Sodium Ions in Hydrated Zeolite Na-Y, Studied by Pulsed Nuclear Magnetic Resonance of ^{23}Na at 295 K

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The free induction decay of ^{23}Na of hydrated zeolite Na-Y has been measured at 295 K. Its intensity as a function of the length of the exiting pulse proves that a whole spectrum of 4 sodium ions per cage is observed. By ion exchange it is found that only the sodium ions in the six-membered rings (site S2) contribute to the observable NMR-signal.

By means of ^{23}Na-nuclear magnetic resonance sorption of various sorbates in zeolites of faujasite-type and type A has been studied, using the electric quadrupole of the ^{23}Na nucleus as a probe of the electric field gradients at the corresponding ion site, for a review see e. g. Lechert [1, 2]. But until now only broad-line NMR of ^{23}Na has been used, which is not well suited to obtain the absolute intensity of the NMR-signal, for which a double integration of the measured derivative of the spectrum is necessary and no easy calibration is available.

Therefore, we decided to measure the ^{23}Na-resonance by pulsed NMR, where the initial intensity V_0 of the free induction decay is proportional to the number of sodium nuclei observed and can be calibrated against the proton-signal of the same sample. Truely because of the dead-time of about 10 μs, this method is limited to line-widths of less than about 30 kHz. Consequently, we investigated hydrated (water activity of 0.80) faujasites, where the ^{23}Na-resonance is known to be motionally narrowed at 295 K by the rapid diffusion of the sorbed water molecules [3].

In order to get a well defined situation to begin with, zeolite Na-Y with a Si/Al-ratio of 2.36 has been used. This Si/Al-ratio gives 7 sodium ions per cage: 3 of them are localized in or before the double six-membered rings in the sodalite units (sites S1 and S1′) whereas 4 ions occupy site S2 near the middle of the six-membered rings between the sodalite units and the supercages (see Figure 1). This Si/Al-ratio assures that there are no non-localizable ions in the supercages, i. e. a possible "cation-solution" can not be expected. For a review of cation positions see e. g. Smith [4].

The pulsed ^{23}Na-NMR was done at 16 MHz with a Bruker B-KR 322 s spectrometer using a self-made probe head, especially built to prevent spurious ^{63}Cu-signals and "ringing" [5]. ^{23}Na-intensities and pulse lengths were calibrated against the proton-signal of the sorbed water of the same sample at the same frequency, using elementary relations and known water sorption capacity.

The ^{23}Na free induction decay, observed after 10 μs, was well exponential with a transverse relaxation time of 190 ± 20 μs. For a quantitative analysis it is necessary to know whether the observed part of the signal corresponds to a whole spectrum or only to the central line of a broad spectrum of spin 3/2. This can be decided by measuring the intensity of the signal as a function of the length t_p of the exiting pulse. Whereas for the exitation of a whole spectrum the classical formula holds:

$$V_0 = K M_0 \sin(\gamma B_1 t_p) \tag{1}$$

where M_0 = equilibrium magnetization, B_1 = exiting RF-field strength, γ = magnetogyric ratio and K = apparatus constant, the corresponding formula for the central line of a spin 3/2 is given by [6]

$$V_0 = K M_0 (4/10) \sin(2\gamma B_1 t_p)\,. \tag{2}$$

Thus the intensity of a spin 3/2 central line contains 40% of the whole intensity and is rotating twice as fast as the whole spectrum.

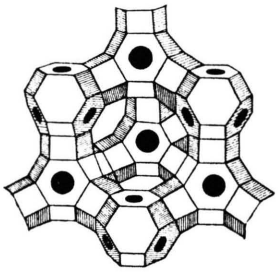

Fig. 1. Model of the alumosilicate frame-work of faujasites showing ion site S2 (full black circles). Ion sites S1 and S1′ are in and before the double six-membered rings.

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We have measured the ^{23}Na-intensity as a function of the pulse length t_p up to 50 μs. As the observable part of the free induction decay was well exponential and the longitudinal relaxation time $T_1 \approx 400$ μs, the correct initial intensity V_0 was obtained by extrapolating to the beginning of the RF-pulse [7]. The results are given in Fig. 2 together with the theoretical function of a whole spectrum of 4 sodium ions per cage, calculated by the first equation. As can be seen clearly, the rotating frequency corresponds well to an exitation of a whole spectrum, the differences between measured and calculated zero-crossings being within the limits of error as well as the deviations of the initial intensity V_0 from a single sinodial exitation function. No superposition of a separate signal of a central line, rotating twice as fast as the theoretical function, can be detected at a detection limit of about 10%.

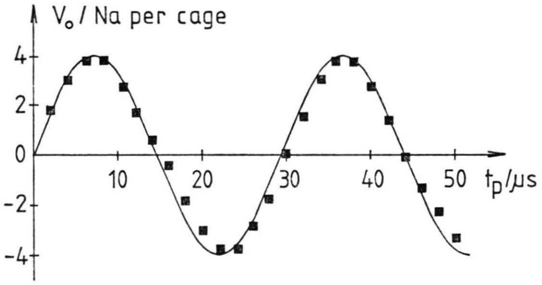

Fig. 2. Initial intensity V_0 of the ^{23}Na free induction decay of hydrated ($a_W = 0.80$) Na-Y zeolite at 295 K as a function of the pulse length t_p: ■ experimental points, full line is calculated for the full exitation of the spectrum of 4 sodium ions per cage by Equation (1).

The intensity of 4 sodium ions per cage suggests that the ^{23}Na-signal originates from the sodium ions in site S2. It has been concluded from ion-exchange studies [8] and proved by water exchange kinetics [9] that these S2-ions can be exchanged selectively against Ca-ions, if the exchange is performed at ambient temperature. We have prepared such a sample (Ca, Na)-Y and looked for its ^{23}Na-signal: At a detection limit of 3% no NMR-signal could be detected any more after this ion-exchange. This proves that the ^{23}Na-signal of hydrated Na-Y zeolites originates only from ions in site S2, the signal from the remaining 3 ions in sites S1 and S1′ being too broad (greater than about 30 kHz) to be detected.

Further studies concerning the temperature dependence, cation exchange and variation of the Si/Al-ratio of faujasites and type A zeolites are in progress.

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