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

Spectroscopic background: Upon adsorption of **ammonia at Lewis acid sites** on solid catalysts, broad ^{1}H MAS NMR signals occur at **δ_{1H} = -0.5 to 3 ppm**, which are caused by ammonia coordinated at Lewis acid sites [1-7]. Due to the above-mentioned resonance position, these ammonia signals may overlap with ^{1}H MAS NMR signals of SiOH and other surface OH groups of oxides (see Table 1 in Section “method 12”). For quantitative studies, therefore, it is useful to evaluate the difference spectra of the catalyst samples before and after ammonia adsorption. As an advantage, on the other hand, the ^{1}H MAS NMR signals of ammonia molecules coordinated at Lewis acid sites have an intensity corresponding to three ^{1}H spins per Lewis acid site, which allows a determination of the number of these sites with high accuracy. For the quantitative evaluation of the ^{1}H MAS NMR signals of ammonia molecules coordinated at Lewis acid sites, the procedure described by Equ. (3) of Section “method 12” is utilized. For the calculation of the number of Lewis acid site able to coordinate ammonia molecules (NH_3), the number of ^{1}H spins obtained by this equation must be divided by three.

For demonstrating the above-mentioned method, the ^{1}H MAS NMR spectra of Lewis acidic solid catalysts before and after ammonia adsorption are shown in **Fig.1** (Fig. 3 in Ref. [3]). The spectrum of dehydrated and unloaded γ-Al_2O_3 in **Fig. 1a** consists of signals at δ_{1H} = -0.2 and 1.7 ppm due to different types of external and internal AlOH species. Adsorption of ammonia on this **γ-Al_2O_3** causes a strong increase of the signal intensity in the shift range of **δ_{1H} = -0.3 to 2.6 ppm** (**Fig. 1b**). This additional signal intensity is cause by ammonia coordinated at Lewis acid sites. The weak signal at δ_{1H} = 6.7 ppm hints at the formation of ammonium ions at few Broensted acidic OH groups. The spectrum in **Fig. 1c** corresponds to the difference spectrum of **Fig. 1a and 1b**. Evaluation of the signal intensity of the difference spectrum for the chemical shift range of δ_{1H} = -0.3 to 2.6 ppm gives the number of ammonia molecules coordinated at Lewis acid sites according to the procedure described above. ^{1}H MAS NMR studies of ammonia-loaded **TiO_2/anatase** and zeolite **52Li,48Na-Y** gave the difference spectra in **Figs. 1d and 1e** consisting of signals of ammonia coordinated at Lewis acid sites at **δ_{1H} = 1.8 ppm and 0.8 ppm, respectively**.

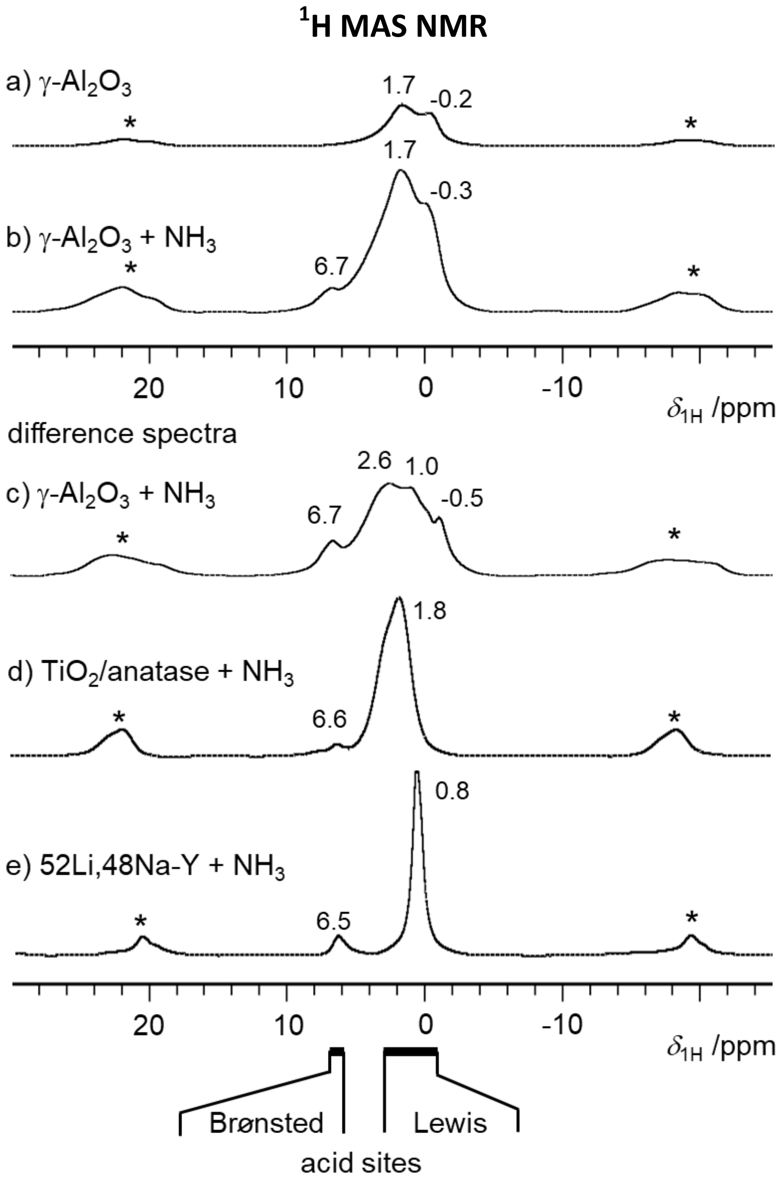

Fig. 1

As another example, **Fig. 2** shows the ^{1}H MAS NMR spectra of dehydrated zeolite DeaY (dealuminated zeolite Y of Degussa) before (a) and after modification with $AlCl_3$ (b) and subsequent calcination at 723 K, recorded before (top) and after (middle) ammonia loading. The bottom spectra are the difference spectra of the middle and the top spectra. The spectrum of the dehydrated parent zeolite DeaY in **Fig. 2a**, top, solely consists of a weak SiOH signal at δ_{1H} = 1.6 ppm. Upon loading of ammonia, an additional signal can be observed at δ_{1H} = 6.4 ppm, which hints at the formation of ammonium ions and, therefore, the presence of Broensted acid sites. In addition, there is a broad signal at δ_{1H} = 2.0 ppm due to ammonia molecules

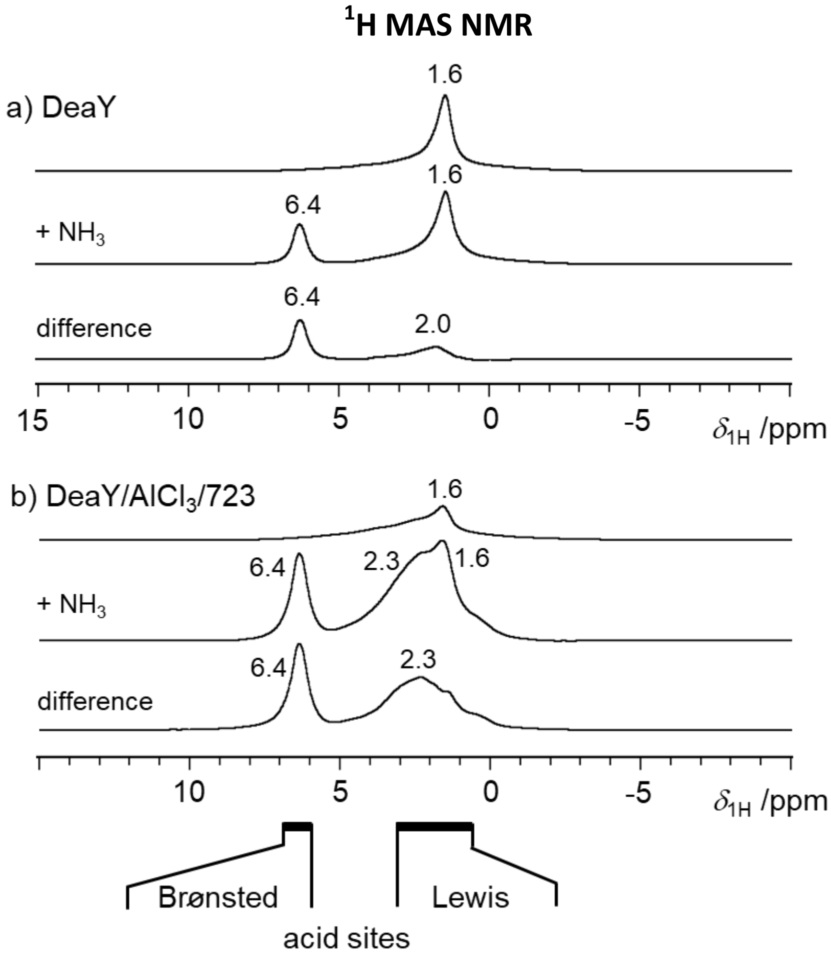

Fig. 2

coordinated at Lewis acid sites. The evaluation of the integral intensity of the latter ^{1}H MAS NMR signal gave a number of 0.005 mmol g^{-1} ammonia molecules coordinated at Lewis acid sites. Adsorption of ammonia at the dehydrated zeolite DeaY/$AlCl_3$/723 led to the ^{1}H MAS NMR spectra in **Fig. 2b**. A significant increase of the ammonium signal (δ_{1H} = 6.4 ppm) and of the signal of ammonia molecules coordinated at Lewis acid sites ($\delta_{1H} \cong$ 2.3 ppm) is visible. The evaluation of integral intensity of the latter ^{1}H MAS NMR signal gave a number of 0.100 mmol g^{-1} ammonia molecules coordinated at Lewis acid sites. This high density of Lewis acid sites indicates the potential of the ACl_3 treatment for the formation of this kind of surface sites on porous support materials.

For reviews on the above-mentioned topics, see Refs. [8], [9], and [10].

Catalyst preparation: At first, a standard activation of the solid catalyst inside a „sample tube system 1“ at „vacuum line 1“ is performed (see link “*In Situ* Solid-State NMR Techniques”). 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 metal bottle with ammonia gas (see Figs. 4 and 5 in in the Section “vacuum line 2”) are connected at „vacuum line 2“. 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 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 ammonia 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. 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. 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 dehydrated sample into the MAS NMR rotor is 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 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.^{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 ν_0 = 400.1 MHz, with a sample spinning rate of ν_{rot} = 8 kHz, $\pi/2$ single pulse excitation, and a repetition time of 10 s. Chemical shifts are referenced to small particles of silicon rubber ($\delta_{1\mathrm{H}}$ = 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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