of negatively charged, tetrahedrally coordinated framework aluminium atoms. Depending on the structure type of zeolites and their cation exchange degree, the ^{1}H 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 bondings with neighbouring framework oxygen atoms (Scheme 1c). This effect was recent investigated in detail by combination of ^{1}H MAS NMR and quantum chemical methods [17].

Generally, bridging OH groups (Si(OH)Al) are formed in crystalline aluminosilicates, but also in silicoaluminophosphates. In the latter case, phosphorus atoms in an aluminophosphate framework (e.g. AlPO-5) are replaced by silicon atoms, which cause negatively charged framework aluminium atoms being not compensated by the replaced positively charged phosphorus atoms. At these framework positions, therefore, Si(OH)Al groups are formed and as responsible for the ^{1}H MAS NMR signals at δ_{1H} = 3.6 and 4.6 ppm in the spectrum of SAPO-5 zeolites with different silicon contents in **Fig. 2** (see Fig. 8 in Ref. [18]).

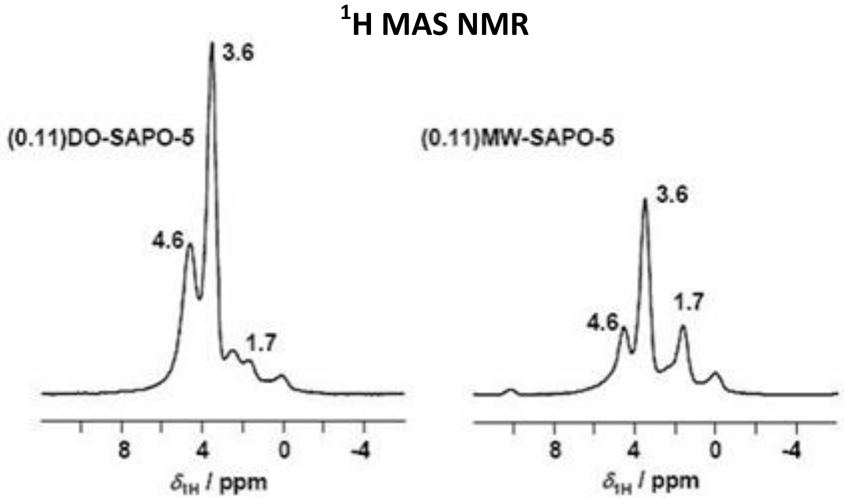


Fig. 2

For the assignment of signals occurring in the ^{1}H MAS NMR spectra of solid catalysts, the correlation of the chemical shift δ_{1H} and the FTIR wavenumber $\tilde{\nu}_{OH}$ of hydroxyl groups is useful. By comparing OH stretching vibrations and ^{1}H MAS NMR chemical shifts of OH groups in various dehydrated zeolites, the following equation (1) was derived [19]:

$$\delta_{1H} / \text{ppm} = 57.1 - 0.0147\, \tilde{\nu}_{OH} / \text{cm}^{-1} \qquad (1)$$

for non-interacting hydroxyl groups. For hydroxyl groups involved in hydrogen bondings, the correlation (2) was found [19]:

$$\delta_{1H} / \text{ppm} = 37.9 - 0.0092\, \tilde{\nu}_{OH} / \text{cm}^{-1} \qquad (2)$$

According to Eq. (2), the FTIR band observed by Zholobenko et al. [20] in the spectra of dehydrated zeolites H-ZSM-5 at $\tilde{\nu}_{\mathrm{OH}}$ = 3250 cm^{-1} corresponds to a ^{1}H MAS NMR signal at $\delta_{1\mathrm{H}} \approx 8.0$ ppm. In the ^{1}H MAS NMR spectra of zeolite H-ZSM-5, a corresponding broad low-field signal was observed at $\delta_{1\mathrm{H}}$ = 6 to 7 ppm [21, 22].

An important advantage of solid-state NMR spectroscopy is the linear correlation between the signal intensity and spin concentration for spin I = ½ nuclei in general and for spin I > ½ nuclei in the case of non-selective excitation with very short radio frequency pulses. A suitable way to quantify, e.g., the concentration of hydroxyl protons in solid catalysts by ^{1}H MAS NMR spectroscopy is the comparison of the signal intensities of the 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 external intensity standard [15, 16, 23, 24]. For quantitative studies, the repetition time of the 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 catalyst sample under study denoted “i” is calculated by [3, 25]:

$$c_\mathrm{i} = c_\mathrm{st}\, m_\mathrm{st}\, A_\mathrm{i} \,/\, (m_\mathrm{i}\, A_\mathrm{st}) \qquad (3)$$

with the concentration, c_st, the weight, m_st, and the total integral, A_st, of the ^{1}H MAS NMR signal of the standard sample denoted “st”, and the weight, m_i, and the total integral, A_i, of the ^{1}H MAS NMR signal of the catalyst sample “i” under study. The determination of the concentration of different OH types in the sample under study is performed by decomposition of the different signals in the ^{1}H MAS NMR spectrum. The obtained relative intensities and the total concentration, c_i, give the concentrations of the specific OH types.

For reviews on the above-mentioned topics, see Refs. [26] and [27].

Catalyst preparation: At first, a standard activation of the solid catalyst inside a „sample tube system 1“ at „vacuum line 1“ (see link “*In Situ* Solid-State NMR Techniques”) is performed. The activation starts with an evacuation at room temperature for ca. 10 minutes followed by a temperature ramp from room temperature to 393 K within 2 hours. At this temperature, the sample is dehydrated for 2 hours. Subsequently, the temperature is increased up to 723 K within 3 hours and evacuated at this temperature for 12 hours. After this treatment, the sample tube system is closed via the vacuum valve and disconnected from „vacuum line 1“ after this line was ventilated with air. The transfer of the dehydrated sample into the MAS NMR rotor is performed without air contact, e.g. in a mini glove box purged with dry nitrogen gas (see Section “mini glove box” via link “*In Situ* Solid-State NMR Techniques”).

^{1}H MAS NMR studies: The sample tube with the activated catalyst is transferred into an MAS NMR rotor inside a glove box, e.g. as that described in Section „mini glove box“, under flowing protecting gas, such as nitrogen, and sealed with a gas-tight rotor cap. ^{1}H MAS NMR spectra are recorded, e.g., at a Bruker AVANCE III 400 WB spectrometer using a 4 mm MAS NMR probe at a ^{1}H resonance frequency of 400.1 MHz, with a sample spinning rate of 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 signal intensities, an external intensity reference with similar spectroscopic properties like the samples under study are suggested (e.g. activated Na,H-Y zeolite). The intensity contributions of spinning sidebands must be considered for the quantitative evaluation of the signals intensities. Chemical shifts are referenced to small particles of silicon rubber ($\delta_{1\mathrm{H}}$ = 0.07 ppm) at low spinning rates of ν_{rot} = 1 to 2 kHz. This reference is easier to handle in MAS NMR rotors in comparison with TMS (tetramethylsilane) with boiling point of 299 to 301 K.

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