Synthesis and structure of zinc oxide clusters encapsulated in zeolite LTA

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We report the synthesis and structure, obtained through Rietveld analysis of powder synchrotron X-ray diffraction data, of zinc oxide clusters encapsulated in zeolite LTA.

There is currently considerable interest in the study of zinc oxide nanoparticles and clusters formed within zeolite crystallites, which is based on potential applications in optics, electronics, sensors and photocatalysis.[1–4] Recent work has concentrated on the characterisation of the materials by spectroscopic methods such as UV–VIS and diffuse reflectance IR spectroscopy,[1–3] but to date there is no crystallographic information on the structure and location of such clusters. A variety of different synthetic routes have been used for the preparation of zinc oxide clusters in zeolites.[1–4] On account of our longstanding interest in metal-zeolite reactions,[5,6] we have adopted the method of Lee *et al.*,[3] who synthesised zinc oxide clusters in zeolite Y through oxidation of the zinc-loaded zeolite, and have applied it to a range of zeolites. As a first step we decided to examine the zinc-loaded zeolites prior to oxidation, and report that in zeolite A (LTA) oxygen-containing clusters are already present at this stage of the synthesis.

The zinc ion-exchanged form of zeolite A (Zn-A) was prepared from as-synthesised Na-A by conventional ion-exchange methods.[7] The zinc-loaded material was prepared through the reaction of dehydrated Zn-A (12 h, 500 °C under vacuum) with Zn powder in a sealed, evacuated (1×10^{-5} mbar) quartz tube. A homogeneous yellow powder was obtained after reaction for 7 days at 500 °C, with a small excess of zinc metal deposited on the ends of the tube. For structural studies to be carried out, a small amount of the sample was placed in a 0.7 mm diameter glass capillary and sealed with epoxy resin in an argon-filled glovebox. X-Ray powder diffraction data were collected at room temperature at station X3B1 at the National Synchrotron Light Source, Brookhaven National Laboratory, USA. The wavelength of the radiation (0.69884 Å) was chosen to minimise any sample absorption problems.

Least squares refinement of our structural model was carried out with the GSAS suite of programs.[8] The starting model was based on the framework coordinates for dehydrated Zn-A obtained by McCusker and Seff,[9] who used the primitive cubic space group $Pm\bar{3}m$ with a lattice constant of *ca.* 12.2 Å. A detailed justification for the use of $Pm\bar{3}m$ in the analysis of X-ray diffraction data from zeolite A has been given by Cruz *et al.*[10] There was no evidence in our data to suggest the need to use a doubled unit cell. After refinement of the background (automated linear interpolation), lattice parameter, peak profiles and framework atomic positions, difference Fourier maps were used to find the positions of three zinc sites. These sites were located at the centre of the sodalite cage (0, 0, 0), in the 6-ring (just inside the sodalite cage) (0.18, 0.18, 0.18) and inside the sodalite cage along the body diagonal (0.13, 0.13, 0.13). Refinement of the fractional occupancies of these sites gave a total zinc content of approximately nine ions per unit cell, three more than necessary to balance the negative charge of the framework.

Difference Fourier maps were used to check for any residual electron density. One peak was found inside the sodalite cage at (0, 0, 0.17). Examination of the bond distances between this site and the zinc site at the centre of the sodalite cage suggested that this new site was actually occupied by oxygen as the bond length of 2.08 Å would be much too short for a Zn–Zn interaction. No sites were found in the α-cage. After further refinement of atomic positions, isotropic thermal parameters and further fitting peak profiles, final difference Fourier maps were again calculated and showed no electron density due to further atomic positions. This refinement (labelled A) converged with $\chi^2 = 2.71$, $R_{wp} = 7.53\%$, $R_p = 5.83\%$, $D_{wd} = 0.807$ and $R_{F^2} = 8.41\%$. Owing 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. This second refinement (B) converged with $\chi^2 = 1.83$, $R_{wp} = 7.32\%$, $R_p = 5.37\%$, $D_{wd} = 1.080$ and $R_{F^2} = 8.86\%$. There was little difference in the structural models obtained from each refinement; the atomic positions, fractional occupancies and isotropic thermal parameters were all within two standard deviations, except for the fractional occupancy of O(4) which was within four standard deviations. Final atomic coordinates, fractional occupancies and isotropic thermal parameters for refinement A are given in Table 1. Observed, calculated and difference plots are shown in Fig. 1. A close visual inspection indicates the main features in the difference plot can be attributed to imperfect modelling of the peak shapes, rather than a mismatch in intensities.

The presence of a non-framework oxygen site implies that a cluster comprising only zinc atoms has not been formed. McCusker and Seff[9] also found non-framework oxygen in Zn-A dehydrated at 600 °C, which was ascribed to water molecules coordinated to Zn^{2+}. In the present work the average unit cell composition[11] is approximately $Zn_{2.75}O_{2.7}/Zn_6[Al_{12}Si_{12}O_{48}]$. It

Table 1 Crystallographic data from refinement A

Atom	*x/a*	*y/a*	*z/a*	Occupancy	$10^2\ U_{iso}/Å^2$	Site Symmetry	Multiplicity
Si/Al	0	0.1839(2)	0.3630(2)	1	1.06(9)	*m*(100)	24
O(1)	0	0.1820(6)	0.5	1	1.2(3)	*mm*2(010)	12
O(2)	0	0.3109(5)	0.3109(5)	1	1.6(3)	*mm*1(011)	12
O(3)	0.1149(4)	0.1149(4)	0.3086(4)	1	2.2(2)	*m*(+ − 0)	24
Zn(1)	0.1346(2)	0.1346(2)	0.1346(2)	0.76(1)	2.3(1)	3*m*(111)	8
Zn(2)	0	0	0	0.74(1)	2.2(4)	*m*3*m*	1
Zn(3)	0.1835(9)	0.1835(9)	0.1835(9)	0.26(1)	4.7(6)	3*m*(111)	8
O(4)	0	0	0.175(3)	0.45(2)	5.8(17)	4*mm*(001)	6

a = 11.9061(1) Å.

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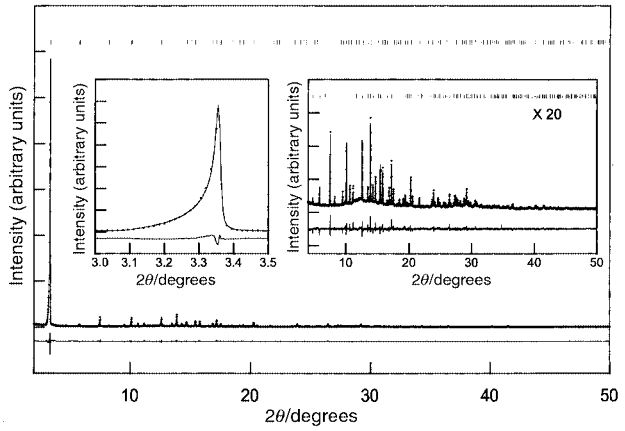

Fig. 1 Final Rietveld fits for refinement A (first peak included) showing observed (dots), calculated (solid line) and difference plots.

is unlikely the extra framework oxygens in this case are due to residual water molecules as the oxidation state of the added zinc atoms would then be close to zero. Likewise, if hydroxy groups were present, the oxidation state of the extra zinc atoms would be approximately +1. If O(4) is considered as O^{2-}, however, the extra zinc atoms can then be considered to be Zn^{2+}. Rittner *et al.*[12] have shown that zinc vapour reacts readily with zeolite H-Y to form a Zn^{2+}-exchanged product. For these reasons we propose that zinc oxide clusters have been formed as a result of the reaction of zinc metal with residual water molecules that remain coordinated to zinc ions within the zeolite after dehydration at 500 °C.

The model obtained from this refinement shows that clusters are formed in the sodalite cage of zeolite A (Fig. 2) as opposed to the larger α-cage as recently proposed by Lee *et al.*[3] The sum of the fractional occupancies of Zn(1) and Zn(3) is approximately unity, without the use of constraints. This is an expected consequence of the distance between the two sites, which is too short for both to be occupied simultaneously. Relatively short Zn–O bond distances supplemented by bond valence sum calculations[12] suggest that Zn(3), located at the centre of the 6-ring, can be considered as Zn^{2+} coordinated only to the oxygen atoms which form the 6-ring. McCusker and Seff[9] found a zinc site in approximately the same position in dehydrated Zn-A. In addition, the fractional occupancies of Zn(1) and Zn(2) are approximately equal, suggesting that each atom at Zn(2) is surrounded by eight at Zn(1). It seems logical to conclude that zinc atoms occupy Zn(1), recessed into the sodalite cage, only when bonded to O(4) atoms. We therefore propose that clusters are formed from Zn(1), Zn(2) and O(4) in approximately 75% of the sodalite cages, and the remaining 25% contain eight Zn^{2+} ions at Zn(3) coordinated to the 6-rings. As there is no evidence of a superstructure, the occupancy of the sodalite cages by the clusters must be random.

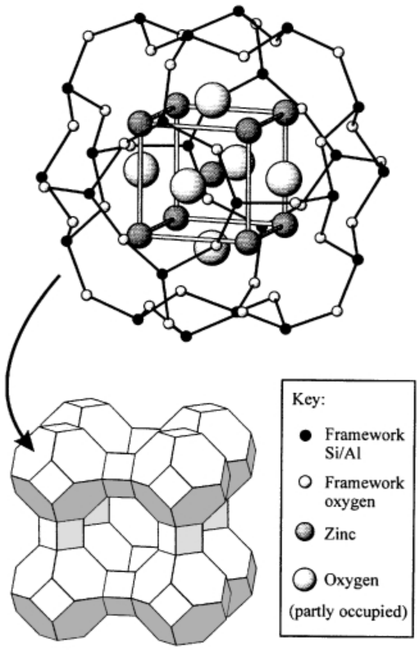

Fig. 2 Structure of zeolite LTA showing the proposed cluster arrangement in the sodalite cage. The oxygen sites are partially occupied.

The proposed cluster is illustrated in Fig. 2 with a zinc atom at the centre of the sodalite cage [Zn(2)] surrounded by eight zinc atoms [Zn(1)] at a distance of 2.78 Å. By symmetry there are six possible oxygen sites each at a distance of 2.08 Å from Zn(2) and 2.32 Å from four atoms at Zn(1). As the results indicate an average of three to four oxygen atoms per cluster, the exact geometry remains unknown. Although the difference between the extra zinc and oxygen contents obtained from the refinement is not significant, there is a possibility that the clusters are slightly oxygen deficient and this may account for the yellow colour of the compound. It is possible that the oxygen content is limited by the small number of water molecules remaining in the zeolite after high temperature dehydration.[9] Experiments aimed at varying the oxygen content are in progress.

One further interesting feature of the structure is that at 11.906 Å, the lattice parameter for this sample is one of the smallest reported for zeolite A. Depmeier has related the lattice parameters of a wide range of zeolite A samples to a framework distortion resulting in the O(3) atoms of the 6-ring being drawn into the sodalite cage and an approximately linear T–O(1)–T angle.[14] It is likely, therefore, that a range of unusual crystallographic parameters, such as the small lattice parameter and the T–O(1)–T angle of 178.5°, observed in this compound result from a framework distortion occasioned in part by cluster formation in the sodalite cage.

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