Flexibility of the Zeolite RHO Framework; Relocation of Cadmium accompanying Transformation of the Unit Cell at High Temperatures

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Upon heating Cd^{2+}-exchanged zeolite RHO, a relocation of the extra-framework cation accompanies the transformation from the acentric (**A**) to centric (**C**) structure type; this relocation from the eight ring to a six ring site, which are 5.7 Å apart, is the largest observed in a zeolite.

Over the past decade a number of studies have dealt with the flexibility of zeolite RHO.[1–5] This open aluminosilicate framework is an appealing candidate for study for several reasons: it is structurally simple, with exceptional flexibility,[1–6] ensuring that the structural response to changes in environment will be large and readily observable, and it is a commercially useful catalyst.[7] The centric (**C**) and acentric (**A**) structural variants, with symmetry $Im\bar{3}m$ and $I\bar{4}3m$ respectively, are favoured under different conditions of temperature and composition. Conditions of unit cell expansion, hydration and high temperature, for example, favour the **C** structure. On the other hand, the **A** structure, characterized by a distortion from circular to elliptical double 8-ring (D8R) apertures (Fig. 1), is favoured at lower temperature, by small ions with large charge densities,[5,6] for example Ca^{2+}, and upon dehydration. a simple semi-empirical parameter, Δ, which relates the degree of ellipticity of the 8R (Fig. 1) to the unit cell distortion was introduced early on in these studies.[2] Further, distance least-squares (DLS) modelling was also used in conjunction with this parameter, most recently to predict the limits of the considerable distortion in this framework.[6] In these studies the assumption has been that the positions of the extra-framework cations change little as a function of temperature.

We report here the relocation of Cd^{2+}-ions from the 8R-site into the single 6-ring (S6R) site in the framework of zeolite RHO (Figs. 1 and 2). This process was studied *in situ* using a high temperature device employing a Pt-strip, which serves as both heater and sample support. This heater is attached to a Scintag PAD-X diffractometer. Data sets, taken upon heating and cooling (Fig. 2), were collected in the range $5 < 2\theta < 80°$, with a step of 0.02° in 2θ, and a counting time of 3 seconds per step, using Cu-Kα radiation. A solid-state detector and a single-channel analyser, rather than a monochromator, were set to discriminate against the Kβ radiation.

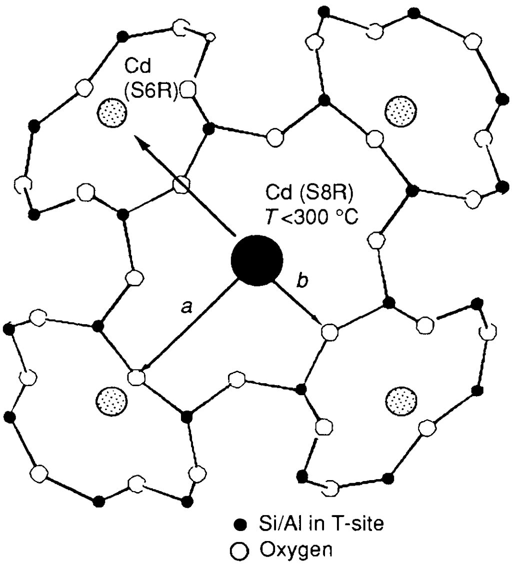

Fig. 1 Representation of the 8-ring (S8R) and 6-ring (S6R) sites in the acentric (**A**) form of zeolite RHO possessing space group symmetry $I\bar{4}3m$. Upon heating above 200 °C (Fig. 2) the Cd^{2+} ion in the S8R (site 6*b*) moves to one of the S6R sites (site 8*c*). The parameter, Δ, described in the text and in the previous studies,[1–6] indicates the difference between the major and minor axes ($a - b$) of the elliptical pore openings. In the centric (**C**) form the 8-rings apertures are circular ($\Delta = 0$).

The hydrated zeolite sample at room temperature consists of a single phase with $a = 15.03$ Å. Upon heating and loss of water the cell parameter a decreases to a minimum of 14.480(2) Å at 200 °C where the symmetry† is $I\bar{4}3m$ (Fig. 2). Subsequently it begins to increase with increasing temperature (Fig. 2). This behaviour is in keeping with other *in situ* studies[3,6] on this and other exchanged forms of zeolite RHO. However, at 300 °C the powder diffraction pattern is consistent with the presence of equal quantities of two phases (Fig. 2) both with cubic symmetry but possessing distinct values of the cubic cell parameter. Both values, 14.588(5) and 15.033(3) Å, are larger than for the single phase at 200 °C (Fig. 2). although annealing for up to 16 h at this temperature did not favour one phase over the other, increasing the temperature to 500 °C led to a single phase with a powder diffractogram distinct from that of the lower temperature phase. Upon cooling, the high temperature phase, confirmed by structure analysis† to have symmetry $Im\bar{3}m$, persists below 300 °C and two phases are observed at 150 °C. Structure refinement of the sample at 300 °C confirmed the presence of equal amounts of the **A** and **C** phases. The differences between the two phases coexisting at 300 °C concern not only the symmetry of the framework, but also the placement of the Cd^{2+} ion; this is near the centre of the single 8-ring (S8R) in the lower temperature **A** phase

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† *Structural details:* Structural refinement was initiated using the starting atomic positions for Cs-RHO.[2] Chemical analysis, $Na_{0.06}Cs_{0.22}Cd_{4.8}Si_{37}Al_{11}O_{96}$, was used to ensure the majority of the extra-framework scattering was from Cd^{2+}, and not from Cs^+ or Na^+, the ions used to synthesize the starting RHO, which was ion exchanged to obtain the sample used in this study. The chemical analysis also allowed the constraint of the T-site chemistry (Fig. 1). The overall temperature factor, positional parameters and the site occupancies at the S6R-site (1/4,1/4,1/4) and the S8R-site (0.423[2],0,0) assuming occupany only by Cd, were refined. The position of the Cd^{2+} was determined from Fourier difference synthesis to be at the S6R-site at 510 °C and at the S8R-site at 200 °C. Attempts to move Cd from the ideal position at (1/4,1/4,1/4) resulted in convergence towards that position following several cycles of least-squares. All calculations were carried out using the GSAS[8] suite of programs. For the low temperature **A** phase a soft constraint on the T–O bond length [1.64(1) Å] was applied. No constraints were imposed on the other refinements. Data collected at 300 °C were modelled using both **A** and **C** phases. Statistics for the three refinements are as follows: at 200 °C, $R_{WP} = 0.29$, goodness of fit parameter (χ^2) = 1.84; at 300 °C, $R_{WP} = 0.38$, $\chi^2 = 1.21$ (scale factors for the phase with symmetries $I43m$ and $Im3m$ present in this sample are 0.074 and 0.078, respectively); and at 500 °C $R_{WP} = 0.23$, $\chi^2 = 2.12$. R_{WP} and χ^2 are defined in a number of previous publications dealing with Rietveld refinement of RHO.[1–6,8]

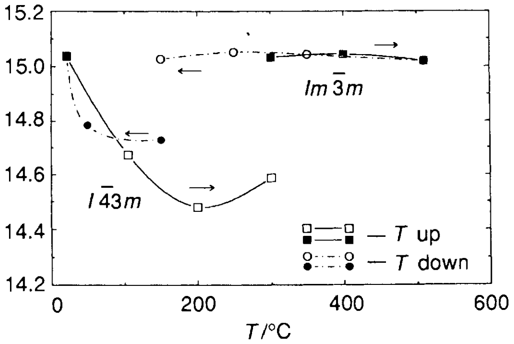

Fig. 2 Variation in cubic unit cell parameter with temperature. Arrows indicate the increase (squares) and decrease in temperature. Note the temperatures at which the $Im\bar{3}m$ and $I\bar{4}3m$ phases coexist are 300 °C upon heating and 150 °C upon cooling. The room temperature data were collected on hydrated material before and after heating. This cycle was found to be reproducible over several cycles.

but has shifted to the S6R-site in the higher temperature **C** phase (Fig. 1). The distance over which the Cd^{2+}-ion migrates, between the S6R and D8R-sites, is approximately 6 Å; this is the largest reported for a metal ion in a zeolite.

This situation contrasts with that for the similarly sized Ca^{2+} ion.[9] In this case the framework is forced to distort to accommodate the coordination geometry of the less polarizable[10] Ca^{2+}, which remains in tetrahedral coordination in the D8R up to 500 °C. On the other hand, the Cd^{2+} ion migrates to the S6R, where the average Cd–O distance, 2.49(2) Å, is close to that expected for 6-fold coordinated Cd^{2+} (2.3 Å) from consideration of ionic radii.[9] With increasing temperature, rather than imposing a distortion upon the framework, as is the case[6] for Ca^{2+}, the Cd^{2+}-ion instead migrates. The shift is to the coordinatively more favourable S6R as the expansion around the D8R makes it difficult for the Cd^{2+} ion to satisfy its coordination requirements in that site. The presence of a two-phase region, alluded to in the literature[6] in other forms of this zeolite, is unusual. Especially interesting is the stability of this situation at intermediate temperatures perhaps signifying the energetic equivalence of the S8R and D8R sites under these conditions.

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