Method for the determination of the strength of Lewis acid sites by adsorption of ¹³C-2-acetone and ¹³C CPMAS NMR

Spectroscopic background: Adsorption of ¹³C-2-acetone on Lewis acidic extraframework species in dealuminated zeolites H,Na-Y (deH,Na-H) leads to characteristic ¹³C CPMAS NMR signals in the chemical shift range of δ_{13C} = 230 to 240 ppm [1-4]. As an example, Fig. 1c (Fig. 5 in Ref. [4] and Fig. 9.2 in Ref. [5]) shows the ¹³C MAS NMR spectrum of ¹³C-2-acetone adsorbed on a steamed and non-hydrated (water-free) zeolite deH,Na-Y/81.5. The signal at δ_{13C} = 218 ppm with a shoulder at $\delta_{13C} \approx 215$ ppm is due ¹³C-2-acetone adsorption at weakly acidic Broensted sites and physisorption at AlOH groups, respectively. The broad ¹³C CPMAS NMR signal at δ_{13C} = 230 to 240 ppm, which does not exist in the spectrum of the parent zeolite H-Y before the dealumination, indicates the presence of Lewis acid sites. For comparison, ¹³C MAS NMR spectra of ¹³C-2-acetone adsorbed on a pure flame-derived silica without any acid sites and on a flame-derived silica/alumina with a molar aluminum fraction of 10 % are shown in Fig. 1a and Fig. 1b, respectively, without any indication for the presence of Lewis acid sites (no signals at $\delta_{13C} = 230$ to 240 ppm).





For aluminum-modified Na- and H-ZSM-5 zeolites, ¹³C CPMAS NMR signals at $\delta_{13C} \approx$ 235 ppm caused by ¹³C-2-acetone adsorbed at Lewis acid sites due to extraframework aluminum species were found [6]. In the case of ¹³C-2-acetone adsorption on surfaces with strong Lewis acid sites, such as on pure ZrO₂, ¹³C CPMAS NMR signals at $\delta_{13C} = 73$ to 76 ppm hint at conversion products of an aldol reaction of the ¹³C-2-acetone (**Fig. 2d**). In contrast, the spectra of ¹³C-2-acetone adsorbed on flamederived silica-zirconia (SZ/x with x = 100 means pure zirconia), prepared by flamespray pyrolysis (FSP), show no signals of probe molecules interacting with Lewis acid sites (**Figs. 2a to 2c**), but of those at strong Broensted acid sites ($\delta_{13C} = 224$ to 226 ppm). Summarizing, ¹³C-2-acetone is a suitable probe molecule for the ¹³C solidstate NMR detection of weak Lewis acid sites by signals at $\delta_{13C} = 230$ to 240 ppm) and strong Lewis acid sites by signals at $\delta_{13C} = 73$ to 76 ppm, caused by products of an aldol reaction.

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



Fig. 2

Catalyst preparation: Before the ¹³CPMAS 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 https://michael-hunger.de

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 K within 3 hours and the sample was evacuated at this temperature for 12 hours. After this treatment, the sample tube system was closed via the vacuum valve and disconnected from the vacuum line (after this line was ventilated with air).

Subsequently, the sample tube system and the vessel with ¹³C-2-acetone were connected at "vacuum line 2" as shown in Fig. 7 of Section "vacuum line 2", accessible via link "In Situ Solid-State NMR Techniques". If the ¹³C-2-acetone (99.5%, SIGMA-ALDRICH) was utilized for the first time, gas impurities were removed by thrice freezing and evacuation. For this purpose, put the acetone vessel into a dewar with liquid nitrogen and open the valve of the vessel after the acetone became rigid to evacuate the gas inside 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). Then, open the valve of the acetone vessel until an acetone 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 a dewar with liquid nitrogen and open the valve of this sample tube system. During acetone adsorption, warm up the catalyst sample 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 acetone molecules. For the removal of acetone physisorbed at SiOH and AIOH groups, the evacuation time can be 2 to 10 hours. Close the valve of the sample tube system and disconnect it from the vacuum line (after this line was ventilated by air).

¹³**C MAS NMR studies:** The ¹³C-2-acetone-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. The above-mentioned ¹³C cross-polarization (CP) MAS NMR spectra were recorded at a Bruker AVANCE III 400 WB spectrometer with a ¹³C resonance frequency of $v_0 = 100.6$ MHz, using a 4 mm MAS NMR probe with a https://michael-hunger.de

sample spinning rate of $v_{rot} = 8$ kHz, a contact time of 4 ms, and a repetition time of 4 s. For decreasing the ¹³C CPMAS NMR line width, high-power ¹H decoupling was applied during recording the induction decays of the ¹³C spins. Chemical shifts are referenced to adamantane powder ($\delta_{13C} = 38.55$ and 29.50 ppm) at spinning rates of $v_{rot} = 2$ to 3 kHz. This reference is easier to handle in MAS NMR rotors than liquid tetramethylsilane (TMS, $\delta_{13C} = 0$ ppm) with a boiling point of 299 to 301 K.

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