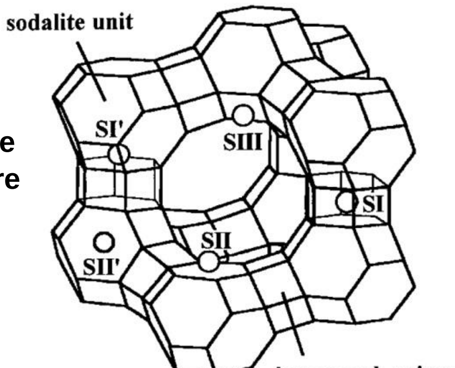
Characterization of cesium-containing catalysts by ^{133}Cs solid-state NMR

Spectroscopic background: ^{133}Cs nuclei have a spin of I = 7/2 and a quadrupole moment of Q = -0.343 x 10^{-30} m^2. Therefore, ^{133}Cs NMR signals of cesium atoms in solids are only weakly affected by quadrupolar interactions. The ^{133}Cs isotope has a natural abundance of 100 % and a sensitivity of 4.8 x 10^{-2} in comparison with ^{1}H nuclei (1.0), making this isotope a suitable candidate for NMR studies of solids. For basic principles of solid-state NMR, see lectures “Solid-State NMR Spectroscopy” for Bachelor students or PhD seminars, accessible via the link “Lectures for Students”.

Like sodium cations (see Section “method 3”), also cesium cations at extra-framework positions compensate negative framework charges of solids, such as caused by tetrahedrally coordinated framework aluminum atoms in zeolites. Cesium cations in zeolites are coordinated to framework oxygen atoms and located on well-defined cation sites of the zeolite structure (see e.g. **Fig. 1** for the faujasite structure of zeolites X and Y [1]). Furthermore, cesium is an important catalytic promotor, e.g. for the production of higher alcohols [2-5]. Therefore, cesium-containing solid catalysts are in the focus of solid-state NMR studies in the field of heterogeneous catalysis [3-15].



cation sites of the faujasite structure

Fig. 1

Combined solid-state NMR and X-ray powder diffraction investigations of a homologous series of cesium-exchanged zeolites allowed the assignment of ^{133}Cs MAS NMR signals caused by cesium cations at crystallographically non-equivalent cation sites [10]. Studies of faujasite-type zeolites revealed cesium cations at SI sites in the center of hexagonal prisms, SI' sites close to the center of 6-membered oxygen rings in sodalite cages, SII sites close to the center of 6-ring windows in the supercages, and at SIII sites close to 4-membered oxygen rings in the supercages (see **Fig. 1**) [10]. In **Fig. 2a**, the ^{133}Cs MAS NMR spectrum of a dehydrated **zeolite Cs,Na-Y** (n_{Si}/n_{Al} = 2.6) with the cesium exchange degree of 70 % is shown [1]. This spectrum was recorded at the resonance frequency of ν_0 = 52.5 MHz and with the sample spinning rate of ν_{rot} = 22 kHz. Based on the above-mentioned previous work [10], the observed ^{133}Cs MAS NMR signals were assigned to cesium cations at **SII (δ_{133Cs} = -73 ppm), SIII (δ_{133Cs} = -92 ppm), SII' (δ_{133Cs} = -107 to -115 ppm),** and **SI' (δ_{133Cs} = -152 to -155 ppm) sites**. Cesium hydroxide guest compounds, **CsO_xH_y**, introduced into zeolite Cs,Na-Y by impregnation and subsequent calcination, create additional base sites and cause a broad ^{133}Cs MAS NMR signal at **δ_{133Cs} = -15 ppm** (**Fig. 2b**).

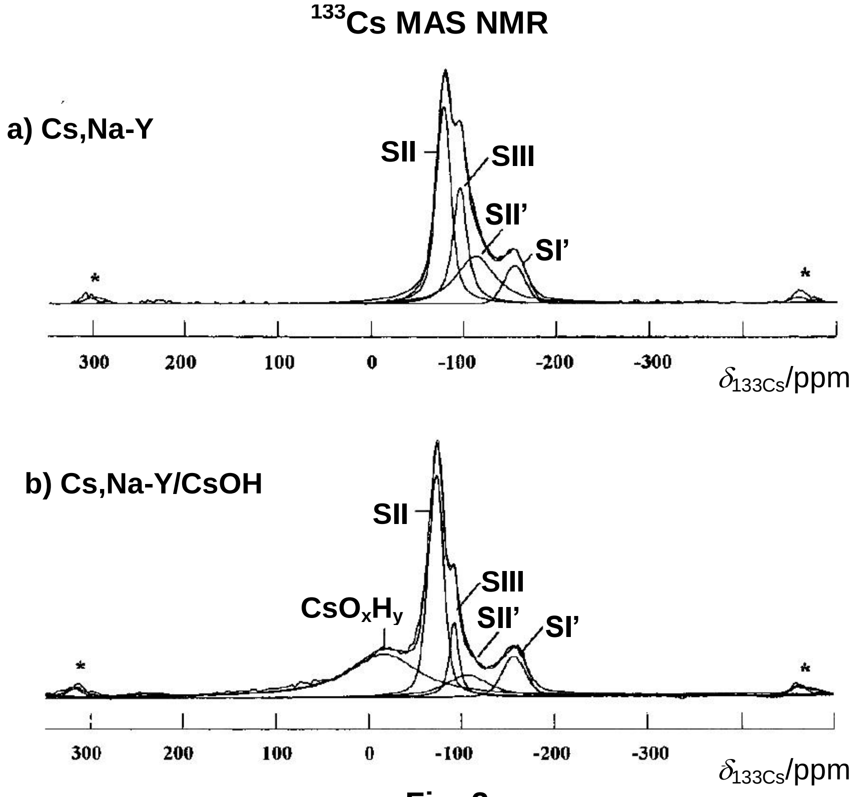


Fig. 2

^{133}Cs MAS NMR investigations carried out at resonance frequencies of ν_0 = 52.4 MHz and ν_0 = 26.2 MHz indicated a negligible quadrupole interaction of cesium cations in faujasite-type zeolites [10]. Therefore, the spinning sidebands (asterisks in **Figs. 2 to 4**) are due to chemical shift anisotropy. This makes the ^{133}Cs MAS NMR spectroscopic properties of cesium cations in zeolites more like nuclei with spin I = 1/2 than quadrupolar nuclei. On the other hand, the large ^{133}Cs chemical shift range makes the signals in ^{133}Cs MAS NMR spectra very sensitive to the environment of cesium cations in zeolites.

Variable temperature MAS NMR (VTMAS NMR) spectroscopy allows the study of the mobility of cations in zeolite catalysts [1, 8]. In **Fig. 3**, ^{133}Cs MAS NMR spectra of

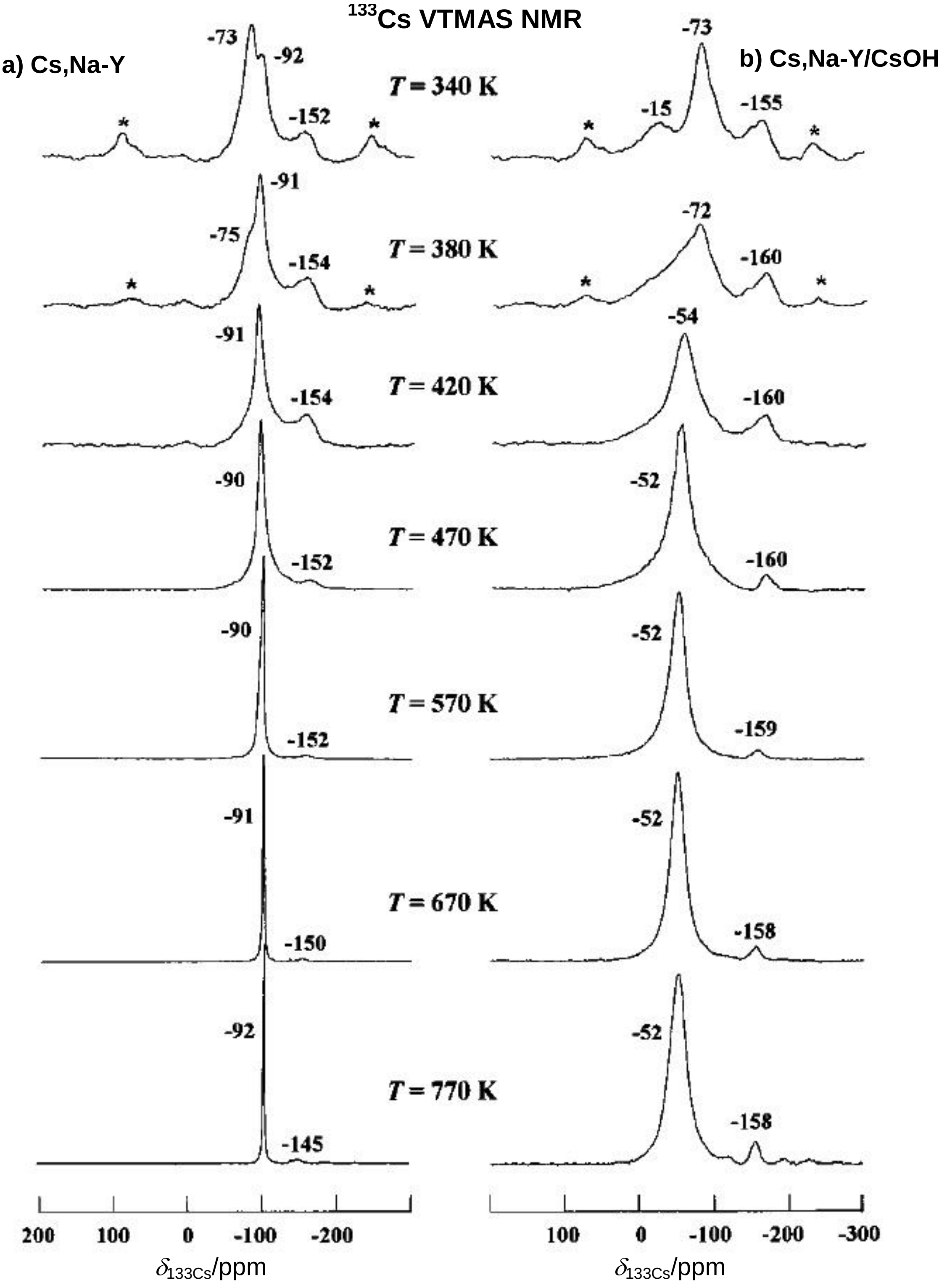


Fig. 3

dehydrated zeolites Cs,Na-Y (a) and Cs,Na-Y/CsOH (b), recorded at temperatures between T = 340 K and T = 770 K are shown [1]. According to these spectra, cesium cations in zeolite CsNaY are rigidly located at their crystallographic cation sites up to 340 K, as indicated by signals identical to those in **Fig. 2**. A further increase of the temperature causes a decrease of the spinning sidebands and a narrowing of the central lines. At T = 770 K, the spectrum in **Fig. 3a** consists of a narrow line at $\delta_{133\mathrm{Cs}}$ = -92 ppm, hinting at a rapid exchange of most of the cesium cations between their crystallographically non-equivalent sites. The weak signal at $\delta_{133\mathrm{Cs}}$ = -145 ppm is due to cesium cations located at less accessible SI′ sites in sodalite cages. According to the spectra in **Fig. 3b**, also cesium atoms contributing to CsO_xH_y guest compounds are involved in the rapid exchange with cesium cations located at SII and SIII sites, but not with those at SI' sites responsible for the signal at $\delta_{133\mathrm{Cs}}$ = -158 ppm for T = 770 K. Hence, the VTMAS NMR experiments demonstrate that cesium cations in zeolites are very mobile at temperatures, which are typical for catalytic applications.

One of the most important catalytic applications of cesium-containing basic zeolites is the **side-chain alkylation of toluene with methanol** [2-5]. Therefore, the interaction of methanol and toluene with cesium cations in zeolites Y was studied by ^{133}Cs MAS NMR spectroscopy [3, 4]. An interesting effect of the methanol adsorption on zeolites Cs,Na-Y and Cs,Na-Y/CsOH at room temperature is the absence of ^{133}Cs MAS NMR sidebands in **Figs. 4a and 4c** [3]. This observation is characteristic for mobile species with correlation times smaller than the reciprocal MAS frequency [16]. Hence, the methanol molecules are not rigidly bound to cesium cations responsible for the signals at $\delta_{133\mathrm{Cs}}$ = -52 ppm and $\delta_{133\mathrm{Cs}}$ = -32 ppm.

Another situation exists for the ^{133}Cs MAS NMR spectra of zeolites Cs,Na-Y and Cs,Na-Y/CsOH loaded with toluene in **Figs. 4b and 4d** [3]. In these spectra, very broad ^{133}Cs NMR MAS sideband patterns due to the low-field signals at $\delta_{133\mathrm{Cs}}$ = -40 ppm and $\delta_{133\mathrm{Cs}}$ = -20 ppm occur. Utilizing the method introduced by Herzfeld and Berger [17], the simulation of the broad sideband patterns yields a chemical shift anisotropy of $\Delta\sigma$ = -450±20 ppm and an asymmetry parameter of η = 0.5±0.1 for the spectra in **Figs. 4b and 4d**. The large chemical shift anisotropy indicates a very anisotropic distribution of the valence electrons, which are responsible for the shielding of the nuclei of the cesium cations. Furthermore, these cations contribute to the adsorbate complexes formed by adsorption of toluene. This effect hints to a strong interaction of toluene molecules with cesium cations, possibly via a one-side docking.

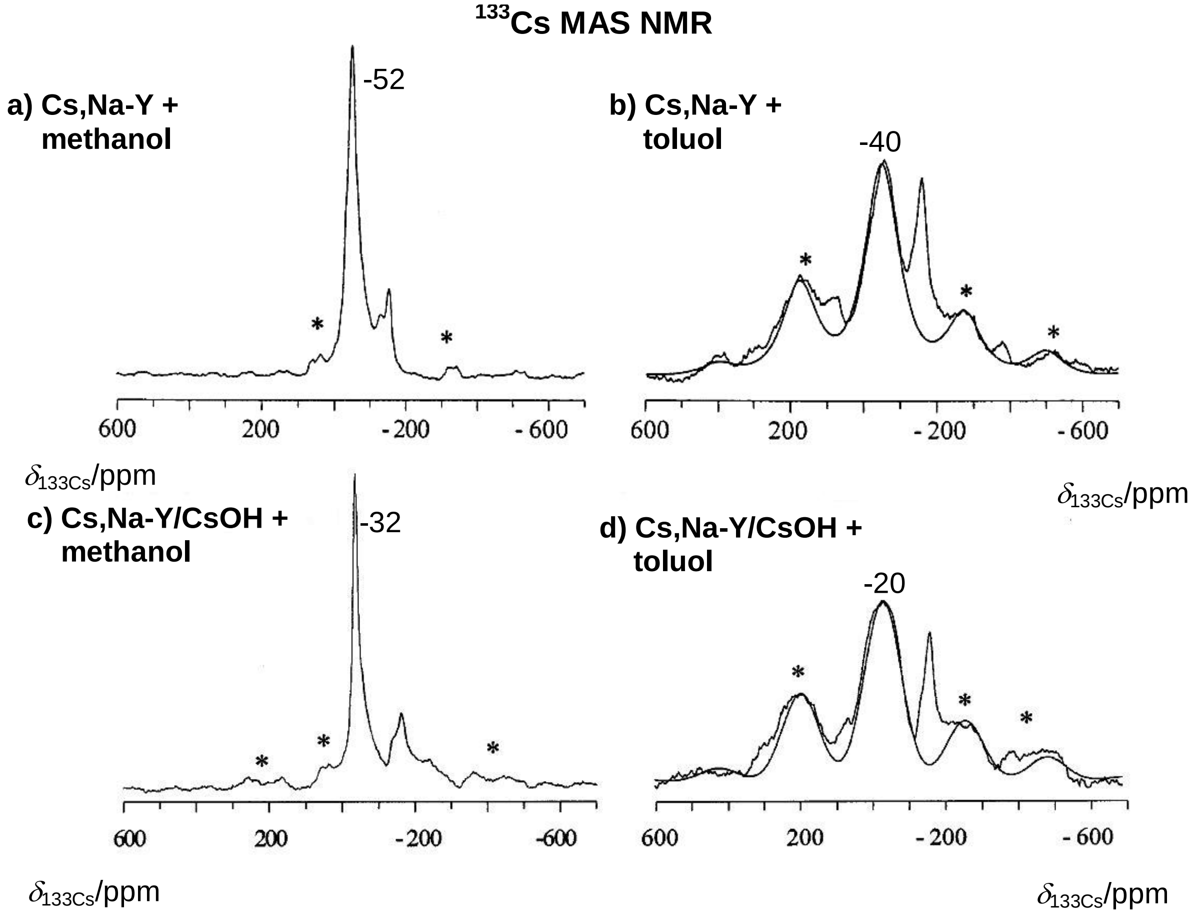


Fig. 4

Numerous additional ^{133}Cs solid-state NMR studies focused on the local structures of cesium cations in hydrated and dehydrated zeolites A and mordenite (see e.g. Refs. [7-9] and Ref. [6], respectively). In the ^{133}Cs MAS NMR spectra of **hydrated cesium-exchanged mordenite (Cs-MOR)**, a single line at the chemical shift of **δ_{133Cs} = -64 ppm** with a weak quadrupole coupling constant of **C_Q = 210 kHz** was found [6]. After **dehydration of zeolite Cs-MOR**, the ^{133}Cs MAS NMR spectrum consists of three components at chemical shifts of **δ_{133Cs} = -157 ppm, δ_{133Cs} = -186 ppm, and δ_{133Cs} = -24 ppm**, due to **cesium cations located at SII, SIV and SVI sites** of the mordenite (MOR) structure, respectively. The determined quadrupole coupling constants were **C_Q = 3.1 MHz for cesium cations at SII and SIV** sites and C_Q **= 3.2 MHz for cesium cations at SVI** sites [6].

Catalyst preparation: Often, the observation of well-separated ^{133}Cs MAS NMR signals, which are not affected by a rapid exchange, requires a dehydration of the powder samples at temperatures of T = 473 K or higher. For this purpose, the dehydration of the solid catalyst inside a „sample tube system 1“ at „vacuum line 1“ (accessible via the 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 473 K or higher 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. In this case, 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”, accessible via the link “*In Situ* Solid-State NMR Techniques”).

^{133}Cs solid-state NMR studies: The ^{133}Cs MAS NMR spectra shown in Figs. 2 to 4 were recorded at the resonance frequency of ν_0 = 52.5 MHz, after a single-pulse excitation (π/8 to π/12), and with the repetition time of 3 s. For reaching high resolution of the ^{133}Cs MAS NMR spectra, the sample spinning rate has to be at least ν_{rot} = 10 kHz and was ν_{rot} = 22 kHz in some cases. The VTMAS NMR experiments were performed utilizing a 7mm high-temperature MAS NMR probe DSI-740 of Doty Scientific Instruments. Referencing of the chemical shifts was performed to saturated CsCl solution ($\delta_{133\mathrm{Cs}}$ = 0 ppm).

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