An ordered array of cadmium clusters assembled in zeolite A

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We report the assembly of a cubic array of cationic cadmium clusters encapsulated in zeolite A, and its characterization through Rietveld analysis of powder synchrotron X-ray diffraction data and high resolution transmission electron microscopy.

A defining feature of zeolite molecular sieves is a regular intracrystalline pore space in which, uniquely, it is possible not only to stabilize unusual cluster species, but also to arrange these with a well defined geometry relative to each other. Zeolite frameworks thus can act as 'molecular scaffolding' for the assembly of ordered cluster arrays or 'cluster crystals', whose properties may depend not only on those of the individual clusters, but also, importantly, on the interactions between neighbouring clusters.[1] With cluster sizes limited by the zeolite cages to approximately 1 nm or less, these may be regarded as the ultimate nanoscale materials.

Of the many cationic clusters reported to form in zeolites, whose properties have attracted considerable research interest,[1] a majority have been alkali metal species. However, due to the instability of these materials towards air, attention has naturally wandered to other groups of the periodic table. The ability of mercury to form polycations is now well documented,[2] and indeed, the uptake of mercury metal by both silver and mercury zeolites was reported over thirty years ago by Barrer and Whiteman,[3] who found that Hg_2^{2+} and larger Hg_x^{2+} (where $x > 2$) polycations formed within the zeolite. More recently, it has been postulated on the basis of Raman measurements that cadmium may also form linear polycations, Cd_3^{2+} and Cd_4^{2+}, encapsulated within zeolites.[4] Interestingly, the reaction of zinc metal with dehydrated Zn–A was found to result in the formation of zinc oxide clusters.[5]

With these results in mind, cadmium-loaded cadmium ion-exchanged zeolite A (LTA framework) was synthesized in an attempt to produce heavy metal clusters and to study their distribution and geometry through crystallographic methods and high resolution electron microscopy. $Cd_{3.8}$/Cd–A, *i.e.* cadmium ion-exchanged zeolite A containing 3.8 additional cadmium atoms per primitive unit cell, was prepared by heating dehydrated Cd–A[6] with Cd powder under vacuum in a sealed quartz tube at 500 °C for up to 3 days. Powder X-ray diffraction (XRD) data were collected at room temperature at Station X3B1 at the National Synchrotron Light Source, Brookhaven National Laboratory, Upton, USA using a wavelength of 0.69884 Å. The bright yellow sample was contained in a 0.7 mm glass capillary sealed under argon. High

resolution transmission electron microscopy (HRTEM) images were recorded on a modified JEOL JEM-200CX electron microscope operating at 200 kV, giving an interpretable resolution of about 0.185 nm.

Least-squares fitting of the powder XRD data was carried out using the GSAS suite of programs.[7] The starting model was that of Jang *et al.*[8] for dehydrated Cd–A in the primitive cubic space group $Pm\bar{3}m$ with a lattice parameter of approximately 12.2 Å.[9] After refinement of the background (automated linear interpolation), lattice parameter, peak profiles and framework atomic positions, difference Fourier maps helped locate three additional cadmium sites: at the centre of the sodalite cage (0, 0, 0), along the body diagonal displaced from the six-ring into the sodalite cage (0.134, 0.134, 0.134) and in the plane of the eight-ring in the larger α-cage (0, 0.5, 0.4). Inclusion of these sites greatly improved the fit and after refinement of the cadmium atomic positions, fractional occupancies and isotropic temperature factors, difference Fourier maps contained no peaks attributable to further sites. However, due to the small fractional occupancy of the cadmium atom in the α-cage six-ring site (0.20, 0.20, 0.20) identified by Jang *et al.*,[8] and the large standard deviation of the thermal parameter, this site was removed with little effect on the fit. After further fitting of the peak shapes the refinement converged with $\chi^2 = 8.21$, $R_{wp} = 7.36\%$, $R_p = 5.30\%$, $D_{wd} = 0.376$ and $R_{F^2} = 4.75$; the resulting atomic coordinates, fractional occupancies and isotropic temperature factors are shown in Table 1.[10]

The majority of the cadmium atoms were found to lie in the sodalite cage. Careful examination of the fractional occupancies and bond distances suggests cadmium clusters are formed in this location. The distances between the cadmium atom in the centre of the sodalite cage Cd(3) and the cadmium sites located on the body diagonal were 2.849 and 3.49 Å for Cd(1) and Cd(4) respectively. The former distance is reasonable for a Cd–Cd interaction, but the latter is too long indicating that Cd(3) must be bonded to Cd(1) and that Cd(4) takes no part in cluster formation. Further evidence of cluster formation between Cd(1) and Cd(3) is given by the fractional occupancies of Cd(1) and Cd(3), which refined to values close to each other without the use of constraints. A fractional occupancy of 0.788 for Cd(3) suggests that (within statistical error) approximately 75% of the sodalite cages contain the large cluster. Each Cd(3) is surrounded by an average of 7.5 Cd(1) atoms, resulting in the average cluster composition $Cd_{8.5}^{x+}$. A range of compositions such as Cd_9^{y+}, Cd_8^{z+}, *etc.* is possible, but this cannot

Table 1 Atomic parameters from $Cd_{3.8}$/Cd–A

Atom	x/a	y/a	z/a	Occupancy	$10^2 U_{iso}/Å^2$	Site Symmetry	Multiplicity
Si/Al	0	0.1808(2)	0.3661(2)	1	1.08(8)	*m*(100)	24
O1	0	0.1970(5)	0.5	1	3.06(27)	*mm*2(010)	12
O2	0	0.2982(4)	0.2982(4)	1	1.62(22)	*mm*2(011)	12
O3	0.1116(2)	0.1116(2)	0.3207(3)	1	0.87(16)	*m*(+−0)	24
Cd1	0.1348(3)	0.1348(3)	0.1348(3)	0.701(13)	1.48(9)	3*m*(111)	8
Cd2	0.3985(7)	0	0.5	0.096(2)	6.09(58)	*mm*2(100)	12
Cd3	0	0	0	0.788(6)	3.35(20)	*m3m*	1
Cd4	0.1651(7)	0.1651(7)	0.1651(7)	0.279(13)	1.55(28)	3*m*(111)	8

$a = 12.2005(1)$ Å

be determined by diffraction methods alone. Cd(1) is bonded to the framework *via* the oxygen atoms of the six-ring at a distance of 2.303 Å. Bond valence sum calculations[11] suggest the oxidation state of Cd(1) to be +1, while the long Cd(1)–Cd(3) distance of 2.849 Å implies the oxidation state of Cd(3) may be zero (the Cd–Cd distance in Cd metal is 2.98 Å). The Cd(1)–Cd(1) distance of 3.240 Å is probably too long for significant bonding interactions to occur. Therefore we propose the clusters to be $Cd_n^{(n-1)+}$, for example Cd_9^{8+} as shown in Fig. 1. The high nominal charge on such clusters is stabilized by coordination of almost all of the atoms to the anionic zeolite framework.

Of the remaining cadmium atoms, Cd(4) is coordinated to the zeolite framework *via* the oxygen atoms of the six-ring. The Cd–O bond distance of 2.11 Å is comparable with the sum of the ionic radii of Cd^{2+} and O^{2-} (2.16 Å),[12] suggesting that the oxidation state of Cd(4) is +2. Bond valence sum calculations confirm this assignment. As Cd(4) and Cd(1) are too close together to coordinate to the same six-ring window, and as around 75% of the sodalite cages contain large clusters, it is logical to conclude that the remaining 25% contain Cd(4) only. Finally, Cd(2) is located in the plane of the eight-ring in the larger α-cage. The Cd–O bond distances are 2.460 Å and 2.740 Å, suggesting that the oxidation state of Cd(2) may also be +1. Again bond valence sum calculations are consistent with this interpretation. The Cd–Cd distance of 2.477 Å is slightly longer than the 2.35 Å reported in the literature for Cd_2^{2+} encapsulated within zeolites,[13] but shorter than the reported distance of 2.576 Å in $Cd_2(AlCl_4)_2$.[14] The fractional occupancies indicate there are approximately $0.5Cd_2^{2+}$ ions per unit cell. Both the position and occupancy of this site is similar to that reported by McCusker and Seff.[13] However, in their sample the cadmium site in question lay out of the plane of the eight-ring. In the work of Jang *et al.*[8] there was a site in a similar position assigned to Cd_2^{2+}, but in contrast to the compounds prepared by us, and by McCusker and Seff,[13] where Cd_2^{2+} was coordinated only to the framework oxygens of the eight-ring, the Cd_2^{2+} ion found by Jang *et al.*[8] also had interactions with other cadmium atoms forming a larger Cd_5^{4+} species.

Taking all Cd species into account, our sample has the unit cell composition $Cd_{2.232}(Cd_2)_{0.576}(Cd_{8.5})_{0.788}$–A. HRTEM images of the sample (Fig. 2) show a patchwork of sharply defined areas of dark and light contrast with the very strong image contrast providing evidence of heavy cadmium-loading, later confirmed by EDX analysis. Perhaps as a consequence of this, and unusually for zeolite samples, the material was very stable under the electron beam with no structural decomposition observed. The image is
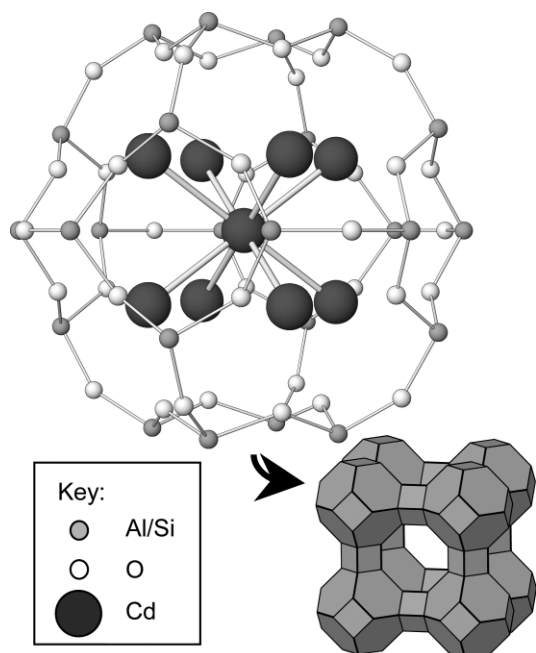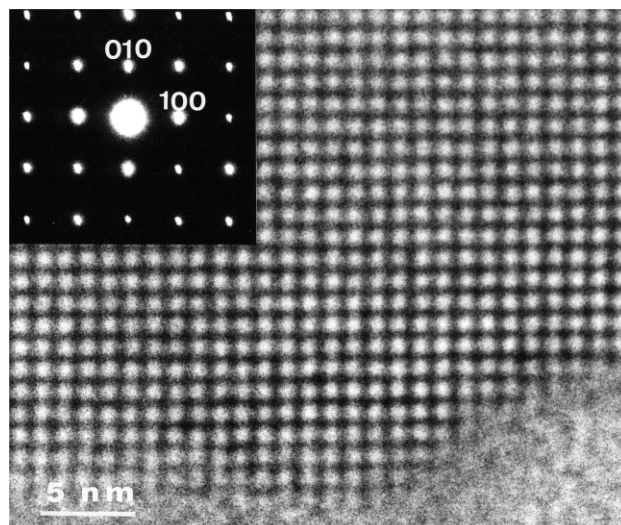
Fig. 2 HRTEM image and SAED pattern (insert) of Cd$_{3.8}$/Cd–A.

fully consistent with the presence of a cubic array of high nuclearity clusters occupying most of the sodalite cages separated by nearly empty α-cages. The lack of superlattice reflections in X-ray or selected-area electron diffraction (SAED) patterns (Fig. 2) confirms that the clusters are randomly distributed throughout the zeolite. Our structural model of a high symmetry and high nuclearity cluster species, with most of the cadmium atoms in the compound located in the sodalite cages, is markedly different from the results of previous work,[4,8,13] although the formation of Cd_2^{2+} in the eight-rings of zeolite A provides a common feature. It is clear that the nature of cadmium clusters formed in zeolites can vary considerably depending on the synthesis conditions.

Notes and references

1 See, for example, P. A. Anderson, *Mol. Sieves*, 2002, **3**, 307 and references therein.

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10 Due to the pronounced asymmetry and large intensity of the first peak the refinement was carried out again with this peak excluded to avoid excessive bias. The refinement converged with χ^2 = 3.31, R_{wp} = 5.83%, R_p = 4.52%, D_{wd} = 0.686 and R_{F^2} = 5.10. There was no significant difference in the structural model obtained from this refinement with atomic positions, fractional occupancies and isotropic thermal parameters all within two standard deviations.

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Key:
- Al/Si
- O
- Cd

Fig. 1 Cadmium cluster (Cd$_9^{8+}$) in the sodalite cage of zeolite A.