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The dynamic desorption of krypton from the zeolite chabazite

S. P. Cork,[a] G. Cressey,[b] R. H. Jones,*[a] S. J. Teat[c] and V. L. Zholobenko[a]
[a] *The School of Chemistry and Physics, Keele University, Staffordshire, UK ST5 5BG*
[b] *The Natural History Museum, Cromwell Road, London, UK SW7 5BD*
[c] *CCLRC Daresbury Laboratory, Daresbury, Warrington, Cheshire, UK WA4 4AD*

Received (in Cambridge, UK) 7th July 2004, Accepted 14th September 2004
First published as an Advance Article on the web 5th November 2004

DOI: 10.1039/b410366c

Single crystal diffraction studies of the zeolite chabazite show that at high loading krypton atoms are forced to occupy sites with unfavourable interatomic Kr–Kr separations but upon desorption of Kr the remaining Kr atoms can now occupy sites with no such unfavourable separations.

Chabazite is a naturally occurring zeolite which has recently attracted attention for the non-cryogenic separation of nitrogen and oxygen.[1] To fully understand the mode of operation in this system it is desirable to determine the location of sorbed molecules within the zeolite and how the occupancy of these sites varies as a function of temperature and coverage. This problem is thus similar to that of finding the location of reactant molecules in zeolite catalysts but with the added complication that relative site occupancies of guest molecules now become important. Noble gases particularly, for example krypton and xenon, have long been used as probe molecules for the location of sorption sites in zeolites. A variety of techniques have been used to investigate the location of these sites including MASNMR,[2] X-ray powder diffraction,[3] neutron powder diffraction,[4] resonant powder diffraction,[5] and single crystal diffraction.[6,7] When powder diffraction methods were employed it has proved possible to determine the variation of the occupancy of the guest molecules as a function of temperature,[3,4] and powder diffraction methods have proved the only feasible method of obtaining such results.

There are several reasons for this. First, zeolites are inherently weak scatterers of X-rays due to the large amounts of empty space within them; second, many zeolites yield only small single crystals. The net effect of this is that it becomes impossible to collect a unique data set in a practical time. However, the construction of single crystal instruments at synchrotron sources[8] equipped with area detectors[9] have made rapid collection of high quality data possible. For example, it has been possible to observe the removal of a template from microporous materials during calcination.[10] In this work we report a variable temperature single crystal study on a chabazite containing krypton as the guest species, to our knowledge the first such example involving a weakly sorbed guest molecule.

Chabazite is built from double six-membered rings (D6R) linked by tilted four-membered rings to give the overall structure.[11] The largest ring aperture is an eight-membered ring. Chabazite is usually found naturally in its calcium rich form with an idealised composition of $Ca_2Al_4Si_8O_{12}\cdot 12H_20$. The space group of chabazite is $R\bar{3}m$ with $a \sim 9.4$ Å, $\alpha \sim 94.2°$.

A large crystal (0.4 × 0.25 × 0.2 mm) was obtained from the Natural History Museum, (sample BM 1914/15, composition $Si_{8.61}Al_{3.39}O_{24}Ca_{1.54}$ $K_{0.32}$ $Na_{0.10}$), was placed in a glass capillary and dehydrated at 350 °C for 12 h under dynamic vacuum with the final pressure being $\sim 10^{-5}$ Torr. The sample was cooled and 500 Torr of krypton was admitted and the sample was sealed. Data were collected on station 9.8,[9] of the Daresbury SRS, over the temperature range 100–290 K.[12] A starting model was derived from a literature study of dehydrated chabazite for the 100 K data set,[11] using only the framework cations. Extra-framework cations were easily located with difference Fourier maps in sites corresponding to literature values. The majority of sites probably contain a mixture of Ca and K ions and refinement of the sites was treated as such. Except for one site which, because of the short Na–O contacts, was treated as a Na atom. While the distribution of cations between these sites should be treated with caution the total number of cations at a site is accurate because Ca^{2+} and K^+ are isoelectronic, and to a first approximation have identical scattering factors.

Further difference maps revealed electron density peaks away from the framework. These peaks were included in the refinements as Kr atoms, with the temperature factors being given the same value. It became apparent that one of these peaks corresponded to the oxygen atom of a water molecule and was included as such since inclusion of a water molecule formed a distorted octahedron of oxygen atoms around one of the calcium ions. Any of the supposed krypton sites whose occupancy did not differ significantly from zero were discarded. The process of locating and refining krypton atoms was iterated until a stable structure resulted. The model obtained for the 100 K data set was used as a starting model for the 190 K data set.

The cations are located at sites that correspond to those found in either dehydrated Ca or K chabazites.[11] One of the cations is located at the centre of a double six ring, the next lies upon a three fold axis but within the main cage. The final cation is located in a position which is similar to that found for a low occupancy site for potassium in a dehydrated potassium chabazite.[13]

A total of 5 krypton sites were located. All of these are shown together with the symmetry related sites in Fig. 1. It can be seen that the krypton atoms are located in two regions at opposite ends of the cage. At 100 K the occupancies and interatomic contacts (Kr–O) are as follows. Kr(1) (0.18(3) per unit cell) is located in the main 8-membered window of the zeolite with a total of 7 contacts, which range between 3.72 and 4.12 Å. The sites which are occupied by Kr(2) (0.30(3) per unit cell) are found over the 4-membered rings which constitute one of the faces of the double 6-membered rings and have 7 contacts which are between 3.53 and 4.10 Å. Kr(3) (0.10(2) per unit cell) has a total of 6 contacts between 3.70 and 3.62 Å; Kr(4) (0.26(2) per unit cell) has contacts, which span 3.67 to 4.17 Å. The final site Kr(5) (0.31(2) per unit cell) has contacts of 3.38 to 3.84 Å. For these sites the nearest physically reasonable distances to cations are Kr(1)–Ca(2) 2.84(2) Å, Kr(1)–Ca(3) 3.02(5) Å, Kr(2)–Ca(2) 2.88(4) Å, Kr(2)–Ca(3) 2.96(3) Å, Kr(3)–Ca(3) 3.64(1) Å (3 contacts), Kr(4)–Ca(3) 3.38(2) Å (2 contacts) and Kr(5)–Ca(2) 3.30(3) Å.

From the large number of positions of krypton sites and their

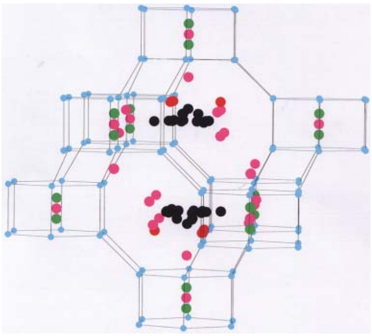

Fig. 1 View of chabazite showing clustering of krypton sites and extra-framework cations. Legend: black Kr, green Na, purple (Ca/K) blue Si, red O (water molecule). Framework oxygen atoms removed for clarity.

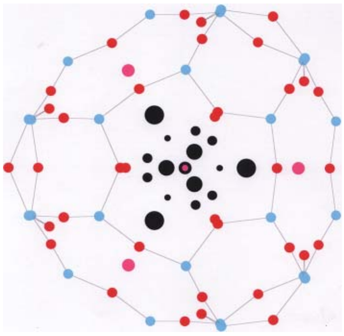

Fig. 2 Projection showing location of krypton sites and nearest cation sites. Note the displacement of Kr(5) towards the 8-membered window. Legend: black Kr (in ascending order of circle size Kr(1), Kr(2), Kr(3), Kr(4), Kr(5)), purple (Ca/K) (smallest Ca/K(2) largest Ca/K(3)), blue Si, red O. The scale can be noted from the following Kr–Kr contacts: Kr(2)–Kr(2) is 0.62 Å, and Kr(5)–Kr(5) is 3.42 Å.

occupancies it might be difficult to designate which of these sites is the most stable. If occupancy were the sole criterion, Kr(5) would be most stable but it has Kr–O contacts, which are less than the sum of the van der Waals radii (3.38 Å), and shorter than those seen in Kr encapsulated in vitreous silica (3.45 Å).[14] However the use of variable temperature diffraction has enabled us to suggest a possible arrangement of stability for these sites. Of the five sites four of them Kr(1), Kr(2), Kr(3) and Kr(4) have minimum Kr–O contacts in excess of 3.53 Å which is comparable to the sum of the van der Waals radii. For these four sites, the maximum occupancy is limited to 2 per unit cell due to unfavourable Kr–Kr contacts either with other krypton atoms or with symmetry related krypton atoms. This is demonstrated more clearly in Fig. 2 which shows a projection of these sites and the surrounding framework atoms. The situation is further complicated by the presence of the extra-framework cations, when these are taken into account the number of krypton sites that can occupy any one of these sites is further reduced, by the presence of cations M(2) and M(3) (where M(2) and M(3) are the cations within the main cage). The final site Kr(5) is located much further off the three fold axis (Fig. 2) and moved effectively towards the windows (eight-membered rings) into the cage and has Kr(5)–Kr(5) contacts of 3.42 Å which are less than the sum of the van der Waals radii but much greater than those seen for the other Kr–Kr distances observed, in the structure. The amount of Kr that can be introduced at site Kr(5) is also limited by interactions with cation sites. However not all the cation sites are fully occupied and if Kr(5) was fully occupied then the number of krypton atoms at this site per unit cell, would be 6.

The effect of heating upon the occupancies of these sites is given in Fig. 3a. It can be seen that for some of the sites there is in fact an increase in the occupancy upon heating. This is shown more clearly in Fig. 3b where the amount of the krypton (%) at a given site at each temperature is plotted. It can be seen that Kr(5), which has the highest occupancy at 100 K, now has one of the lowest occupancies. In addition, there is a marked increase in the relative amount of krypton at sites 1 and 2. It will be recalled that these sites make contacts with the framework, which are comparable to the sum of the van der Waals radii and are thus relatively stable but because of unfavourable Kr–Kr contacts can only have a limited capacity for sorbed krypton atoms. When the total amount of krypton sorbed at a given temperature is such that these sites can accommodate the majority of the krypton atoms it is these sites that are preferentially occupied.

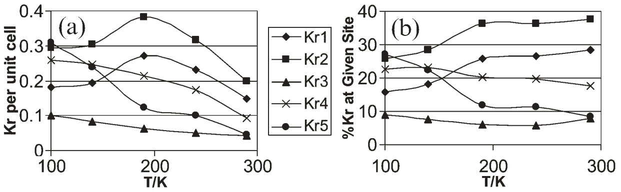

Fig. 3 (a) Variation of Kr occupancy at a site as a function of temperature. (b) Percentage of Kr occupying a site as a function of temperature.

In conclusion we have located the sites of krypton atoms within a naturally occurring chabazite. By varying the temperature it is shown that at low temperatures (high loading) krypton atoms are forced into sites having Kr–Kr contacts which are less than the sum of the van der Waals radii, and thus of higher energy. On raising the temperature, as krypton is desorbed the remaining krypton is able to occupy sites which do not have these unfavourable Kr–Kr interactions and thus are of lower energy. This is the first time to our knowledge that single crystal methods have been used to study a weakly bound guest species in this manner. Thus by using a combination of single crystal diffraction and varying the temperature we have been able to obtain information of the mode of desorption of a guest species from a zeolite at the atomic level with much enhanced accuracy and precision, which has enabled the mechanism of desorption to be studied. Furthermore, it shows that inferences of the stability of structures that are determined from diffraction data at one temperature on a zeolite sorbate complex should be treated with caution.

We wish to thank the EPSRC and CCLRC for support.

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12 Crystallographic details: formula $Si_{8.61}Al_{3.39}$ $O_{24}Ca_{1.54}$ $K_{0.32}$ $Na_{0.10}$ $Kr_x(H_2O)_{0.52}$ rhombohedral, space group = $R\bar{3}m$, number of parameters = 70: T = 100 K, a = 9.2743(7) Å, α = 91.597°(1), μ = 0.77 mm^{-1}, total number of reflections = 14001, number of unique reflections = 1836, number of observed reflections ($I > 2\sigma(I)$) 1382, R_{obs} = 0.0864, R_{total} = 0.0956, wR^2 = 0.1975, CCDC 244274; T = 140 K, a = 9.2935(7) Å, α = 91.604(1)°, μ = 0.72 mm^{-1}, total number of reflections = 14219, number of unique reflections = 1852, number of observed reflections ($I > 2\sigma(I)$) 1404, R_{obs} = 0.0597, R_{total} = 0.0696, wR^2 = 0.1756, CCDC 244271; T = 190 K a = 9.2833(7) Å, α = 91.617°(1), μ = 0.72 mm^{-1}, total number of reflections = 14187, number of unique reflections = 1846, number of observed reflections ($I > 2\sigma(I)$) 1385, R_{obs} = 0.0588, R_{total} = 0.0695, wR^2 = 0.1724, CCDC 244272; T = 240 K, a = 9.2943(7) Å, α = 91.625(1)°, μ = 0.63 mm^{-1}, total number of reflections = 14235, number of unique reflections = 1853, number of observed reflections ($I > 2\sigma(I)$) 1386, R_{obs} = 0.0563, R_{total} = 0.0673, wR^2 = 0.1712, CCDC 244273; T = 290 K, a = 9.3086(7) Å, α = 91.638(1)°, μ = 0.47 mm^{-1}, total number of reflections = 16639, number of unique reflections = 1602, number of observed reflections ($I > 2\sigma(I)$) 2387 (number of parameters = 69), R_{obs} = 0.0572, R_{total} = 0.0764, wR^2 = 0.1769. CCDC 244270. See http://www.rsc.org/suppdata/cc/b4/b410366c/ for crystallographic data in .cif or other electronic format.
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