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Alkali Metal Loaded Zeolite LiA: Evidence for Highly Symmetrical Rb$^-$ and K$^-$

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We present NMR evidence for the existence of Rb$^-$ and K$^-$ in metal-loaded LiA zeolite, in an environment with surprisingly high symmetry. For the first time quantitative information about these species has been obtained.

Metal-loaded zeolites were first synthesized in 1966 by Rabo et al.[1] and have attracted persistent study because of the unusual ions, clusters, and filamentary structures which can form.[2] One such species is the remarkable alkalide anion, M$^-$. NMR spectroscopy, in tandem with X-ray structural studies, has become the major tool in the study of these rare anions. They have a unique NMR signature because of a characteristic high-field shift and usually a low sensitivity to chemical shielding and quadrupolar interactions in comparison to alkali cations. This is attributed to the two additional s electrons on M$^-$ which produce a significantly larger ion and a spherical charge distribution that is highly effective in screening the p electrons. Recognition of this basic difference thus allows the assignment of NMR resonances of M$^-$ in nonaqueous solutions[3] and in solids where both M$^+$ and M$^-$ coexist.[3,4] We previously reported the unexpected occurrence of Na$^-$ in a K-loaded NaA zeolite.[5a] Since then Na$^-$ has also been observed in Rb-loaded NaA.[5b,6] Such zeolite-bound alkalide ions, however, have not yet been detected in crystallographic studies, presumably because of their relatively low concentration. Thus, much about the origin, location, and stability of Na$^-$ remains unknown.

We have examined two series of cation-exchanged NaA zeolites, RbNaA and LiA, loaded to various levels with Rb by vapor absorption.[7] In the series of ^{87}Rb NMR spectra[8] obtained for Rb$_x$/LiA, where *x* is the number of Rb added per primitive unit cell (u.c.), one very narrow line stands out at -87 ± 1 ppm, Figure 1.3,4. It is the only resonance observed for $x \leqslant 3$ the strongest one for $x = 5$, and disappears for $x = 10$. For $x = 5$ and 10, other broader lines are visible at −45 and +105 ppm. These are also seen in Rb$_5$/NaA, Figure 1.2, and Rb$_x$/RbNaA zeolites and we tentatively attribute them to Rb$^+$ and diamagnetic Rb-containing cluster species, respectively. The −45 ppm assignment is made by analogy with anhydrous RbNaA, which shows only one line, at −56 ppm, Figure 1.1, for Rb$^+$. The sharp line does not appear in the ^{87}Rb spectra of Rb$_5$/NaA and the Rb$_x$/RbNaA series. Instead a line corresponding to Na$^-$ appears in the ^{23}Na NMR spectrum at −52.6 ppm (reference: 1 M NaCl solution) when $x = 4$ Rb/u.c.

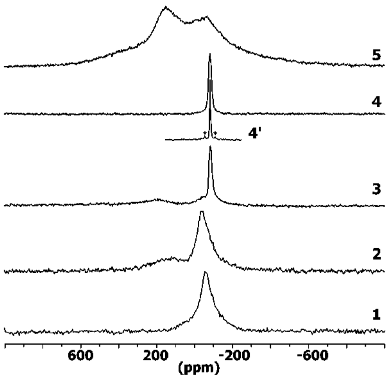

Figure 1. ^{87}Rb NMR static spectra of (1) dehydrated RbNaA zeolite, and rubidium-loaded samples: (2) Rb$_5$/NaA; (3) Rb$_5$/LiA; (4) Rb$_3$/LiA (3.5 kHz MAS shown in (4′), * = spinning sidebands); and (5) Rb$_{10}$/LiA.

The line at −87 ppm has interesting NMR characteristics, which together strongly suggest that it should be assigned to Rb$^-$:

(1) Its shift falls within the known range of +120 to −197 ppm for Rb$^-$ in condensed phases,[4,9] and outside the known range for Rb$^+$ of +328 to −56 ppm.[6,10] In solution,[9] however, and in three solid crown ether complexes[4] Rb$^-$ shifts fall in the narrow range of −185 to −197 ppm, which appears to be "typical" for relatively isolated Rb$^-$. Two exceptional Rb$^-$ shifts occur at +33 ppm in Rb$^+$(C222)Rb$^-$ and +120 ppm in Rb$^+$(18-crown-6)Rb$^-$,[4] associated with dimers of Rb$^-$ and chains of Rb$^-$ (in further contact with Rb$^+$), respectively. These shifts provide ample evidence that Rb$^-$ has some sensitivity to its environment; even the "typical" shifts are 17−29 ppm downfield from the calculated shift of Rb$^-$ in the gas phase.[3e,f] Thus although a shift of −87 ppm is unusual for Rb$^-$ such an assignment is not unreasonable, especially since the Rb$^-$ would likely have numerous cations as nearest neighbors, as discussed later.

(2) Its line width of 2.7 kHz is significantly less than those for any Rb$^+$ signals in zeolite A, including Rb$^+$ in fully hydrated RbNaA (7.6 kHz at 130.9 MHz, and field dependent), but of the same order as for Rb$^+$ in the cubic environment of RbCl solid (1.3 kHz).

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[†] NRCC Contribution No. 43875.

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[6] This work.

[7] Zeolite A (Na$_{12}$Al$_{12}$Si$_{12}$O$_{48}$, Strem) was ion-exchanged (at pH 10 and 297 K for 24 h, repeated 5 times) to give LiA (~98% Li) and RbNaA (65−70% Rb). Crystallinity was confirmed by powder X-ray diffraction and ^{27}Al and ^{29}Si MAS NMR. No dealumination of the framework was detected. Vacuum-dehydrated zeolites (heated slowly then held at 450 °C for 48 h at $<10^{-4}$ Torr) were reacted with a known amount of alkali metal vapor in sealed, evacuated quartz reaction vessels at 250 °C for 48 h. Each sample was sealed into a 5 mm o.d. quartz tube sidearm, and its crystallinity confirmed by ^{27}Al NMR.

[8] NMR spectra were obtained on Bruker DSX-400, AMX-300, and MSL-200 spectrometers (^{87}Rb at 130.9, 98.2, and 65.5 MHz, respectively, and ^{39}K at 18.67 MHz/DSX-400), using a quadrupolar spin−echo pulse sequence (sweepwidths up to 700 kHz). Reference: 1 M aqueous RbNO$_3$ at 0 ppm. No metallic Rb (Knight shift 6540.6 ppm, this work) was detected in any of the samples. Samples in quartz tubes were spun at 3.5−4 kHz in a 7 mm ZrO$_2$ spinner using a Bruker HPMAS probe. EPR spectra were recorded on a Bruker ESP 300 spectrometer operating at X-band frequencies (~9 GHz).

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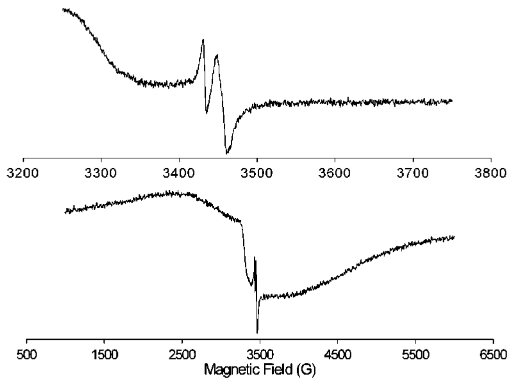

Figure 2. EPR spectra of Rb_3/LiA at 77 K: broad sweep (bottom) and short sweep of central region (top). Four resonances: (1) very broad, 2300 G; (2) 130 G, $g = 2.077$; (3) 4.5 G, $g = 2.0018$; (4) 14.6 G, $g = 1.9897$.

(3) More exciting is the observation that its shift and line width are field-independent. This means that the quadrupolar coupling constant (QCC) is zero or very close to zero, thus locating the anion on an extremely symmetrical site. A field-independent line width means there is no shielding anisotropy. Thus the MAS sidebands, Figure 1.4′, must arise from field-independent anisotropic interactions: possibly dipolar couplings, or an extremely narrow 1st order quadrupolar line shape. Rb^- in the organic alkalides show QCC values of the order of 0.87−6.3 MHz. Such values are not very large for ^{87}Rb, and significantly less than for Rb^+ in the same systems which have QCC ranging from 5.77 to 16.6 MHz.[4b] In fact we find that because of very large QCC values much of the Rb in our systems is NMR invisible (see below).

(4) Its shift is temperature independent. The species therefore has no hyperfine contact with the 4 paramagnetic species detected by EPR in the Rb_x/LiA series, Figure 2, and if it is Rb^- this is an indication of its effective isolation from such species.

Because the QCC is effectively zero we can be certain that the intensity of the suggested Rb^- line corresponds to all 3 transitions of the spin $^3/_2$ ^{87}Rb nucleus, and by comparison with the intensity of Rb^+ signals in known amounts of RbCl we can determine the fraction of the total Rb represented by this signal. It is small, about 2.0, 4.5, 2.1, and 0.0% in Rb_1, Rb_3, Rb_5, and Rb_{10}/LiA, respectively, and reaches a maximum at Rb-loadings between 2 and 3 Rb/u.c. Therefore, in the Rb_3/LiA sample there are about 14 Rb^- per 100 u.c. The disappearance at 10 Rb/u.c. is likely due to excess Rb encroaching on all available space, leading to loss of symmetry, bonding interactions, and involvement in cluster species. Similar quantitative NMR measurements on anhydrous RbNaA show that less than 3% of the Rb is detected.

The zero QCC of the suggested Rb^- line is very significant since it places strong constraints on the location of the alkalide ion. Provided that the cations are symmetrically disposed, there are 2 sites in the crystal which can give isotropic framework symmetry, namely the centers of the large (α) and small sodalite (β) cages. A third, less likely, possibility, which would give rise to isotropic lines, is the presence of dynamic averaging over anisotropic sites related by tetrahedral, octahedral, or cubic symmetry. We tend not to favor the latter as this is likely to lead to residual 2nd order shifts as we found for Rb^+ and Na^+ in hydrated RbNaA and NaA, respectively.[11]

In LiA there are Li^+ ions in the 8-ring faces of the α-cages and almost in the plane of the 6-ring faces which join the α- and β-cages.[12] If the Rb^- ionic radius is 3.2 Å[13] it is unlikely to be in the β-cage, since there would be van der Waals overlaps of 0.15 Å with a cube of Li^+ and 0.38 Å with O atoms. It could fit, however, if the Rb^- radius were 2.09 Å as suggested for the compound $Na_{16}Rb_7Sb_7$,[14] where the Rb^- forms the center of an Rb_7^{5+} cluster. Possible further evidence against Rb^- being in the β-cage is that we do not see the same NMR line in Rb-loaded LiY zeolite, which also has sodalite cages.[15] The α-cage, however, has ample room for the $r = 3.2$ Å Rb^- at the cage center, well away from the negatively charged framework and possibly surrounded by cations. Even if Li^+ were displaced by Rb^+ above the 6-ring and in the 8-ring windows (in RbA the Rb^+ sits 1.654 Å above the 6-ring[16]), there could still be at least 0.3 Å between Rb^+ and Rb^-.

Although we have referred to the species as Rb^-, one should not discount the possibility that it constitutes the center of a high-symmetry cluster involving cations and/or even numbers of neutral atoms, since there are many other atoms still not accounted for. We note the hole at the center of K_8 and K_{12} clusters found by X-ray and neutron diffraction in the α-cages of K-loaded K_5/KA.[17] Also, Seff has located atoms at the center of high-symmetry clusters in both the β-cages and supercages of zeolite X.[18] Indeed, the results of optical and magnetic measurements on Na, K, and Rb-loaded NaA, KA, and RbA were interpreted in terms of cationic metal clusters, though alkalides were not considered.[19]

To explain the formation of an electron-rich species, we must conclude that favorable coordination sites for Li^+ and Rb^+ force the extra electrons to locate elsewhere, e.g. as Rb^-, whose presence at the center of a cage lined with framework cations also helps offset cation−cation repulsions, and as clusters.

In the ^{39}K NMR spectrum of K_5/LiA we have observed a very similar, solitary, sharp line at −45 ppm (width 740 Hz) relative to K^+(aq), which by analogy we assign to K^-. K^- has previously been assigned to lines at −105 ppm in several crown ether complexes and at +19 ppm in Cryptand 222.[4b,20] K, like Rb, often has a QCC large enough to render the resonances invisible and, in fact, K^+ signals cannot be detected in anhydrous KA zeolite. In hydrated KA zeolite, however, we observe a line assigned to K^+ at −33 ppm (width 1.8 kHz). Note that the known shift ranges of K^+ and K^- overlap.

In conclusion, it appears that dehydrated LiA zeolite is an active medium for the generation of the rare alkalide anions Rb^- and K^- via metal vapor deposition. Work continues to see whether Cs^- will also form in LiA, though so far it seems that Na^- does not. While we can conclude that the NMR visible alkalides in LiA must occupy a very symmetric site, most probably at the center of the α-cage, its exact environment and the nature of the other species present remain to be clarified. Structural studies with powder diffraction and double resonance NMR[21] should provide further evidence.

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