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

Spectroscopic background: The chemical shifts of carbonyl atoms in ^{13}C-2-acetone dissolved in $CDCl_3$ and in a 100 % sulphuric acid solution are δ_{13C} = 205 and 245 ppm, respectively [1]. Based on the experimentally determined dependence of the resonance positions of carbonyl atoms in ^{13}C-2-acetone dissolved in aqueous sulphuric acid with varying concentration, a scale of the Broensted acid strength was introduced [1] (**Fig. 1, last line**, and Fig. 5, last line, in Ref. [1]) corresponding to a higher acid strength for a higher ^{13}C chemical shift value of adsorbed ^{13}C-2-acetone. In this scheme, furthermore, the ^{13}C chemical shift range for **^{13}C-2-acetone adsorbed at Broensted acid sites** of zeolites covers the range of **δ_{13C} = 215 ppm** for zeolite H,Na-X with low acid strength **up to δ_{13C} = 223 ppm** for zeolite H-ZSM-5 with high acid strength.

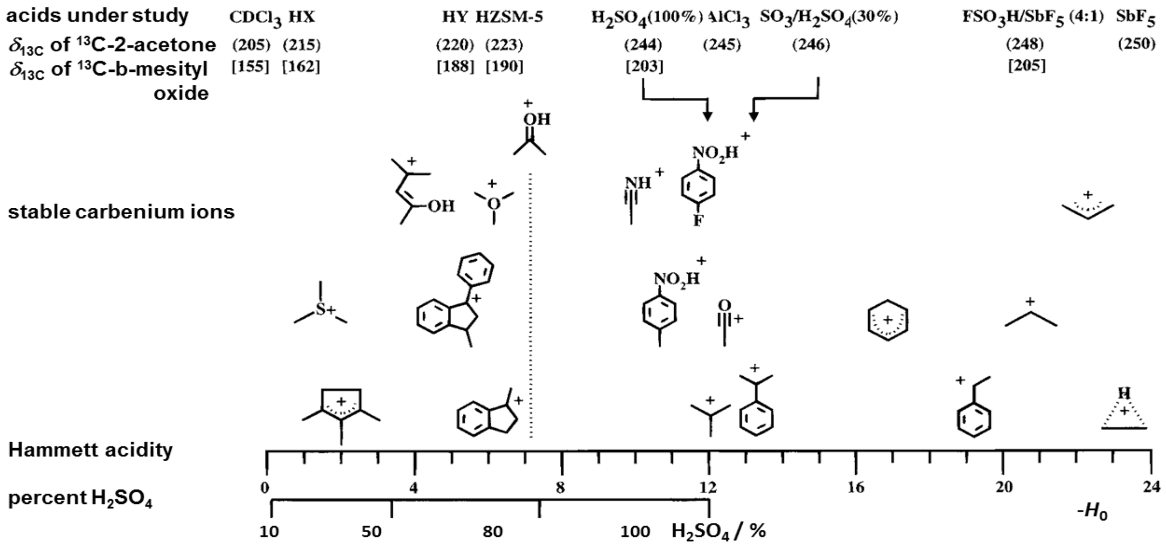

Fig. 1

A number of research groups [1-5] studied various solid catalysts by adsorption of ^{13}C-2-acetone and obtained the following sequence of the ^{13}C NMR shifts of carbonyl atoms corresponding to an increasing Broensted acid strength of these materials:

Silica (δ_{13C} = 210.0 ppm [2]) < H-SAPO-5 (δ_{13C} = 216.8 ppm [3]) < H-SAPO-34 (δ_{13C} = 217.0 ppm [4]) < H,Na-Y (δ_{13C} = 219.6 ppm [3]) < H-MOR (δ_{13C} = 221.8 ppm [3]) < H-[Ga]ZSM-5 (δ_{13C} = 222.8 ppm [3]) < H-ZSM-12 (δ_{13C} = 223.4 ppm [3]) < H-ZSM-5

(δ_{13C} = 223.6 ppm [3]) < H-ZSM-33 (δ_{13C} = 225.4 ppm [3]) < $H_3PW_{12}O_{40}$ and $AlPW_{12}O_{40}$ (δ_{13C} = 235 ppm [5]).

Based on the ^{13}C CPMAS NMR spectra of aluminium-modified Na- and H-ZSM-5 zeolites in **Fig. 2**, a sequence of the ^{13}C chemical shifts of adsorbed ^{13}C-2-acetone and of the Broensted acid strength of [6]:

Al/Na-ZSM-5/1 (δ_{13C} = 218 + weak 223 ppm) < Al/NaZSM-5/2 (δ_{13C} = 218 + 223 ppm) < H-ZSM-5 (δ_{13C} = 223 ppm) < Al/H-ZSM-5/1 (δ_{13C} = weak 218 + 223 + weak 225 ppm) < Al/H-ZSM-5/2 (δ_{13C} = 225 + weak 228 ppm)

was found. ^{13}C CPMAS NMR signals at δ_{13C} = 210 ppm are due to ^{13}C-2-acetone adsorbed at SiOH groups, while signals at $\delta_{13C} \approx$ 235 ppm are caused by Lewis acid sites due to extra-framework aluminium. These aluminium species, which are introduced inside zeolite pores, enhance the acid strength of the Broensted sites in their vicinity. According to **Fig. 2**, aluminium-modified H-ZSM-5 zeolites have a higher acid strength than modified Na-ZSM-5 zeolites. These Al/H-ZSM-5 catalysts are at the upper limit of the Broensted acid strength of zeolites and, therefore, also of the ^{13}C chemical shift range of adsorbed ^{13}C-2-acetone on Broensted acidic zeolites.

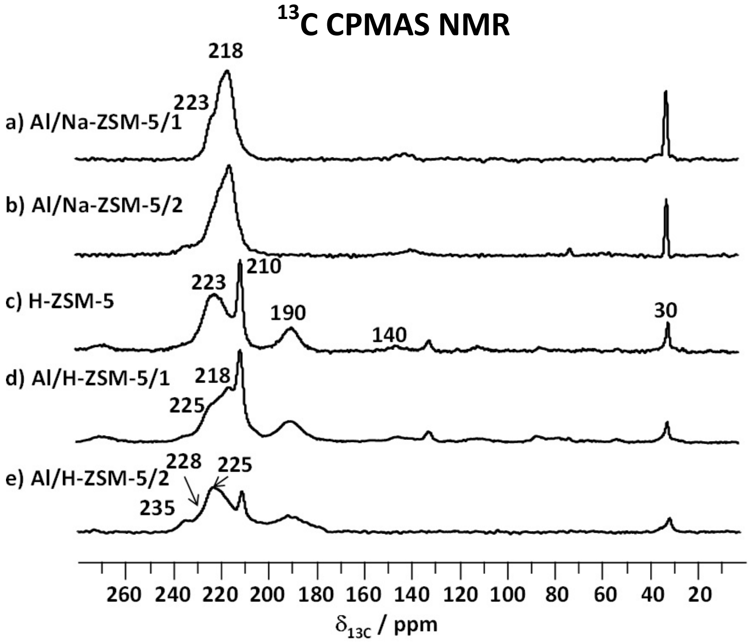

Fig. 2

Similarly, the Broensted acid strength of flame-derived silica-zirconia (*SZ*/*x* with *x* = 100 means pure zirconia), prepared by flame-spray pyrolysis (FSP), was investigated

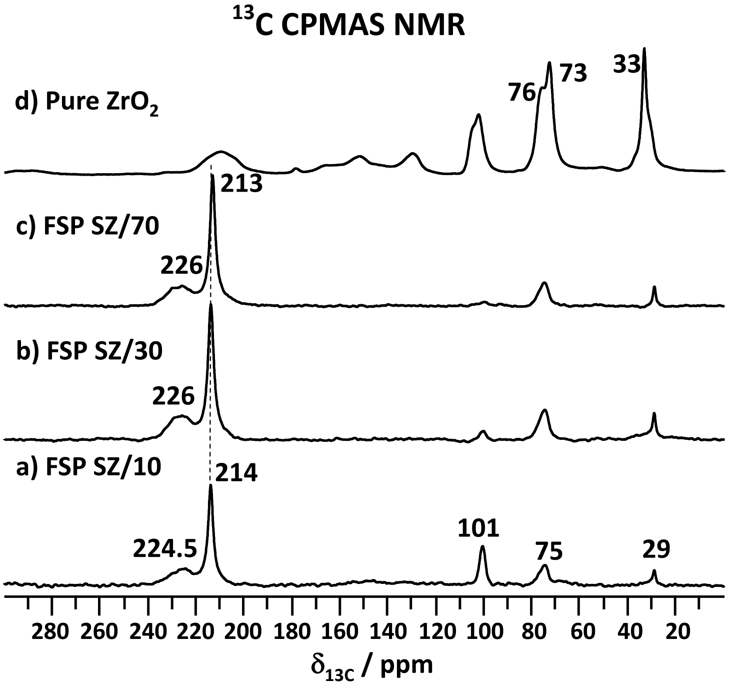

Fig. 3

by adsorption of ^{13}C-2-acetone and ^{13}C CPMAS NMR (see **Fig. 3**) [7]. Signals at δ_{13C} = 226 ppm for SZ/x samples with x = 30 and 70 hint at the presence of Broensted acid sites with an acid strength comparable with that of the strongest zeolites (compare with **Fig. 2**). The signals at δ_{13C} = 73-76 ppm in the ^{13}C MAS NMR spectrum of **Fig. 3d** are caused by the products of an aldol reaction of the ^{13}C-2-acetone at strong Lewis acid sites of pure ZrO_2. For reviews on the application of ^{13}C-2-acetone as molecular probe molecules for Lewis sites on solid catalysts, 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 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 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”).

^{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 the 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 100.6 MHz, with a sample spinning rate of 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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