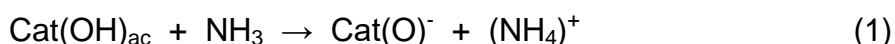


Method for the determination of the density of Broensted acid sites by adsorption of ammonia and ^1H MAS NMR

Spectroscopic background: For quantifying the number of Broensted acid sites on solid catalysts (Cat), adsorption of ammonia as probe molecule is a very suitable method. Upon formation of **ammonium ions NH_4^+** by protonation of the ammonia molecules adsorbed at **Broensted acidic OH groups**, $(\text{OH})_{\text{ac}}$:



a narrow signal occurs at $\delta_{\text{H}} = 6.5$ to 7.0 ppm in the ^1H MAS NMR spectrum [1-11]. Due to this resonance position, the ammonium signal does not overlap with most of the OH signals of solid catalysts (see Table 1 in Section “method 12”). Furthermore, the narrow line width of ^1H MAS NMR signals of ammonium ions and their intensity, which is four times larger in comparison with the ^1H MAS NMR signal of the acidic OH groups of the unloaded material, allows a determination of the number of accessible Broensted acid sites with high accuracy. For the quantitative evaluation of the ^1H MAS NMR signals of ammonium ions, the procedure described by Equ. (3) of Section “method 12” is utilized. For the calculation of the number of Broensted acid site (H^+) able to protonate adsorbed ammonia molecules (NH_3) to ammonium ions (NH_4^+), the number of ^1H spins obtained by the above-mentioned Equation (3) must be divided by four.

For example, **Figs. 1a and 1b** show ^1H MAS NMR spectra of two SAPO-34 materials

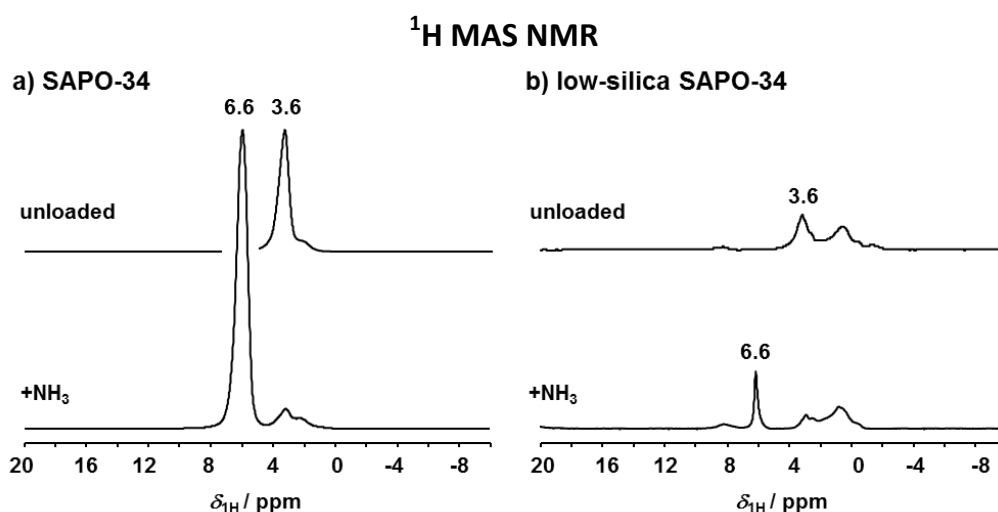


Fig. 1

with different silicon contents of $n_{\text{Si}}/(n_{\text{Al}}+n_{\text{P}}+n_{\text{Si}}) = 0.171$ and 0.010 , respectively (Fig. 4 in Ref. [8]). The signals at $\delta_{1\text{H}} = 3.6$ ppm in **Figs. 1a and 1b**, top, are due to Si(OH)Al groups of SAPO-34. Upon loading of 100 mbar ammonia on the dehydrated samples and subsequent evacuation at 453 K for 2 h, signals of ammonium ion appear at $\delta_{1\text{H}} = 6.6$ ppm (**Figs. 1a and 1b**, bottom). The intensity of this ammonium signal for SAPO-34 (**Fig. 1 a**) indicates that 95% of the Si(OH)Al groups act as accessible Brønsted acid sites. In the case of the low-silica SAPO-34 (**Fig. 1b**), only 70% of the Si(OH)Al groups causing a ^1H MAS NMR signal at $\delta_{1\text{H}} = 3.6$ ppm form ammonium ions with a signal at 6.6 ppm .

In the case of amorphous solid catalysts with weak Brønsted acid sites, such as silica-zirconia (SZ/ x with $x = 100$ means pure zirconia), prepared by flame-spray pyrolysis (FSP), the ammonia-loaded catalyst samples are evacuated at 393 K for 2 h. The ^1H MAS NMR spectra in **Fig. 2** indicate that also these materials exhibit Brønsted acid site able to protonate ammonia (Fig. 5 in Ref. [9]). The intensities of the signals of ammonium ions at $\delta_{1\text{H}} = 6.7$ and 6.8 ppm depend on the zirconia contents ($x = 10$ and 70), which evidence that the incorporation of zirconia atoms into the silica framework is the reason for the formation of Brønsted acid sites. For reviews on the above-mentioned topics, see Refs. [8], [12], and [13].

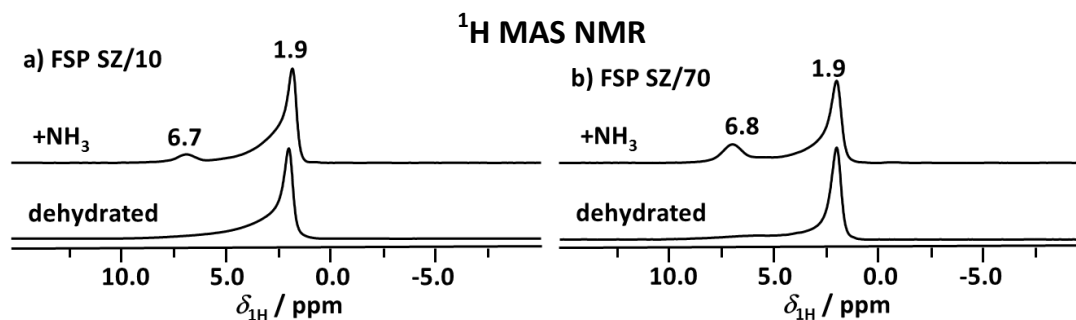


Fig. 2

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, <https://michael-hunger.de>

the sample tube system is closed via the vacuum valve and subsequently connected with “vacuum line 2” allowing the loading of ammonia via the metal bottle filled with ammonia gas (see Figs. 4 and 5 in the Section “vacuum line 2” accessible via link “*In Situ* Solid-State NMR Techniques”). 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 ammonia bottle until an ammonia pressure of ca. 100 mbar is reached in the “vacuum line 2” and close the valve of the metal bottle. 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 ammonia adsorption, warm up the catalyst sample 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. Subsequently, close the valve of the sample tube system and disconnect it after the vacuum line was ventilated by air. Then, connect the sample tube system with the ammonia-loaded catalyst with “vacuum line 1”. For removing physisorbed ammonia from the catalyst surface, an evacuation of the catalyst sample at “vacuum line 1” with a heating ramp of 1h to 453 K and at this temperature for additional 2 h is performed. For removing physisorbed ammonia from weakly acidic catalysts, such as amorphous aluminosilicates or silica-zirconia, an evacuation temperature of 393 K is suggested. Finally, the valve of the sample tube system is closed and it is disconnected from the line after ventilation by air. 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”).

¹H MAS NMR studies: The sample tube with the ammonia-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. ¹H MAS NMR spectra are recorded, e.g., at a Bruker AVANCE III 400 WB spectrometer using a 4 mm MAS NMR probe at a ¹H 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.

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