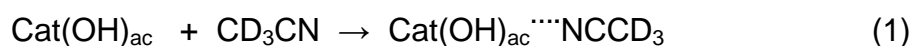


Method for the determination of the strength of Brønsted acid sites by adsorption of acetonitrile and ^1H MAS NMR

Spectroscopic background: Weakly basic probe molecules interact with Brønsted acid site via H-bonds and do not cause a complete proton transfer to the probe molecules. In the ^1H MAS NMR spectrum of the OH groups acting as Brønsted acid sites on solid catalysts (Cat), the formation of H-bonds is accompanied by a characteristic resonance shift, $\Delta\delta_{\text{1H}}$, of their ^1H MAS NMR signals to higher chemical shift values (low-field shift). This resonance shift corresponds to a decrease of the electronic shielding of the ^1H nuclei of the interacting hydroxyl protons. Simultaneously, the O-H bond distance is slightly increased, which is the initial step of a hydroxyl proton transfer to adsorbed probe molecules or potential reactants. The latter property is characteristic for hydroxyl protons acting as Brønsted acid sites ($(\text{OH})_{\text{ac}}$). Therefore, the resonance shift, $\Delta\delta_{\text{1H}}$, of the ^1H MAS NMR signals of hydroxyl protons upon adsorption of a weak base, such as acetonitrile (CD_3CN), interacting via the nitrogen atom:



is used as a measure of the strength of Brønsted acid sites (see **Fig. 1** shown below and Fig. 4 in Ref. [1]) [1-9].

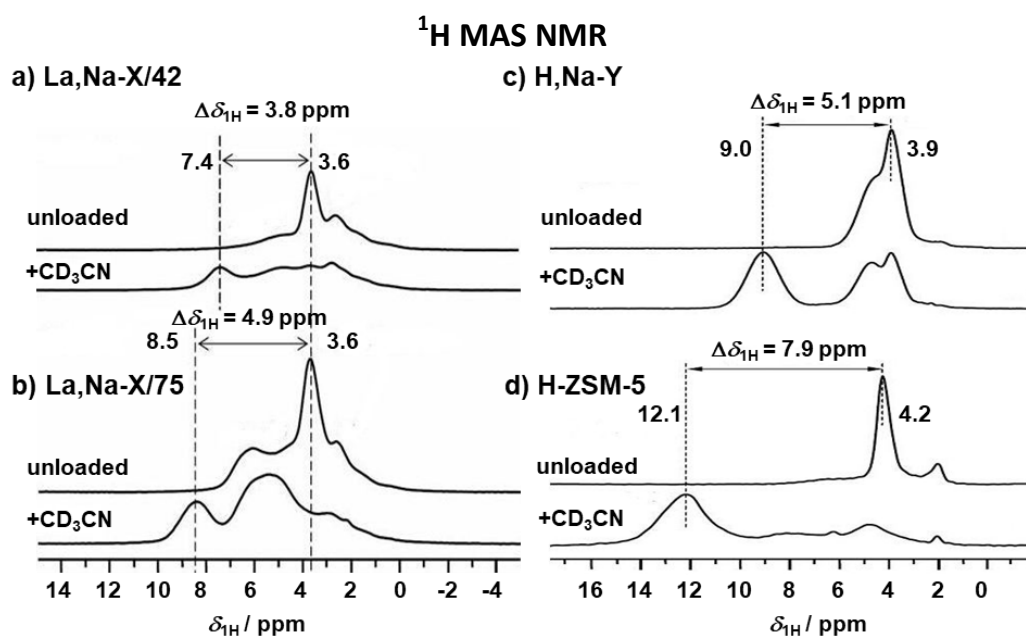


Fig. 1

Large adsorbate-induced resonance shifts, $\Delta\delta_1$, occurring after loading of the catalysts under study, e.g. with acetonitrile, corresponds to a high acid strength of the interacting Brønsted site and *vice versa*. In a similar manner, the wavenumber shift, $\Delta\nu_{\text{OH}}$, of hydroxyl groups in the FTIR spectra of solids catalysts upon adsorption of carbon monoxide is utilized for characterizing the strength of Brønsted acid sites [10].

Table 1 gives a summary of adsorbate-induced low-field shifts, $\Delta\delta_{1\text{H}}$, of the ^1H MAS NMR signals of hydroxyl protons with different Brønsted acid strength occurring after adsorption of acetonitrile (Table 3 in Ref. [1] and values of Fig. 1 in Ref. [9]).

Low-field Shift $\Delta\delta_{1\text{H}}$ / ppm	Type of OH Group Interacting with CD_3CN
1.2	AlOH groups in the metal-organic framework MIL-53(Al)
3.0	SiOH groups on silica
3.6	Si(OH)Al groups of zeolite H,Na-X ($n_{\text{Si}}/n_{\text{Al}} = 1.3$)
3.8	Si(OH)Al groups of zeolites La,Na-X/42 and Al,Na-X/32 (cation exchange degrees of 42 and 32 %, respectively, $n_{\text{Si}}/n_{\text{Al}} = 1.3$)
4.4	Si(OH)Al groups of zeolites Al,Na-X/61 (cation exchange degree of 61 %, respectively, $n_{\text{Si}}/n_{\text{Al}} = 1.3$)
4.9	Si(OH)Al groups of zeolite La,Na-X/75 (cation exchange degree of 75 %; $n_{\text{Si}}/n_{\text{Al}} = 1.3$)
5.1	Si(OH)Al groups of zeolite H,Na-Y ($n_{\text{Si}}/n_{\text{Al}} = 2.7$)
5.3	Si(OH)Al groups of zeolites Al,Na-Y/34 and Al,Na-Y/63 (cation exchange degrees of 34 and 63 %, respectively, $n_{\text{Si}}/n_{\text{Al}} = 2.7$)
5.6	Si(OH)Al groups of zeolite SAPO-34 ($n_{\text{Si}}/(n_{\text{Al}}+n_{\text{P}}+n_{\text{Si}}) = 0.1$), in [9]
5.7	Si(OH)Al groups of zeolites La,Na-Y/42 and La,Na-Y/74 (cation exchange degrees of 5.7 and 74 %, respectively, $n_{\text{Si}}/n_{\text{Al}} = 2.7$)
6.2	Si(OH)Al groups of zeolite H-MOR ($n_{\text{Si}}/n_{\text{Al}} = 6.7$)
6.5	Si(OH)Al groups of zeolite H-SSZ-13 ($n_{\text{Si}}/n_{\text{Al}} = 8.4$), in [9]
6.7	Si(OH)Al groups of zeolite H-MOR ($n_{\text{Si}}/n_{\text{Al}} = 10$)
6.8	Si(OH)Al groups of zeolite H-EU-1 ($n_{\text{Si}}/n_{\text{Al}} = 10.3$), in [9]
7.0	Si(OH)Al groups of zeolite H,Na-Y ($n_{\text{Si}}/n_{\text{Al}} = 18$)
7.2	Si(OH)Al groups of zeolite H-ZSM-5 ($n_{\text{Si}}/n_{\text{Al}} = 19$)
7.9	Si(OH)Al groups of zeolite H-ZSM-5 ($n_{\text{Si}}/n_{\text{Al}} = 26$)

Table 1

Utilizing DFT methods for calculating acetonitrile molecules interacting with $(\text{H}_3\text{SiO})_3\text{--Si--OH--Al--(OSiH}_3)_3$ cluster models for the $\text{Al}_{12}\text{--O}_{24}(\text{H})\text{--Si}_{12}$ site of zeolite H-ZSM-5 and calculating ^1H and ^{15}N chemical shifts by a Gauge-Independent Atomic Orbital (GIAO) method, the proton affinities PA and $\delta_{1\text{H}}$ as well as $\delta_{15\text{N}}$ values depicted in **Fig. 2** were obtained [13]. According to these data, a linear relationship between the ^1H chemical shift, $\delta_{1\text{H}}$, of the acidic hydroxyl proton and apparent acid strength (PA) exists, regardless of the nature of steric effects [13]. These results support an increasing acid strength of zeolitic bridging OH groups in $\text{CH}_3\text{CN}\cdots\text{H}^+$ complexes with increasing ^1H chemical shifts of these hydroxyl protons. See Section “method 5” for ^{15}N CPMAS NMR studies of ^{15}N -acetonitrile interacting with surface sites on solid catalysts.

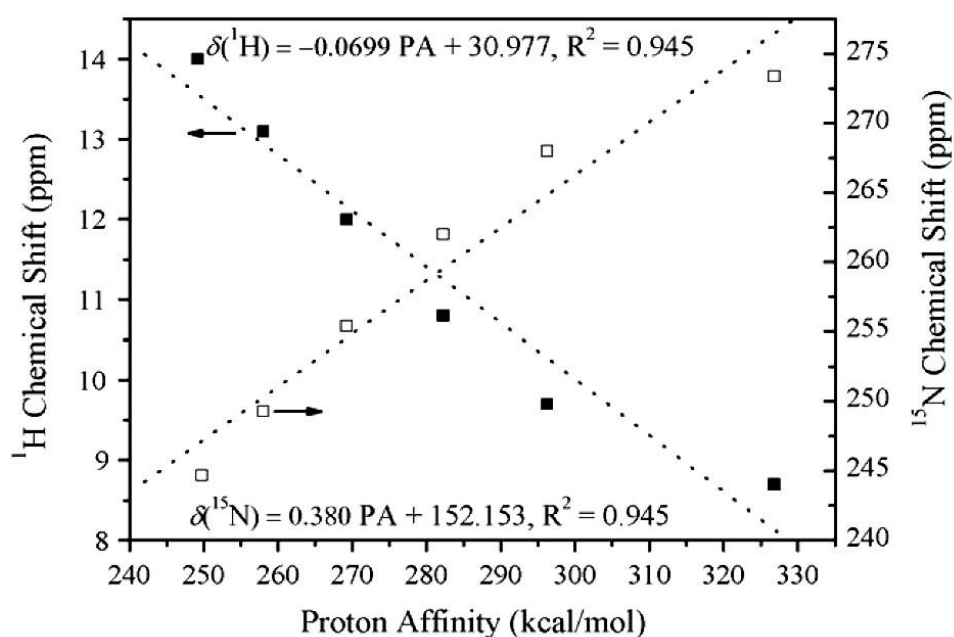


Fig. 2

For reviews on the above-mentioned topics, see Refs. [1], [11], and [12].

Catalyst preparation: Before the ^1H MAS NMR studies, a standard dehydration of the solid catalyst 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 starts with an evacuation at room temperature for ca. 10 minutes followed by a temperature ramp 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. <https://michael-hunger.de>

K within 3 hours and, subsequently, 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). The sample tube system and the vessel with deuterated acetonitrile (CD_3CN , 99.9 %, ACROS) were connected at “vacuum line 2” as shown in Fig. 7 of the Section “vacuum line 2”, accessible via link “*In Situ* Solid-State NMR Techniques”. If the acetonitrile is used for the first time, gas impurities were removed by thrice freezing and evacuation. For this purpose, put the acetonitrile vessel into a dewar with liquid nitrogen. After the acetonitrile becomes rigid, open the valve of the acetonitrile vessel for the evacuation of the gas inside the vessel and, finally, close this valve again. After an evacuation of the line for ca. 10 minutes, close the valve connecting the vacuum line with the pump (large left valve). Open the valve of the acetonitrile vessel until an acetonitrile pressure of ca. 70 mbar is reached in the vacuum line and close the valve of the vessel. Put the lower part of the sample tube, filled with the activated catalyst, into a dewar with liquid nitrogen and open the valve of the sample tube system with the dehydrated catalyst. During the acetonitrile adsorption, warm up the catalyst sample by hand to room temperature and wait 10 minutes for better distribution of the molecules in the sample. Subsequently, slowly open the left valve of the “vacuum line 2” to the pump and evacuate the sample tube for 10 minutes at room temperature for the removal of surplus molecules. For the removal of acetonitrile from SiOH and AlOH groups, the evacuation at room temperature can be increased up to 10 hours. Close the valve of the sample tube system and disconnect it from the vacuum line (after this line was ventilated with air).

^1H MAS NMR studies: The acetonitrile-loaded 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. All above-mentioned ^1H MAS NMR spectra were recorded at a Bruker AVANCE III 400 WB spectrometer with a ^1H resonance frequency of 400.1 MHz, using a 4 mm MAS NMR probe with a sample spinning rate of 8 kHz, $\pi/2$ single pulse excitation, and a repetition time of 10 s. Chemical shifts are referenced to small particles of silicon rubber ($\delta_{\text{H}} = 0.07$ ppm) at low spinning rates of $\nu_{\text{rot}} = 1$ to 2 kHz.

This 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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