# Method for the determination of the strength of Broensted acid sites by adsorption of acetonitrile and $^{1}H$ MAS NMR

***Spectroscopic background:*** Weakly basic probe molecules interact with Broensted acid site via H-bonding and not via proton transfer to the probe molecules. In the $^{1}H$ MAS NMR spectrum of the OH groups acting as Broensted acid sites on solid catalysts (Cat), the formation of H-bondings is accompanied by a characteristic resonance shift $\Delta\delta_{1H}$ of their signals to higher chemical shift values. This resonance shift corresponds to a decrease of the electronic shielding of the $^{1}H$ 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 Broensted acid sites ($(OH)_{ac}$). Therefore, the resonance shift $\Delta\delta_{1H}$ of the $^{1}H$ MAS NMR signals of hydroxyl protons upon adsorption of a weak base, such as acetonitrile ($CD_3CN$) interacting via the nitrogen atom:

$$\mathrm{Cat(OH)_{ac}} + \mathrm{CD_3CN} \rightarrow \mathrm{Cat(OH)_{ac}}\cdots\mathrm{NCCD_3} \qquad (1)$$

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

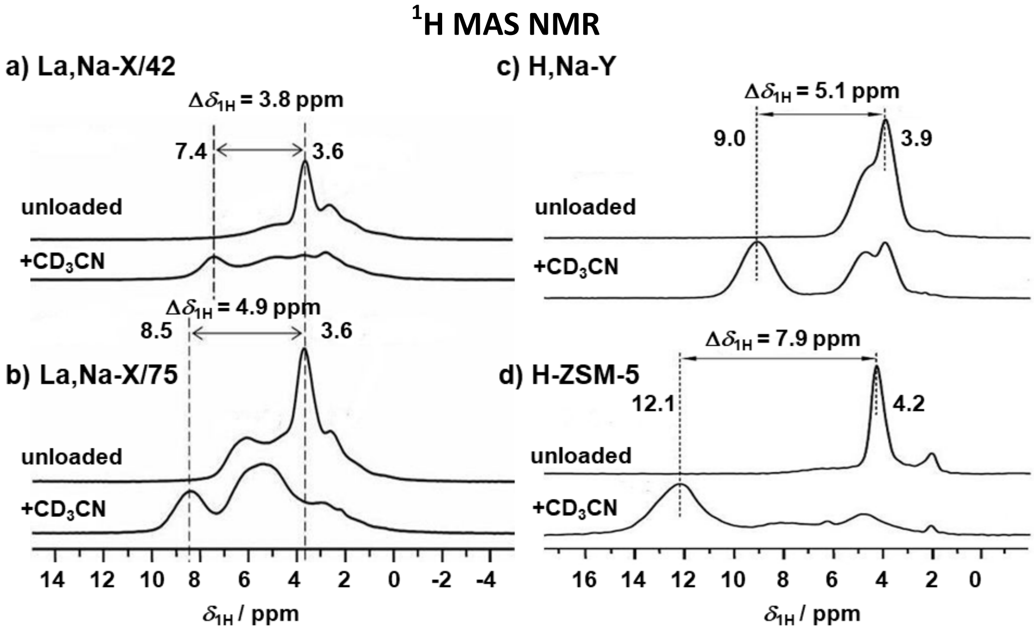

**Fig. 1**

**Large adsorbate-induced resonance shifts $\Delta\delta_{1H}$ after loading of the catalysts under study, e.g. with acetonitrile, corresponds to a high acid strength of the interacting Broensted site and vice versa**. In a similar manner, the wavenumber shift $\Delta\nu_{OH}$ of hydroxyl groups in the FTIR spectra of solids catalysts upon adsorption of carbon monoxide is utilized for characterizing the strength of Broensted acid sites [10].

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

| Low-field Shift $\Delta\delta_{1H}$ / 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 ($n_{Si}/n_{Al}$ = 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, $n_{Si}/n_{Al}$ = 1.3) |
| 4.4 | Si(OH)Al groups of zeolites Al,Na-X/61 (cation exchange degree of 61 %, respectively, $n_{Si}/n_{Al}$ = 1.3) |
| 4.9 | Si(OH)Al groups of zeolite La,Na-X/75 (cation exchange degree of 75 %; $n_{Si}/n_{Al}$ = 1.3) |
| 5.1 | Si(OH)Al groups of zeolite H,Na-Y ($n_{Si}/n_{Al}$ = 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, $n_{Si}/n_{Al}$ = 2.7) |
| 5.6 | Si(OH)Al groups of zeolite SAPO-34 ($n_{Si}/(n_{Al}+n_P+n_{Si})$ = 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, $n_{Si}/n_{Al}$ = 2.7) |
| 6.2 | Si(OH)Al groups of zeolite H-MOR ($n_{Si}/n_{Al}$ = 6.7) |
| 6.5 | Si(OH)Al groups of zeolite H-SSZ-13 ($n_{Si}/n_{Al}$ = 8.4), in [9] |
| 6.7 | Si(OH)Al groups of zeolite H-MOR ($n_{Si}/n_{Al}$ = 10) |
| 6.8 | Si(OH)Al groups of zeolite H-EU-1 ($n_{Si}/n_{Al}$ = 10.3), in [9] |
| 7.0 | Si(OH)Al groups of zeolite H,Na-Y ($n_{Si}/n_{Al}$ = 18) |
| 7.2 | Si(OH)Al groups of zeolite H-ZSM-5 ($n_{Si}/n_{Al}$ = 19) |
| 7.9 | Si(OH)Al groups of zeolite H-ZSM-5 ($n_{Si}/n_{Al}$ = 26) |

**Table 1**

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

***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 the sample is further 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 sample tube system and the vessel with deuterated acetonitrile ($CD_3CN$, 99.9 %, ACROS) are connected at „vacuum line 2“ as shown in Fig. 7 of the Section „vacuum line 2“. If the acetonitrile is utilized for the first time, gas impurities must be removed by thrice freezing and evacuation. For this purpose, put the acetonitrile vessel into liquid nitrogen and open the valve of the vessel after the acetonitrile became rigid to evacuate the gas inside the vessel and 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). Now, 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 liquid nitrogen and open the valve of this sample tube system. During acetonitrile adsorption, warm up the catalyst sample, e.g. 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 to the pump and evacuate the sample tube for 10 minutes at room temperature for removing surplus molecules. For removing the acetonitrile from SiOH and AlOH groups, the evacuation time at room temperature is increased up to 10 hours. Close the valve of the sample tube system and disconnect it from the vacuum line after the line was ventilated. The transfer of the prepared sample into the MAS NMR rotor should be 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 acetonitrile-loaded catalyst is transferred into an MAS NMR rotor inside a glove box, e.g. as that described in Section „mini glove box“, under flowing nitrogen gas, 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. Chemical shifts are referenced to small particles of silicon rubber ($\delta_{1H}$ = 0.07 ppm) at low spinning rates of $\nu_{rot}$ = 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.

***References:***

[1] Y. Jiang, J. Huang, W. Dai, M. Hunger, *Solid-state nuclear magnetic resonance investigations of the nature, property, and activity of acid sites on solid catalysts*, Solid State Nucl. Magn. Reson. 39 (2011) 116-141, DOI: 10.1016/j.ssnmr.2011.03.007.

[2] J.F. Haw, M.B. Hall, A.E. Alvarado-Swaisgood, E.J. Munson, Z. Lin, L.W. Beck, T. Howard, *Integrated NMR and ab-initio study of acetonitrile in zeolites – A reactive complex model of zeolite acidity*, J. Am. Chem. Soc. 116 (1994) 7308-7318, DOI: 10.1021/ja00095a039.

[3] J. Janchen, J.H.M.C. van Wolput, L.J.M. van de Ven, J.W. de Haan, R.A. van Santen, *FTIR spectroscopic and $^1$H MAS NMR studies of the influence of lattice chemistry and structure on Bronsted acidity in zeolites*, Catal. Lett. 39 (1996) 147-152, DOI: 10.1007/BF00805574.

[4] J. Huang, Y. Jiang, V.R. Reddy Marthala, W. Wang, B. Sulikowski, M. Hunger, *In situ $^1$H MAS NMR investigations of the H/D exchange of alkylaromatic hydrocarbons on zeolites H-Y, La,Na-Y, and H-ZSM-5*, Microporous Mesoporous Mater. 99 (2007) 86-90, DOI: 10.1016/j.micromeso.2006.06.041.

[5] J. Huang, Y. Jiang, V.R. Reddy Marthala, Y.S. Ooi, J. Weitkamp, M. Hunger, *Concentration and acid strength of hydroxyl groups in zeolites La,Na-X and La,Na-Y with different lanthanum exchange degrees studied by solid-state NMR spectroscopy*, Microporous Mesoporous Mater. 104 (2007) 129-136, DOI: 10.1016/j.micromeso.2007.01.016.

[6] J. Huang, Y. Jiang, V.R. Reddy Marthala, B. Thomas, E. Romanova, M. Hunger, *Characterization and acidic properties of aluminum-exchanged*

*zeolites X and Y*, J. Phys. Chem. C 112 (2008) 3811-3818, DOI: 10.1021/jp7103616.

[7] C. Lieder, S. Opelt, M. Dyballa, H. Henning, E. Klemm, M. Hunger, *Adsorbate effect on* $AlO_4(OH)_2$ *centers in the metal-organic framework MIL-53 investigated by solid-state NMR spectroscopy*, J. Phys. Chem. C 114 (2010) 16596-16602, DOI: 10.1021/jp105700b.

[8] J. Huang, N. van Vegten, Y. Jiang, M. Hunger, A. Baiker, *Increasing the Broensted acidity of flame-derived silica-alumina up to zeolitic strength*, Angew. Chem. Int. Ed. 49 (2010) 7776-7781, DOI: 10.1002/anie.201003391.

[9] W. Dai, X. Sun, B. Tang, G. Wu, L. Li, N. Guan, M. Hunger, *Verifying the mechanism of the ethene-to-propene conversion on zeolite H-SSZ-13*, J. Catal. 314 (2014) 10-20, DOI: 10.1016/j.jcat.2014.03.006.

[10] H.G. Karge, M. Hunger, H. Beyer, *Characterization of Zeolites - Infrared and Nuclear Magnetic Resonance Spectroscopy and X-Ray Diffraction*, in: J. Weitkamp, L. Puppe (eds.), *Catalysis and Zeolites - Fundamentals and Application*, Springer-Verlag, Berlin, 1999, ISBN: 978-3-662-03764-5, p. 228-230.

[11] W. Yang, Z. Wang, J. Huang, Y. Jiang, *Qualitative and Quantitative Analysis of Acid Properties for Solid Acids by Solid-State Nuclear Magnetic Resonance Spectroscopy*, J. Phys. Chem. C 125(19) (2021) 10179-10197, DOI: 10.1021/acs.jpcc.1c01887.

[12] M. Dyballa, *Solid-State NMR Probe Molecules for Catalysts and Adsorbents: Concepts, Quantification, Accessibility, and Spatial Distribution*, Energy & Fuels 37(23) (2023) 18517-18559, DOI: 10.1021/acs.energyfuels.3c03815.