Method for the identification of Broensted acid sites by adsorption of pyridine and ^{1}H MAS NMR

Spectroscopic background: Strongly basic probe molecules are suitable for distinguishing between acidic and non-acidic sites by a complete proton transfer from the catalyst surface to the adsorbate molecules. In the case of pyridine (Pyr) adsorption at weakly acidic Broensted sites, this molecule interacts via hydrogen bondings leading to a characteristic low-field resonance shift of the ^{1}H MAS NMR signal of the OH group, such as to δ_{1H} ca. 10 ppm for SiOH groups. If pyridine is adsorbed at **strongly acidic Broensted sites**, $(OH)_{ac}$, on a catalyst (Cat), such as at bridging OH groups (Si(OH)Al) in zeolites, it is protonated to **pyridinium ions ($PyrH^+$)**:

$$Cat(OH)_{ac} + Pyr \rightarrow Cat(O)^- + PyrH^+ \qquad (1)$$

causing broad ^{1}H MAS NMR signals at **δ_{1H} = 12 to 20 ppm** [1-8].

As an example, **Figs. 1a and 1b** show ^{1}H MAS NMR spectra of lanthanum-exchanged zeolites Y with cation exchange degrees of 42% and 74%, respectively, recorded upon adsorption of pyridine-d_5 (Fig. 4 in Ref. [6]). The proton transfer from Si(OH)Al groups in supercages of the zeolite Y framework to this probe molecule results in the appearance of a new ^{1}H MAS NMR signal at δ_{1H} = 16 ppm caused by the formation of $PyrH^+$. Simultaneously, the signal of Si(OH)Al groups in supercages at δ_{1H} = 3.9 ppm is strongly decreased, while the signals of non-accessible Si(OH)Al groups in sodalite cages at δ_{1H} = 4.8 ppm and of non-acidic LaOH groups at δ_{1H} ca. 6 ppm remain unchanged. The large line width of the $PyrH^+$ signals and the absence of spinning sidebands for these signals indicate a high mobility of these protonated species in zeolite cages.

DFT calculations delivered a linear correlation of the ^{1}H NMR chemical shift values of the H^+ at pyridinium ions in the range of δ_{1H} = 12.0 to 16.5 ppm with proton affinities of the solid acids of PA = 255 to 315 kcal/mol [9]. According to this correlation, formation of pyridinium ions at stronger Broensted acid sites leads to ^{1}H NMR signals with lower shift values in the above-mentioned shift range and vice versa. This finding is contrary to the resonance shifts obtained for hydrogen bonding of pyridine at weakly acidic Broensted sites. In experimental studies of microporous zeolites,

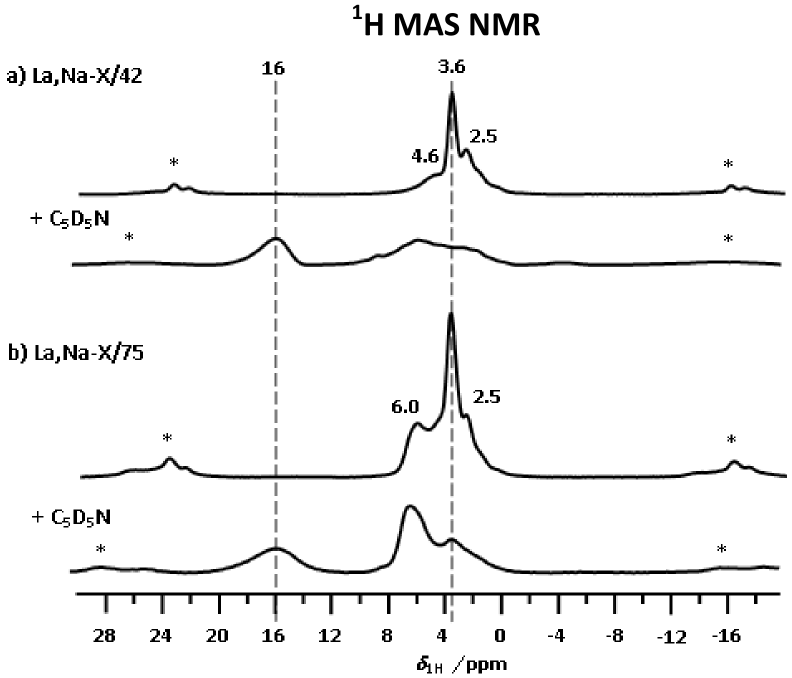

Fig. 1

influences of rapid exchange and limitation in the accessibility of Broensted acid sites for pyridine on the observed ^{1}H resonance positions of this probe molecule occur. Therefore, pyridine is mainly used for assigning the ^{1}H MAS NMR signals of accessible and strongly acidic Broensted sites. For reviews on the above-mentioned topics, see Refs. [8], [10], and [11].

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 sample tube system and the vessel with deuterated pyridine (pyridine-d_5, 99.5%, ACROS) are 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 pyridine is utilized for the first time, gas impurities must be removed by thrice freezing and evacuation. For this purpose, put the pyridine vessel into liquid nitrogen and open the valve of the vessel after the pyridine 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 pyridine vessel until a pyridine pressure of ca. 50 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 pyridine 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 pyridine from SiOH and AlOH groups, the evacuation time can be also 2 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 pyridine-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 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. Chemical shifts are referenced to small particles of silicon rubber (δ_{1H} = 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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