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

Spectroscopic background: Adsorption of ^{13}C-2-acetone on **Lewis acidic extra-framework species** in dealuminated zeolites H,Na-Y (deH,Na-H) leads to characteristic ^{13}C CPMAS NMR signals in the chemical shift range of $\boldsymbol{\delta_{13C}}$ **= 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 ^{13}C MAS NMR spectrum of ^{13}C-2-acetone adsorbed on a steamed and non-hydrated zeolite deH,Na-Y/81.5. The signal at δ_{13C} = 218 ppm with a shoulder at $\delta_{13C} \approx$ 215 ppm is due ^{13}C-2-acetone adsorption at weakly acidic Broensted sites and physisorption at AlOH groups, respectively. The broad ^{13}C 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, ^{13}C MAS NMR spectra of ^{13}C-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 δ_{13C} = 230 to 240 ppm).

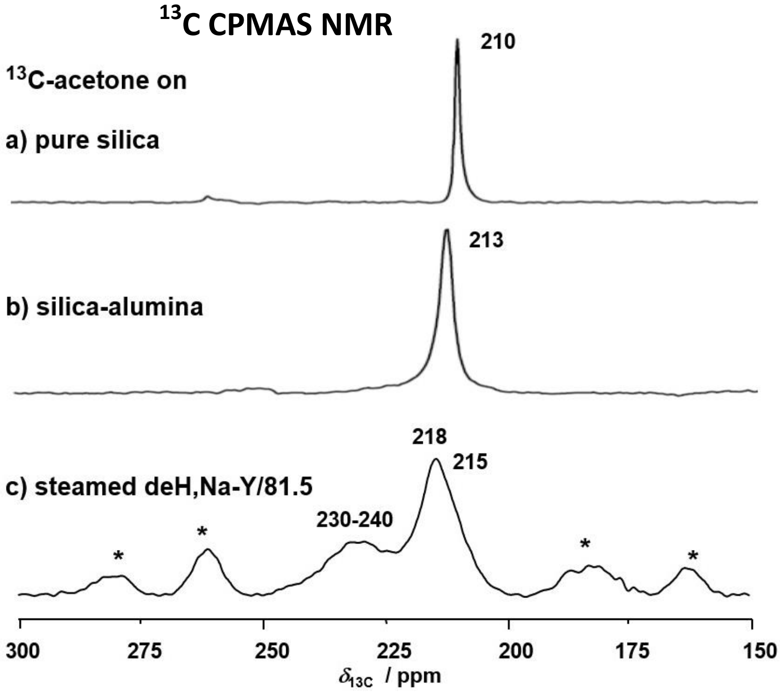

Fig. 1

For aluminium-modified Na- and H-ZSM-5 zeolites, ^{13}C CPMAS NMR signals at δ_{13C} ≈ 235 ppm caused by ^{13}C-2-acetone adsorbed at Lewis acid sites due to extra-framework aluminium were found [6]. In the case of ^{13}C-2-acetone adsorption on surfaces with strong Lewis acid sites, such as on pure ZrO_2, ^{13}C CPMAS NMR signals at δ_{13C} = 73 to 76 ppm hint at conversion products of an aldol reaction of the ^{13}C-2-acetone (**Fig. 2d**). In contrast, the spectra of ^{13}C-2-acetone adsorbed on flame-derived silica-zirconia (SZ/*x* with *x* = 100 means pure zirconia), prepared by flame-spray 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 (δ_{13C} = 224 to 226 ppm). Summarizing, ^{13}C-2-acetone is a suitable probe molecule for the ^{13}C solid-state NMR detection of **weak (signals at δ_{13C} = 230 to 240 ppm) and strong (signals of conversion products at δ_{13C} = 73-76 ppm) Lewis acid sites**. For reviews on the above-mentioned topics, see Refs. [8] and [9].

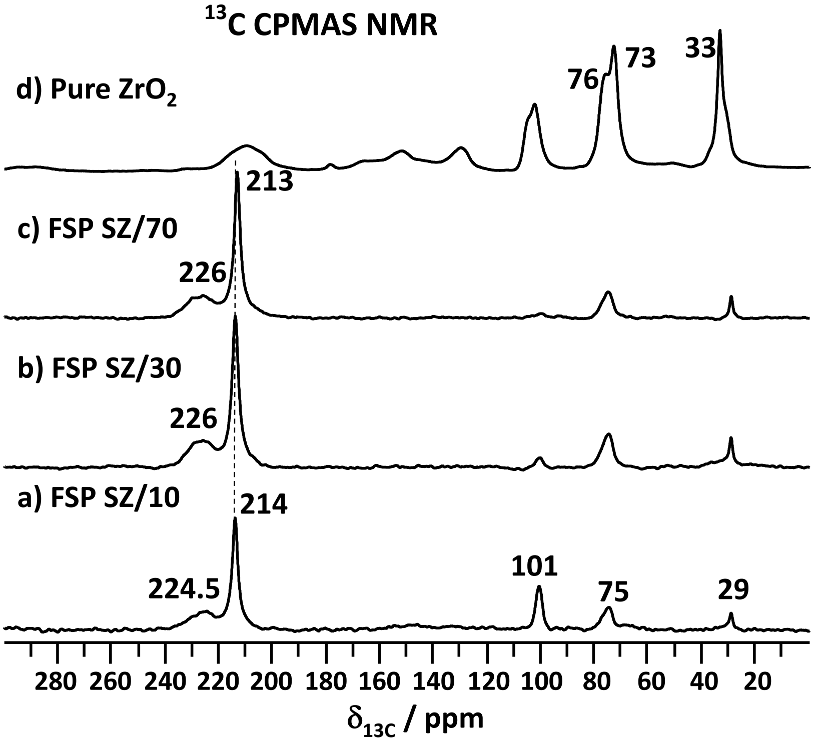

Fig. 2

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, the sample tube system is closed via the vacuum valve and connected with „vacuum line 2“.

The sample tube system and the vessel with ^{13}C-2-acetone are connected at „vacuum line 2“ as shown in Fig. 7 of the Section „vacuum line 2“. If the ^{13}C-2-acetone (99.5%, SIGMA-ALDRICH) is utilized for the first time, gas impurities must be removed by thrice freezing and evacuation (put the acetone vessel into 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). Now, 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 liquid nitrogen and open the valve of this sample tube system. During acetone 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. For removing the acetone from SiOH and AlOH groups, the evacuation time can be also 2 to 10 hours. Close the valve of the sample tube system and disconnect it from the vacuum line after the line was ventilated. The transfer of the dehydrated 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”).

^{13}C MAS NMR studies: The ^{13}C-2-acetone-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. ^{13}C cross-polarization (CP) MAS NMR spectra are recorded, e.g., at a Bruker AVANCE III 400 WB spectrometer using a 4 mm MAS NMR probe at a ^{13}C resonance frequency of ν_0 = 100.6 MHz, with a sample spinning rate of ν_{rot} = 8 kHz, with a contact time of 4 ms, and a repetition time of 4 s. For decreasing the ^{13}C CPMAS NMR line width, high-power ^{1}H decoupling should be applied during recording the induction decay of ^{13}C spins. Chemical shifts are referenced to adamantane powder (δ_{13C} = 38.55 and 29.50 ppm) at spinning rates of ν_{rot} = 2 to 3 kHz. This reference is easier to handle in MAS NMR rotors in comparison with tetramethylsilane (TMS, δ_{13C} = 0 ppm) with boiling point of 299 to 301 K.

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