

^{29}Si and ^{27}Al MAS NMR spectra are affected by alkali metal cluster formation in zeolite LTA

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We report the application of ^{27}Al and ^{29}Si MAS NMR to provide a direct probe of alkali metal cluster formation and distribution in the α -cages of zeolite A (LTA).

The reaction of alkali metals with framework aluminosilicates produces a rich variety of inclusion compounds comprising metal clusters and filamentary structures, confined and ordered, within the intracrystalline channels and cavities.¹ With zeolite pore dimensions typically *ca.* 1 nm or less, these may be regarded as the ultimate nanostructured materials, and as such have justifiably attracted considerable experimental and theoretical attention on account of a range of remarkable electronic, magnetic, optical and catalytic properties.^{2–6} Although the presence in such compounds of low-nuclearity ($n = 6$) paramagnetic clusters is well documented,^{7–12} these are present as minority species in all but a few cases.^{1,2} Pioneering ^{23}Na MAS studies by Nakayama *et al.*¹³ have suggested the possible formation of Na_5^{3+} and Na^- , in zeolites X, Y and A, but in general there is a dearth of information about the diamagnetic species present, in particular higher nuclearity clusters ($n > 10$) presumed to occupy the larger zeolite cages. Here, we report the first application of ^{27}Al and ^{29}Si MAS NMR to provide a direct probe of cluster formation and distribution in the α -cages of zeolite A.

We prepared a number of deeply coloured compounds $M'_x/M-A$ (where A denotes the LTA framework)¹⁴ by exposing alkali metal (M) ion-exchanged and dehydrated zeolite samples to a measured amount of alkali metal (M') vapour in sealed, evacuated quartz tubes.^{15,16} The products, which were virtually black, were subsequently handled under dry Ar. Unusual MAS NMR¹⁷ spectral shifts (Table 1) were observed for several compositions, and for the first time in zeolite A, a number of compounds exhibited two distinct signals (Figs. 1 and 2) for each T_d nucleus ($T_d = ^{27}\text{Al}$ and ^{29}Si), even though the materials were crystallographically single phase.¹⁸ When exposed to air the colour centres were gradually quenched, yielding white powders, whose MAS NMR spectra closely resembled those of the 'empty' dehydrated hosts, with only one T_d signal. Dehydrated zeolite K-A exhibited a single sharp resonance in both the ^{27}Al and ^{29}Si MAS NMR spectra, at the usual shifts for zeolite A (δ *ca.* 58 and -89 , respectively). In metal-loaded

'black' $\text{K}_5/\text{K-A}$, however, sharp T_d resonances shifted to lower frequency, δ 52.5 and -100.2 , respectively, were observed. The magnitudes of the shifts suggest a structural and/or electronic perturbation of the framework.

Topologically, LTA is a cubic array of sodalite cages mutually separated by double 4-ring (D4R) windows to form a large α -cage. Each T_d atom in the structure belongs to one sodalite cage, two α -cages and one double 4-ring. In dehydrated K-A, all the α -cages contain eight K^+ cations that are coordinated to oxygen atoms in the 6-rings and partly balance the negative charge of the framework. The structure has a pseudo unit cell size (assuming no Si, Al ordering) of *ca.* 12.3 Å in space group $Pm\bar{3}m$. In $\text{K}_5/\text{K-A}$, alternate α -cages contain either eight K^+ cations coordinated to 6-rings as in the dehydrated host, or a K_{12}^{4+} cluster whose partly reduced potassium cations occupy 4-ring sites. This results in a doubling of the unit cell to 24.6324 Å in space group $Fm\bar{3}m$.^{16,19} Owing to the strict alternation of the cage contents, the structure retains a single unique crystallographic T_d site.¹⁶ We suggest that the observed low frequency T_d shifts in $\text{K}_5/\text{K-A}$ may be due to an increase in the average $T_d\text{-O-T}_d$ bond angles²⁰ in the cluster-containing material relative to those in the empty host, which is consistent with an observed increase in lattice parameter.^{16,19} It is interesting that there is no paramagnetic T_d shift or broadening of lines observed in this compound, suggesting that the T_d atoms do not interact appreciably with the paramagnetic clusters known to be present.^{16,19}

Similar low frequency NMR shifts were observed for $\text{Cs}_5/\text{K-A}$, but in this case, the deeply coloured material exhibited two sharp resonances for both T_d nuclei (Fig. 1). The first one, labelled line 1, is only slightly shifted relative to the dehydrated host and is assigned to T_d atoms at the vertices of α -cages that contain only 6-ring cations. Line 2 resembles the T_d resonance in $\text{K}_5/\text{K-A}$, both in shift and signal breadth, and therefore is assigned to T_d atoms which are part of one α -cage that contains 6-ring cations and one that contains a 'reduced' cluster. As caesium cations are both less likely to occupy the 4-ring site in preference to potassium, and less likely to be found partly reduced, we speculate that K_{12}^{4+} clusters may again be present. Structural studies are under way to confirm this hypothesis.¹⁸ The relative intensities of the two lines are consistent with the

Table 1 Summary of 156.4 MHz ^{27}Al and 71.5 MHz ^{29}Si MAS NMR shifts (ppm), linewidths [$\Delta\nu_{1/2}$ (Hz)] and intensity ratios of the framework T_d resonances

Material	^{27}Al (line 1)	^{27}Al (line 2)	^{29}Si (line 1)	^{29}Si (line 2)	Ratio 1:2
$\text{Cs}_5/\text{K-A}$	59.3	52.2 (2150, total)	-89.7 (540)	-101.9 (420)	3:2
Exposed $\text{Cs}_5/\text{K-A}$	59.9 (1160)	—	-89.5 (320)	—	—
$\text{K}_5/\text{K-A}$	—	52.5 ^a	—	-100.2 (400)	—
K-A host (dehydrated)	57.7 (890)	—	-89.3 (490)	—	—
$\text{Rb}_7/\text{Rb-A}$	83.8	67.9 (4320, total)	-64.1 (910)	-86.1 (840)	3:1
Exposed $\text{Rb}_7/\text{Rb-A}$	61.0 (940)	—	-86.1 (570)	—	—
Rb-A host (dehydrated)	57.8 (700)	—	-89.1 (490)	—	—

^a ^{27}Al shift measured at 93.8 MHz. For comparison, the 93.8 MHz ^{27}Al shifts of $\text{Cs}_5/\text{K-A}$ are at δ 57.5 and 51.0

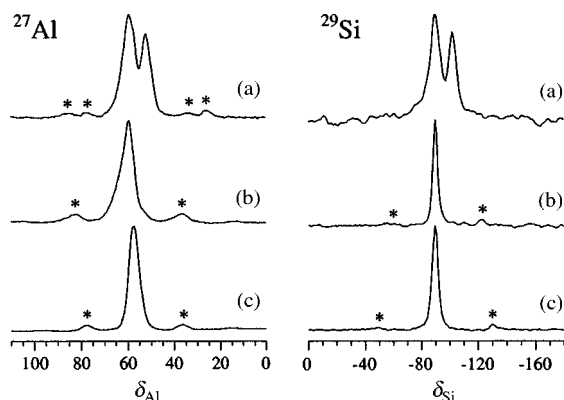


Fig. 1 ^{27}Al and ^{29}Si MAS NMR spectra of (a) 'black' $\text{Cs}_5/\text{K-A}$, and (b) air-exposed 'white' $\text{Cs}_5/\text{K-A}$ and (c) dehydrated 'empty' K-A . Asterisks denote positions of spinning sidebands.

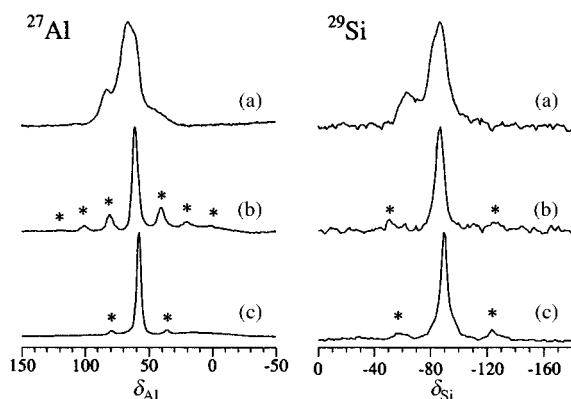


Fig. 2 ^{27}Al and ^{29}Si MAS NMR spectra of (a) 'black' $\text{Rb}_7/\text{Rb-A}$, (b) air-exposed 'white' $\text{Rb}_7/\text{Rb-A}$ and (c) dehydrated 'empty' Rb-A . Asterisks denote spinning sidebands.

presence of a cluster in about one fifth of the α -cages. Exposure of 'black' $\text{Cs}_5/\text{K-A}$ to air resulted in complete loss of colour and a single T_d resonance in both the ^{27}Al and ^{29}Si MAS NMR spectra (Fig. 1).

Two distinct T_d resonances were also observed in 'black' $\text{Rb}_7/\text{Rb-A}$ and these collapsed to a single signal when the samples were exposed to air (Fig. 2). In this case the lines are significantly broader than in the dehydrated host, which may indicate some site distribution (static disorder) or broadening from nearby paramagnetic clusters. Additionally, both lines are shifted to higher frequency relative to the host. The framework in this fully loaded zeolite is also expanded relative to the empty host,¹⁸ therefore there is no straightforward structural explanation for the observed shifts. One plausible explanation is that the

framework in this case is directly affected by paramagnetic clusters of guest atoms, similar to the shift trends observed in 'black' sodalite.¹²

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Notes and references

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- 17 NMR experiments were performed on samples sealed inside quartz MAS rotor inserts (Fluorochem/Wilmad) with epoxy. ^{29}Si MAS spectra were measured at 71.5 MHz, at spinning speeds of up to 4 kHz, using a Chemagnetics 6 mm MAS probe in a Bruker MSL-360 spectrometer. Chemical shifts were measured relative to TMS. Field-dependent ^{27}Al MAS spectra were collected at 93.8 MHz as above, and at 156.4 MHz using a 9.5 mm Chemagnetics probe in a Varian/Chemagnetics Infinity 600 spectrometer. ^{27}Al shifts were measured relative to aqueous AlCl_3 .
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