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^{23}Na MAS NMR Evidence for a New Sodium Cluster and Na$^{\bullet}$ in Metal-Loaded Zeolites[†]

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In the last few years there has been much interest in the formation of metal aggregates in metal-loaded zeolites.[1-4] In the case of zeolites loaded with alkali metals, the focus has been on (i) how the interaction of metallic clusters can lead to bulk metal properties and (ii) the possibility of observing quantum size effects. When sodium or other alkali metals are loaded into anhydrous sodalite and zeolites X, Y, and A, colored materials are obtained ranging from light blue or pink for lightly loaded materials to black for heavily loaded samples. EPR, NMR, and optical techniques[1-5] have been used to study these materials, with EPR giving perhaps the most useful information. In the case of Y and A zeolites, a number of studies have identified the Na$_4^{3+}$ cluster, thought to reside in the β cage, from the characteristic 13-line spectrum with a hyperfine coupling constant of 3.3 mT. Early studies argue for the presence of a second, metallic particle in the Y α cage on the basis of a sharp central line in the EPR spectrum. Anderson and Edwards[2] have argued convincingly that none of the experimental data are, in fact, consistent with such a model and that the sharp line should be attributed to the interaction between Na$_4^{3+}$ clusters in neighboring β cages. Despite a number of attempts, NMR studies[2,3] have failed to show convincing evidence for the presence of distinct species other than cations in the alkali metal-loaded zeolites. In this communication we report the first evidence for new ^{23}Na species in Y, X, and A zeolites as identified by ^{23}Na magic angle spinning (MAS) NMR.

The ^{23}Na NMR spectrum[6] of sodium-loaded NaY zeolite is shown in Figure 1 as a function of loading. In addition to the signal from the cationic Na$^+$ with a peak at −10 ppm, there is a line at +51 ppm for the Na$_{11}$/NaY and at +48 ppm for the Na$_7$/NaY samples (Na$_x$ corresponds to x atoms per unit cell).

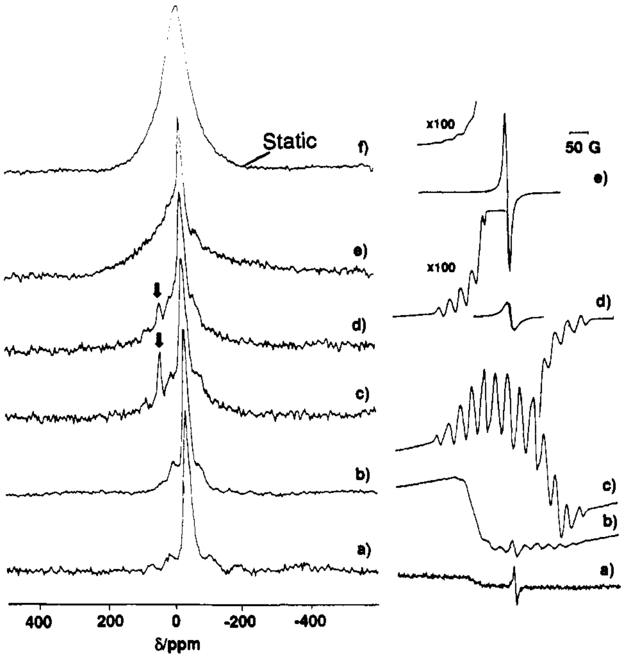

Figure 1. ^{23}Na MAS NMR (left column) and EPR spectra (right column) of NaY zeolite loaded with increasing quantities of Na metal vapor; x equals the approximate number of Na per unit cell: (a) x = 0, (b) x = 3, (c) x = 7, (d) x = 11, (e) x = 22. Also shown is one ^{23}Na spectrum obtained for a static sample: (f) x = 7. The arrows indicate the line arising from the new species.

The measured shift of the spectral line in question is independent of field, so that the line position represents a true chemical shift unaffected by second-order quadrupolar effects. We note that the shift value is well outside the range of normal ^{23}Na chemical shifts and that this line becomes evident only on application of MAS. The appearance and subsequent disappearance of the signal, either by broadening or by shifting and broadening, parallels that of the EPR signal arising from the Na$_4^{3+}$ cluster recorded for the same sample (Figure 1), suggesting that the NMR and EPR signals are in some way related. However, the following calculations demonstrate that the NMR and EPR signals do not represent the same species. If we consider that the EPR signal is essentially isotropic with spin density at the nucleus due mainly to electrons in s orbitals, the expected paramagnetic shift of the nuclear resonance can be calculated from[7]

$$\Delta B/B = -g\mu_B S(S+1)a_N/3g_N\mu_N kT \qquad (1)$$

where a_N is the hyperfine coupling constant (3.3 mT) and μ_B and μ_N are the electronic and nuclear magnetic moments. This gives a shift of 9170 ppm, much larger than the Knight shift of metallic sodium at 1132 ppm and 2 orders of magnitude larger than the observed 50 ppm, which therefore cannot be due to Na$_4^{3+}$. Consequently we postulate that the NMR signal is due to a diamagnetic cluster Na$_m^{n+}$ ($n + m$ is even) and that the shift could be due, at least in part, to the coupling of the electron spins of the Na$_4^{3+}$ and Na$_m^{n+}$ in adjacent β cages. There is precedent for this kind of interaction from ESEEM studies[4,5] on sodium-loaded sodalite, where a hyperfine coupling constant of 0.1 mT was found for the interaction of the Na$_4^{3+}$ cluster with a Na$^+$ in a neighboring cage. If we apply eq 1 to calculate the shift in nuclear resonance frequency for a hyperfine coupling constant of 0.1 mT, we find a value of 30 ppm, certainly of the correct order of magnitude. However, the line did not shift with temperature as predicted by the above equation, so that other

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(6) Weighed quantities of commercial zeolite samples (LZY-52, 4A, 13X) were dehydrated in an all-quartz reaction vessel. Weighed quantities of sodium or potassium in small open quartz tubes were then added to the dried samples in an argon atmosphere glovebox. The reaction vessels were then re-evacuated and sealed and placed in a furnace at 250 °C. The sorption of alkali metal became apparent almost immediately upon heating from the change in color of the sample. In order to ensure completion of the sorption process, samples were left in the furnace for several days. The product was then transferred into a side arm attached to the reaction vessel, which, when sealed off, could be spun (at about 3 kHz) in a spinner suitable for the Chemagnetics pencil probe. Samples containing excess sodium or incompletely reacted samples gave an isotropic resonance due to metallic Na at about 1130 ppm. This line was absent from all the spectra shown in Figure 1. ^{23}Na MAS NMR spectra were obtained at a frequency of 52.9 MHz on a Bruker MSL-200 spectrometer at or 79.35 MHz on a Bruker AMX-300 spectrometer. Sweep widths were 100 kHz, and pulse turning angles were kept small in order to obtain quantitative spectra. ^{23}Na chemical shifts were referenced to solid NaCl.

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shift mechanisms must be considered. Relatively large downfield shifts with respect to the hydrated cation also have been observed for charged silver atom clusters.[8]

Anderson and Edwards' model[2] could account for the appearance of both paramagnetic and diamagnetic clusters at low loading and the subsequent disappearance of their signals as the electrons in different clusters couple more strongly with increasing cage occupancy. The fact that the signal becomes visible relatively easily on application of MAS suggests the presence of weakly anisotropic interactions, much the same as for the Na_4^{3+} cluster, perhaps so because of motional averaging.

It is very significant that signals at similar shift values can be seen in other zeolite samples (+48 ppm in Na/NaA loaded with excess sodium as evident from the metallic shift seen at +1126 ppm, and +50 ppm in Na_{24}/NaX zeolite). Since the sodalite cage is common to both A zeolite and faujasite-type structures, it is consistent with the earlier suggestion that the +50 ppm signal is due to a Na_m^{n+} cluster stabilized inside a sodalite cage. An Na_m^{n+} cluster might be formed by addition of Na to an existing cluster, e.g., Na_5^{3+} from Na_4^{3+} inside the sodalite cage, or by transfer of an electron from a Na to a paramagnetic cluster, though at this stage we have no idea of the relative stabilities of the diamagnetic clusters and which might be stabilized by the zeolite framework.

In the search for new species, some other metal-loaded systems were examined as well, including some in which potassium metal was deposited into Na zeolites. The most interesting result obtained is shown in Figure 2 for a K/NaA (excess K) zeolite. The sample shows a strong signal at −65 ± 2 ppm, quite easily visible in both spun and stationary samples. Again, this is a highly unusual shift for sodium species. The nearest reported resonance shifts range from −58 to −63 ppm,[9,10] referenced relative to dilute aqueous Na^+, and these have been consistently identified with the sodide ion, Na^-. When referenced to solid NaCl (correction factor −5.6 ppm[9]), this range becomes −63.6 to −68.6 ppm. We postulate that the −65 ppm resonance in K/Na zeolite also should be attributed to a sodide ion. It is significant to note that the chemical shift of this spherical anion has shown little sensitivity to its environment,[9] which fits the observations both that the resonance line is isotropic and that it occurs nearly at the same chemical shift as in solid sodides and in alkali metal solutions. We can only speculate as to the mechanism of formation of Na^- in this system. Certainly the reaction $K + Na^+ \rightarrow K^+ + Na$ is favored by the relative electrode potentials. The next step to produce Na^- may be involved in the formation of larger charged potassium clusters such as K_4^{3+}. One possible overall reaction might then be

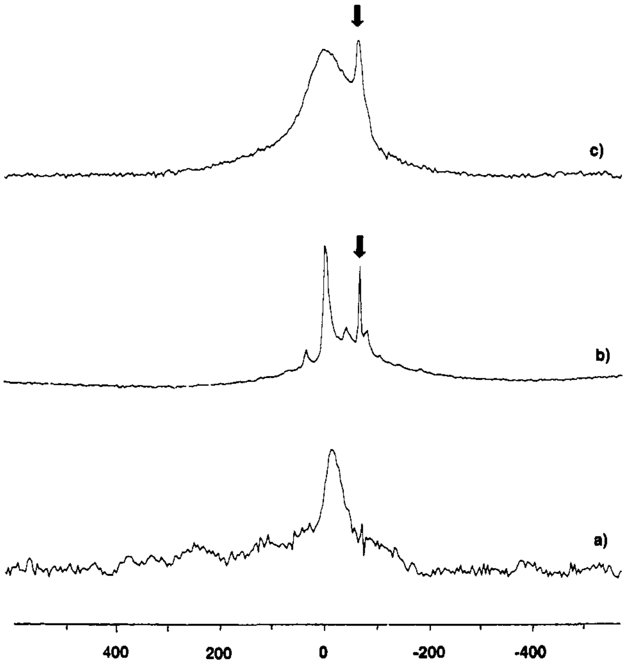

Figure 2. ^{23}Na NMR spectra for a sample of guest-free dehydrated NaA zeolite with MAS (a) and for a sample of K/NaA zeolite with MAS (b) and stationary (c). The arrows indicate the resonance thought to be due to Na^-.

$$4K + 2Na^+ \rightarrow K_4^{3+} + Na^- + Na$$

The Na^- must presumably be isolated in a cage away from contact with other metal atoms or ions, perhaps inside one of the smaller prisms connecting the β cages. The observation of the sodide anion in potassium-loaded NaA zeolite suggests some interesting analogies between electron-rich environments in zeolites, cryptand salts, and strong electron-donor solvents.

Clearly, speciation in metal-loaded zeolites is rather more complex than envisaged previously.

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