A New Assignment of the Signals in ^{23}Na DOR NMR to Sodium Sites in Dehydrated NaY Zeolite

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Spectral simulations of ^{23}Na MAS and double rotation (DOR) NMR spectra of dehydrated NaY zeolite, CaNaY and Mo(CO)$_6$ adsorbed in NaY allow the assignment of four signals to the five different Na$^+$ sites.

Several ^{23}Na NMR techniques have been used to probe the distribution of the sodium cations in zeolites.[1–4] However, NMR spectra of quadrupolar nuclei, like ^{23}Na, are limited in resolution, because of the second-order quadrupolar line broadening of the readily observable central $+1/2 \leftrightarrow -1/2$ transition in these spectra. The double rotation NMR (DOR) technique is able to reduce this line broadening and thus gives a much better spectral resolution.

Recently, Jelinek *et al.*[5,6] measured the ^{23}Na DOR NMR spectrum of dehydrated NaY at 11.7 T. They found three different ^{23}Na DOR NMR signals (centrebands) with the assignments as summarized in Table 1. Subsequently, Hunger *et al.*[7] published a reassignment of the ^{23}Na DOR and MAS spectra with only two distinguishable signals (7.0 and 9.4 T): one is assigned to Na$^+$ cations at site I and the second signal to all other Na$^+$ sites, see again Table 1. The five different sites for Na$^+$ cations in zeolite Y are illustrated in Fig. 1.

Table 1 Assignments of the ^{23}Na DOR NMR signals in dehydrated NaY to the five different sodium sites as given in literature and according to our simulations

Site	δ_{obs} (7.0 T)^a /ppm, ± 1.0	δ_{obs} (9.4 T)^a /ppm, ± 1.0	δ_{obs} (9.4 T)^b /ppm, ± 1	δ_{obs} (11.7 T)^c /ppm, ± 0.3
I	−7.6	−6.4	−6	−4
I′/II′	−71.0	−41.0	−24	−42
II	−71.0	−41.0	−43	−30
III	−71.0	−41.0	−46	−30

[a] Hunger *et al.*[7] The recalculated chemical shift values are given with respect to a NaCl solution; ref. 7 uses solid NaCl as a reference. [b] Present assignments. [c] Jelinek *et al.*[5,6]

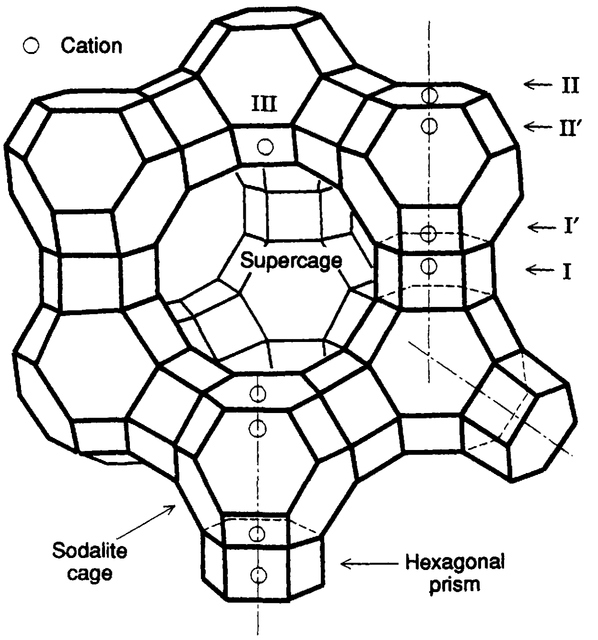

Fig. 1 Structure of zeolite Y. The five different Na$^+$ sites are indicated by roman numerals.

Here, we present evidence that in fact four different Na$^+$ sites can be distinguished with ^{23}Na DOR and MAS NMR, in combination with simulation procedures. The simulations were carried out with the program QNMR.[8] This program, which works in a non-iterative way, requires signal positions, quadrupolar coupling constants (e^2qQ/h), asymmetry parameters (η) and values for line broadening as input variables.

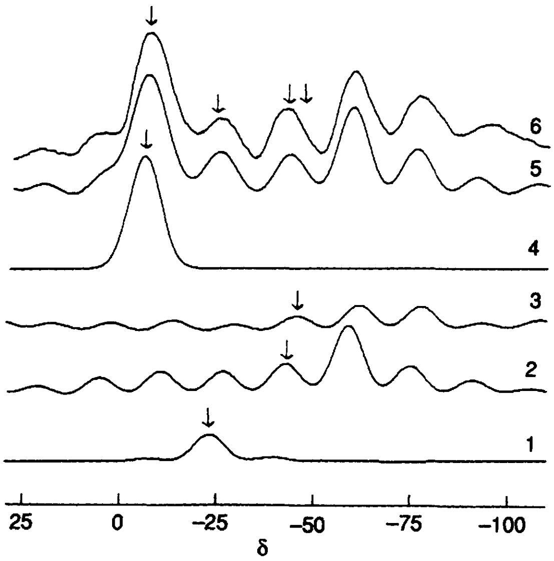

Fig. 2 Individual lines/patterns (traces 1–4), simulated (trace 5) and experimental (trace 6) ^{23}Na DOR spectra (850 Hz) of dehydrated NaY at 9.4 T. Trace 1: site I′/II′; trace 2: site II; trace 3: site III; trace 4: site I. Signals are indicated by arrows.

Table 2 Quadrupolar parameters used for the simulation of the NMR spectra of dehydrated NaY

Site	δ_{iso}/ppm, ± 1^a	P_Q/MHz, ± 0.1^b
I	−6	0.4
I′/II′	−12	2.3
II	−4	4.2
III	5	4.7

[a] δ_{iso} = isotropic chemical shift. [b] $P_Q = e^2qQ/h^*(1 + \eta^2/3)^{1/2}$.

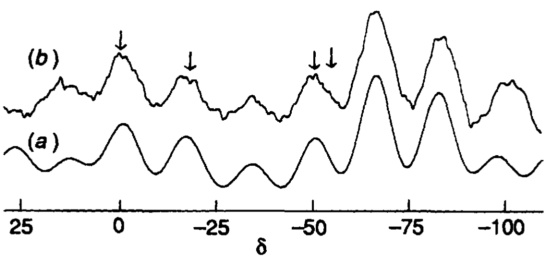

Fig. 3 Simulated (*a*) and experimental (*b*) ^{23}Na DOR spectrum (850 Hz) of Ca$_{19}$Na$_{16}$Y at 9.4 T. Signals are indicated by arrows.

For a given simulation, in which the outer DOR rotor speed, the Larmor frequency and the spin quantum number are fixed parameters, the variables mentioned above and the relative contributions of the different signals are optimized. The results are included in Table 1. Fig. 2 depicts our ^{23}Na DOR NMR spectra of dehydrated NaY at 9.4 T (outer rotor spinning frequency 850 Hz) and the accompanying simulation traces for the different sites. Additional spectra were taken at 700 and 1000 Hz to sustain these results. All spectra were acquired by rotor-synchronized pulsing,[9] consequently only the even sidebands are present.

Arguments for assigning four, rather than two[7] or three[5,6] signals are twofold. (*i*) A considerable part of the signal intensity at δ −24 (9.4 T) does not change position upon changing the DOR rotation speed, both in our study and in that of Hunger *et al.*[7] This points to the presence of a centreband at δ −24 overlapping with sidebands from other sources. (*ii*) In the high-field part of the 9.4 T DOR NMR spectra the distances between lines become irregular (*i.e.* unequal to twice the outer rotor frequency), both in our study and in that of Hunger *et al.*[7] This can only be reconciled with an extra centreband, besides the signal at δ −43, at approximately δ −46, bringing the total number of assigned lines to four (our assignment of the δ −6 line to site I Na$^+$ cations agrees with previous assignments[5–7]). The spectral parameters, summarized in Table 2 originate from simulations of our own measurements. The second-order quadrupolar shifts at 9.4 T of the four centrebands can be obtained by subtracting the values of δ_{iso} in Table 2 from the corresponding values of δ_{obs} in the fourth column of Table 1. In addition, the parameters in Table 2 enable us to simulate the ^{23}Na DOR or MAS spectra at 7 T[7] and 11.7 T,[5,6] excluding some minor changes in relative intensities between signals, which we ascribe to the proven sensitivity of the Na$^+$ distribution in NaY samples to the preparation methods and thermal treatments.[2,10]

Further support for our assignment comes from measurements and simulations of the ^{23}Na DOR NMR spectra (9.4 T) of Ca$_{19}$Na$_{16}$Y. At this level of ion exchange with Ca^{2+} most of the I sites will be occupied by Ca^{2+}. Far-IR spectra (not shown) indicate that most of the Na$^+$ cations are in the supercages (sites II and III) with only a small amount of Na$^+$ retained at sites I and I′/II′. The corresponding ^{23}Na DOR NMR spectra are shown in Fig. 3, the relevant parameters are summarized in Table 3. Again four signals were needed. Interestingly, the P_Q values of the Na$^+$ cations in the supercages are enlarged, implying enhanced electric field gradients at the sites II and III, presumably induced by local changes in the framework geometry.[11]

Table 3 Quadrupolar parameters used for the simulation of the NMR spectra of Ca$_{19}$Na$_{16}$Y and Mo(CO)$_6$/NaY

	Ca$_{19}$Na$_{16}$Y		Mo(CO)$_6$/NaY	
Site	δ_{iso}[a] /ppm, ± 1	P_Q[b] /MHz, ± 0.1	δ_{iso}[a] /ppm, ± 1	P_Q[b] /MHz, ± 0.1
I	−2	0.4	−2	0.4
I′/II′	−4	2.3	−10	2.3
II	−3	4.6	−9	2.8
III	3	5.0	−9	2.8

[a] δ_{iso} = isotropic chemical shift. [b] $P_Q = e^2qQ/h^*(1 + \eta^2/3)^{1/2}$.

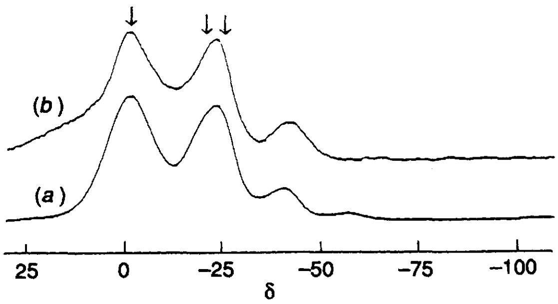

Fig. 4 Simulated (*a*) and experimental (*b*) ^{23}Na DOR spectrum (850 Hz) of Mo(CO)$_6$/NaY at 9.4 T. Signals are indicated by arrows.

Fig. 4 depicts the ^{23}Na DOR NMR spectra of NaY, in which Mo(CO)$_6$ has been adsorbed. Mo(CO)$_6$ is known[12] to interact only with Na$^+$ cations in the supercages (sites II and III). Our results (Table 3) show that the quadrupolar interactions of the supercage Na$^+$ cations have decreased considerably, due to a more symmetric surrounding of these cations upon Mo(CO)$_6$ adsorption, whereas the sodalite cage Na$^+$ cations (sites I′/II′) are not affected. Following the assignments of Hunger *et al.*,[7] some of the intensity between δ −43 and −46 (our spectra) should have been retained. This is in contrast to our observations; our simulations still require separate signals for sodalite- and supercage-Na$^+$ cations.

On the basis of these experiments we feel we have presented evidence for the assignment of four different signals in the ^{23}Na DOR and MAS NMR spectra of NaY zeolite. The distinction between sites II and III can be made, based on the known relative numbers of Na$^+$ cations at these sites.[10] Further experiments are obviously needed to enable the distinction of the sites I′ and II′ by ^{23}Na NMR spectroscopy. Possibly, the DOR sidebands should be minimized as suggested very recently by Samoson.[13] Newer simulation procedures, including *e.g.* chemical shift anisotropy and dipolar interactions could be used to extract more and more precise variables from the DOR spectra.[14,15]

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