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**, (OH)_{ac}:

$$Cat(OH)_{ac} + NH_3 \rightarrow Cat(O)^- + (NH_4)^+$$
(1)

a narrow signal occurs at $\delta_{IH} = 6.5$ to 7.0 ppm in the ¹H MAS NMR spectrum [1-11]. Due to the low-field resonance position, the ammonium signal does not overlap with most of the signals of OH groups on solid catalysts (see Table 1 in Section "method 1"). Furthermore, the narrow line width of ¹H MAS NMR signals of ammonium ions and their high 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 Eq. (3) of Section "method 1" is utilized. For the calculation of the number of Broensted acid site (H⁺), which are able to protonate adsorbed ammonia molecules (NH₃) to ammonium ions (NH₄⁺), the number of ¹H spins obtained by the above-mentioned Eq. (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 $n_{Si}/(n_{AI}+n_P+n_{Si}) = 0.171$ and 0.010, respectively (Fig. 4 in Ref. [8]). The signals at $\delta_{1H} = 3.6$ ppm in **Figs. 1a and 1b**, top, are due to Si(OH)AI 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 $\delta_{1H} = 6.6$ 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)AI groups act as accessible Broensted acid sites. In the low-silica SAPO-34 (**Fig. 1b**), only 70% of the Si(OH)AI groups causing a ¹H MAS NMR signal at $\delta_{1H} = 3.6$ ppm form ammonium ions with a signal at 6.6 ppm .

In the case of amorphous solid catalysts with weak Broensted 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 were evacuated at 393 K for 2 h. The ¹H MAS NMR spectra in **Fig. 2** indicate that also these materials exhibit Broensted acid site able to protonate ammonia (Fig. 5 in Ref. [9]). The intensities of the signals of ammonium ions at $\delta_{1H} = 6.7$ 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 Broensted acid sites. For reviews on the above-mentioned topics, see Refs. [8], [12], and [13].



Fig. 2

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 https://michael-hunger.de

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 this line was ventilated by air). Subsequently, the sample tube system with the dehydrated catalyst was connected with "vacuum line 2" allowing the loading of ammonia via the metal bottle filled with ammonia gas (see Figs. 4 and 5 in 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 dehydrated catalyst, into a dewar with liquid nitrogen and open the valve of the sample tube system. During ammonia adsorption, warm up the catalyst sample 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, which connects the vacuum line with the pump, and evacuate the sample tube for 10 minutes at room temperature to remove surplus molecules. Close the valve of the sample tube system and disconnect it from "vacuum line 2" (after this line was ventilated by air). Then, connect the sample tube system with the ammonialoaded catalyst with "vacuum line 1". For the removal of weakly physisorbed ammonia from the catalyst surface, an evacuation of the catalyst sample at "vacuum line 1" with a heating ramp of 1 h to T = 453 K and at this temperature for additional 2 h was performed. For the removal of physisorbed ammonia from weakly acidic catalysts, such as amorphous aluminosilicates or silica-zirconia, an evacuation temperature of T = 393 K is suggested. Finally, the valve of the sample tube system was closed and it was disconnected from "vacuum line 1" (after this line was ventilated by air).

¹*H* MAS NMR studies: The ammonia-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 at 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, https://michael-hunger.de

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 $v_{rot} = 1$ 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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