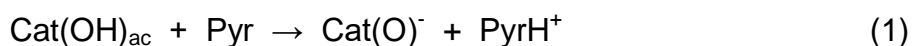


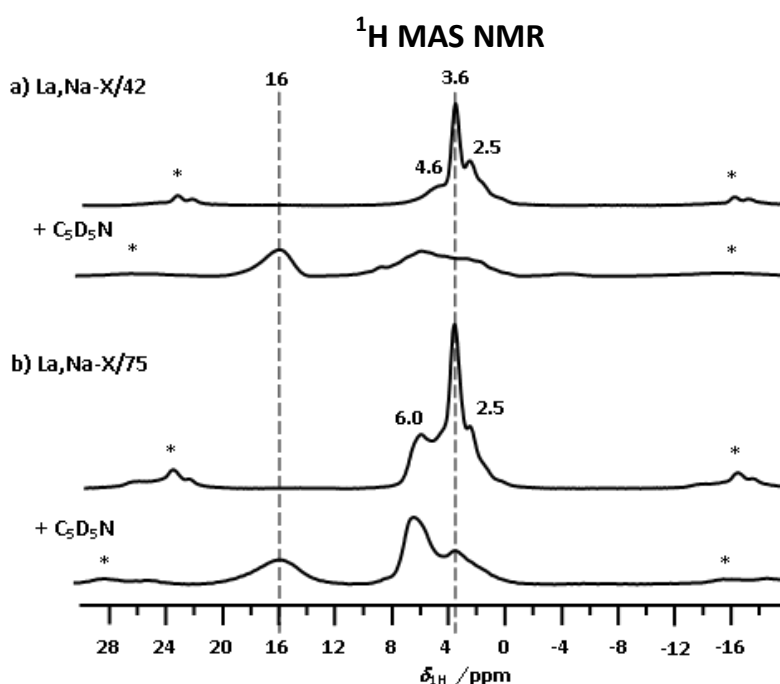
## Method for the identification of Brønsted acid sites by adsorption of pyridine and $^1\text{H}$ MAS NMR

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



causing broad  $^1\text{H}$  MAS NMR signals at  $\delta_{\text{H}} = 12$  to  $20$  ppm [1-8].

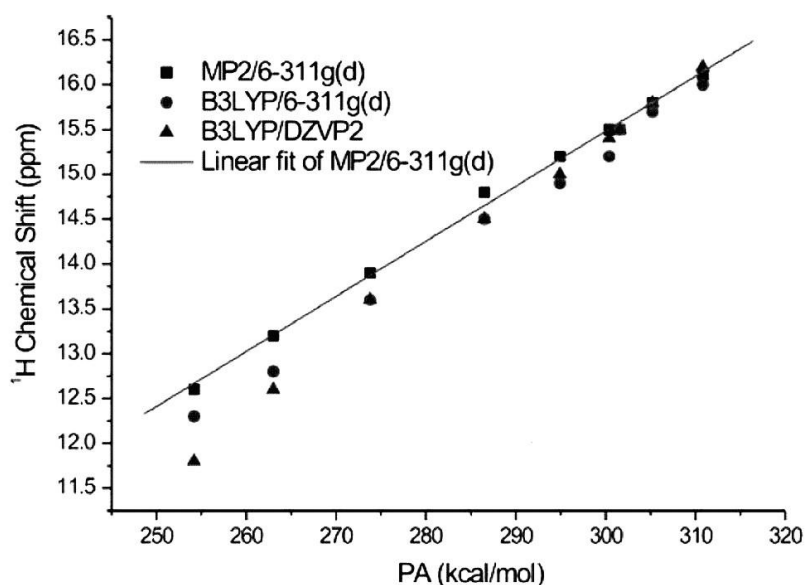
As an example, **Figs. 1a and 1b** show  $^1\text{H}$  MAS NMR spectra of lanthanum-exchanged zeolites Y with cation exchange degrees of 42% and 74%, respectively, recorded upon adsorption of pyridine- $\text{d}_5$  (Fig. 4 in Ref. [6]). The proton transfer from  $\text{Si}(\text{OH})\text{Al}$  groups in the supercages of the zeolite Y framework to this probe molecule results in the appearance of a new  $^1\text{H}$  MAS NMR signal at  $\delta_{\text{H}} = 16$  ppm caused by



**Fig. 1**

the formation of  $\text{PyrH}^+$ . Simultaneously, the signal of  $\text{Si(OH)Al}$  groups in supercages at  $\delta_{\text{H}} = 3.9$  ppm is strongly decreased, while the signals of non-accessible  $\text{Si(OH)Al}$  groups in sodalite cages at  $\delta_{\text{H}} = 4.8$  ppm and of non-acidic  $\text{LaOH}$  groups at  $\delta_{\text{H}}$  ca. 6 ppm remain unchanged. The large line width of the  $\text{PyrH}^+$  signals and the absence of spinning sidebands for these signals indicate a high mobility of these protonated adsorbates in zeolite cages.

Quantum-chemical calculations of  $(\text{H}_3\text{SiO})_3\text{-Si-OH-Al-(SiOH}_3)_3$  cluster models for the  $\text{Al}_{12}\text{-O}_{24}(\text{H})\text{-Si}_{12}$  site of zeolite H-ZSM-5 delivered a linear relationship between the  $^1\text{H}$  NMR chemical shifts,  $\delta_{\text{H}}$ , of the  $\text{H}^+$  species at pyridinium ions in the range of  $\delta_{\text{H}} = 12.0$  to 16.5 ppm with proton affinities in the range of  $\text{PA} = 255$  to 315 kcal/mol (**Fig. 2**) [9]. According to this relationship, the formation of pyridinium ions at stronger Brønsted acid sites leads to  $^1\text{H}$  NMR signals with  $\delta_{\text{H}}$  values and *vice versa*. This finding is contrary to the resonance shifts obtained for hydrogen bonded probe molecules, e.g. in the case of acetonitrile (see Fig. 2 in Section “method 20”). See Section “method 5” for  $^{15}\text{N}$  CPMAS NMR studies of  $^{15}\text{N}$ -pyridine interacting with surface sites on solid catalysts.



**Fig. 2**

In experimental studies of microporous zeolites, rapid exchange and limitation in the accessibility of Brønsted acid sites for pyridine may influence the observed  $^1\text{H}$

resonance positions of this probe molecule. Therefore, pyridine is mainly used for assigning the  $^1\text{H}$  MAS NMR signals of accessible and strongly acidic Brønsted sites. For reviews on the above-mentioned topics, see Refs. [8], [10], and [11].

**Catalyst preparation:** Before the  $^1\text{H}$  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  $T = 393\text{ K}$  within 2 hours. At this temperature, the sample was dehydrated for 2 hours. Subsequently, the temperature was increased up to  $T = 723\text{ K}$  within 3 hours and the sample material 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 the line was ventilated with air).

Subsequently, the sample tube system with the dehydrated catalyst and a vessel with deuterated pyridine (pyridine- $\text{d}_5$ , 99.5%, 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 pyridine- $\text{d}_5$  was utilized for the first time, gaseous impurities were 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 becomes rigid, for an evacuation of 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). Open the valve of the vessel with purified liquid pyridine until a pyridine vapour pressure of ca. 50 mbar is reached in the vacuum line and close the valve of the pyridine- $\text{d}_5$  vessel. Put the lower part of the sample tube containing the dehydrated catalyst into a dewar with liquid nitrogen and open the valve of this sample tube system. During the pyridine adsorption, warm up the catalyst sample, e.g. by hand to room temperature, and wait 10 minutes for a 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 a selective removal of pyridine molecules from weakly acidic SiOH and AlOH groups, the evacuation time can be 2 to 10 hours at room temperature. Close the valve of the sample tube system and disconnect it from the vacuum line (after the line was ventilated by air).

**<sup>1</sup>H MAS NMR studies:** The pyridine-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 nitrogen gas, and, finally, the rotor was sealed with a gas-tight rotor cap. Most of the above-mentioned <sup>1</sup>H MAS NMR spectra were recorded at a Bruker AVANCE III 400 WB spectrometer with a <sup>1</sup>H 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 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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