Entrapment and Controlled Release of Xenon in Cd2+-exchanged Zeolite Rho†

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Thermal relocation of Cd2+ ions and framework flexibility are used to effect the entrapment and controlled release of xenon from the pores of Cd2+-exchanged zeolite rho.

Zeolite rho, which is composed of a body-centred cubic arrangement of truncated cubooctahedra or α-cages linked by double 8-rings (D8R) of the silica and alumina tetrahedra that

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are the primary building blocks of zeolites,[1] has been shown in the acid form to exhibit high activity and selectivity for the synthesis of dimethylamine from methanol and ammonia.[2] Detailed structural characterization studies have also shown the RHO framework to exhibit exceptional flexibility with particular sensitivity to cation, temperature and degree of

hydration.[3] For example, D-exchanged rho shows the largest unit cell with $a = 15.0976(4)$ Å (space group $Im\bar{3}m$), while Ca, D-rho shows the smallest reported unit cell for an aluminosilicate RHO structure with $a = 13.9645(7)$ Å (space group $I\bar{4}3m$). This corresponds to a decrease in lattice volume of greater than 20% in going from D-rho to Ca,D-rho and a change in the crystallographic opening (assuming ionic radii) of the single 8-rings (S8R) of 4.3 Å in D-rho to 1.6 × 6.5 Å in Ca,D-rho.[3,4] Structural studies[3] of the similarly sized Cd^{2+}-ion exchanged into zeolite rho showed a unit cell parameter intermediate between these extremes with $a = ca.$ 14.49 Å. More detailed studies and structure refinements[5] indicated relocation of the Cd^{2+} ions from the 8-membered ring site to the 6-membered ring site in the framework of zeolite rho on heating from room temperature to 300 °C or greater. As illustrated in Fig. 1, the structural results show that below 300 °C, the pore opening is elliptical with Cd^{2+} blocking access to the internal surfaces of the zeolite. Above 300 °C, the pore is essentially circular and is no longer blocked by cations thus allowing full access to the internal surfaces. In this communication, we demonstrate that we can take advantage of this unique flexibility to trap species, specifically xenon, within the zeolite cages and release them in a controlled manner using Cd-exchanged zeolite rho.

A sample of Cd,NH_4-rho, $Cd_{3.3}(NH_4)_{5.42}Na_{0.03}Cs_{0.25}$-$Al_{12.3}Si_{35.7}O_{96}$ (NH_4^+ content is assumed for charge balance), was prepared by conventional NH_4^+-exchange followed by Cd^{2+}-exchange of Na,Cs-rho.[6] The sample of Cd,NH_4-rho was outgassed for 10 days at 400 °C under 1.3 mPa. The sample was then placed in a pressure vessel, charged with 1.4 MPa of Xe, and heated to 350 °C for 2 h. After cooling to room temperature, the pressure was decreased to 0.17 MPa and the sample was transferred to a dry box. The samples were then analysed by thermogravimetric/mass spectral analysis (TG/MS),‡ ^{129}Xe NMR, and in situ X-ray and synchrotron X-ray powder diffraction.

The TG/MS results are given in Fig. 2. Three events (with the corresponding weight losses given in parentheses) are observed at approximately 100 °C (9.8%), 340 °C (5.7%), and 520 °C (0.93%). The ion chromatograms show the low temperature event is associated with the desorption of water ($m/z = 18, 17$). This water was most likely sorbed during transfer from the dry box to the TG apparatus. There are also a couple of small events that appear to be due at least partially to loss of water at $ca.$ 290 °C and at $ca.$ 390 °C. In addition, the event at 520 °C appears to be associated with loss of ammonia

($m/z = 17$). Apparently, the outgassing at 400 °C was not sufficient to deammoniate the Cd,NH_4-rho completely. The event at 340 °C is attributed solely to desorption of xenon ($m/z = 129$). Ion peaks corresponding to all of the isotopes of xenon as well as the +2 ions were observed. The appearance of xenon at this temperature correlates well with the 'unclogging' of the pore as observed in the in situ X-ray powder diffraction results given in Fig. 1 for this Xe-loaded sample and earlier samples[3,5] of Cd-rho not containing Xe. The weight loss associated with this escape corresponds to a loading of approximately 0.85 Xe per α-cage (or 1.7 Xe per unit cell); however, considering the amount of water sorbed, significant amounts of Xe may have been lost.

Preliminary ^{129}Xe NMR of a Xe-loaded Cd-rho shows a resonance at δ 90 ± 5 with a T_1 of the order of tens of seconds at 23 °C.[7] The observed chemical shift is close to that reported for Xe trapped in Na-A zeolite using similar techniques.[8] Although zeolite A has a similar cage structure, it does not exhibit the flexibility and dramatic changes in structure observed for zeolite rho.

Refinements and Fourier difference map calculations based upon synchrotron X-ray diffraction intensity measurements§ of the Xe-loaded Cd-exchanged rho sample collected at 13 K revealed density close to the double 8-ring (D8R), the single 8-ring (S8R) and the single 6-ring (S6R) sites. The occupancy of 3.2 Cd at an S8R site corresponds well to the chemically analysed value of 3.3 Cd per unit cell. This site is close to that found in previous studies.[5] The remainder of the scattering was assigned to Xe.

A series of site occupancy refinements was carried out using oxygen scattering factors; occupation factors greater than 1.0 were presumed to be indicative of partial occupancy by Xe. Because of the expected dominance of the X-ray scattering of Cd and Xe, no attempt was made to differentiate the effects of scattering from NH_4^+ and H_2O. Essentially all the extra-framework sites were found at this stage; those sites with

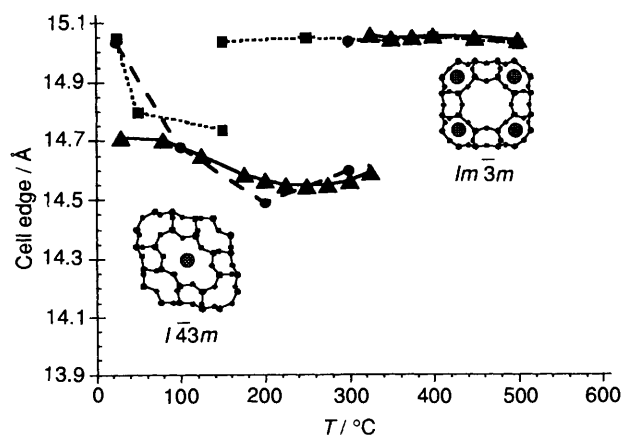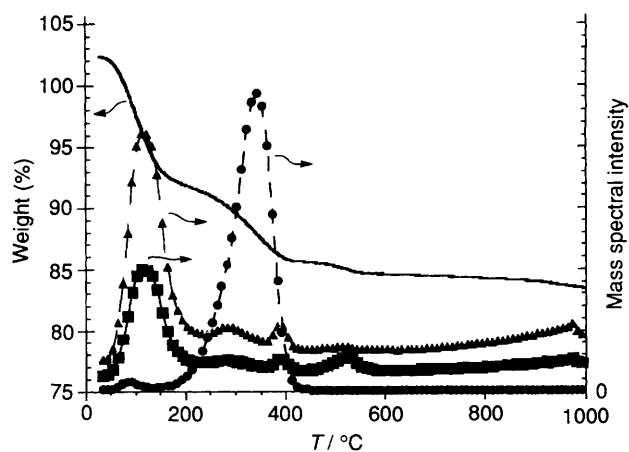Fig. 2 TG/MS plots for Xe-loaded Cd-rho. ■ m/z 17; ▲ m/z 18; ● m/z 129.

Fig. 1 Plot of effect of temperature on cell edge of Cd-rho. The resiting of the Cd^{2+} ion (hatched circle) on heating is also illustrated. ● Up cycle (ref. 5); ■ down cycle (ref. 5); ▲ up cycle (this work).

‡ DuPont 951 Thermal Gravimetric Analyzer interfaced to a Hewlett Packard 5970 Series Mass Spectrometer.

§ Structural X-ray diffraction intensity measurements were performed at the X-7A beamline at the National Synchrotron Light Source using a channel cut Si(111) monochromator and Ge(220) analyser (D. E. Cox, B. H. Toby and M. M. Eddy, Aust. J. Phys., 1988, 41, 117). The X-ray wavelength [λ = 0.69750(3) Å] was determined using CeO_2 as a standard. Data were collected in the range in 5–40° with a step size of 0.01° in 2θ with a counting times of 5 s per step. The data were collected at a nominal temperature of 13 K in a Displex® unit with the sample contained in a 1 mm quartz capillary which was loaded in an inert atmosphere box. The refinement of the crystal structure was initiated in the space group $I\bar{4}3m$. The determination of the cubic unit cell parameter [14.6886(5) Å] is in the range expected for this symmetry.[3] The discrepancy factors obtained were $R_{wp} = 0.078$, $R_p = 0.065$, $\chi^2 = 1.32$, and $R_F = 0.093$.
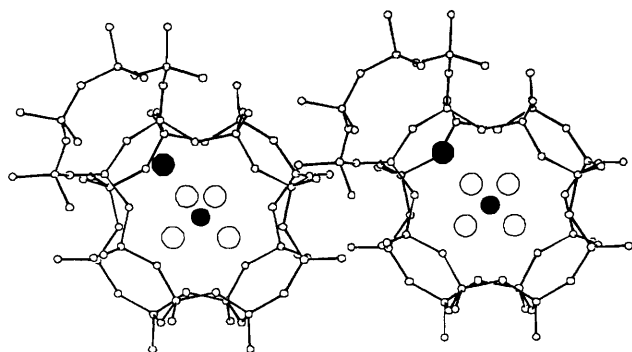
Fig. 3 Stereoscopic view of the distribution of Cd (○) and Xe (●) in the D8R site and in the S6R site. The Cd and Xe sites in the 8-ring are within 2.5 Å of one another and are therefore statistically occupied.

occupancy factors less than 10% of an oxygen atom were removed from the atom list. Four sites were found. Two of these are close to the 8R site, shown in Fig. 3; this site is occupied by 2.4 Xe [at $x,0,0$, $x = 0.540(1)$] and 3.2 Cd [at x,y,y, $x = 0.348(1)$, $y = -0.057(1)$]. The composition of the 8-ring sites is then ($Xe_{2.4}Cd_{3.2}$), close to the maximum of six dictated by space available in this site (Fig. 3). The remaining scattering is in the S6R sites, assigned to 1.26(3) Xe [x,x,x, $x = 0.143(1)$] and scattering modelled as 1.0(1) oxygen [x,x,x, $x = 0.35(1)$]. The total extra-framework scattering found is consistent with ($Cd_{3.2}Xe_{3.7}$) per unit cell.

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