Use of Anomalous X-Ray Diffraction to Determine the Location of Sorbed Krypton in Ferrierite

R. H. Jones,[a] P. Lightfoot[b] and R. M. Ormerod[a]

[a] *Department of Chemistry, University of Keele, Keele, Staffordshire, UK ST5 5BG*
[b] *Department of Chemistry, University of St Andrews, St Andrews, Fife, UK KY16 9ST*

Rietveld refinement of X-ray powder diffraction data collected at two wavelengths, one close to the Kr absorption edge, has enabled the location of three sorption sites of Kr in the zeolite ferrierite to be determined, using anomalous scattering.

Microporous aluminosilicate zeolites constitute an important branch of the so-called uniform heterogeneous catalysts.[1] Crucial to our understanding of the mode of operation of these materials is the location of reactant molecules within the pore structure. Since these are crystalline materials it is possible to use diffraction methods to probe the location of these sorbed molecules. The technique that has found the most widespread applicability relies on the Rietveld profile refinement of powder data, as it is usually impossible to obtain single crystals of sufficient size and quality. Early noteworthy studies include the location of benzene in zeolite Y,[2] pyridine in zeolite L[3] and xenon in zeolite rho[4] using neutron diffraction. The latter two studies were also important in that recourse was made to modelling studies in confirming the position of the sorbed moieties. It has also been possible to use X-rays to locate sorbed species using either laboratory sources[5] or synchrotron sources.[6–9] Almost all of these studies have involved zeolites with a crystallographic symmetry of hexagonal or higher. Here we report the location of Kr in the zeolite ferrierite, which is found in an orthorhombic space group, using synchrotron radiation. A recently exploited advantage of synchrotron radiation involves the tunability of the source which enables an anomalous scattering experiment to be performed. This has recently been used to locate Zn^{2+} ions coordinated to the O atoms of the framework of zeolite Y.[10] We have made use of this technique to study for the first time the location of a sorbed species.

Ferrierite is a zeolite which possesses a two-dimensional pore system. The larger channels are bounded by 10-membered rings, whilst the smaller channels contain 8-membered rings, which link large cavities in the structure.[11] There has been renewed interest in ferrierite as a commercial catalyst for the isomerisation of butenes as precursors in the production of methyl *tert*-butyl ether.[12] Extensive use has been made of noble gases in studying zeolites, for example in their adsorption properties,[13] use of ^{129}Xe NMR,[14] and in modelling studies.[15]

A sample of proton ferrierite was kindly supplied by Dr J. W. Couves of BP plc. The sample was loaded into a glass capillary and was dehydrated at 320 °C for 12 h under dynamic vacuum. The sample was cooled and 631 Torr of Kr was admitted. This corresponds to an approximate loading of 3.5 Kr per unit cell.[16] Data were collected on station 9.1 of the Daresbury synchrotron at 140 K. Two powder patterns were collected, one at 0.8663 Å (*a*), which is close to the Kr absorption edge of 0.86552 Å, and the other at 0.6483(1) Å (*b*). The step increment for each pattern was 0.01° and the time for each step increment was 9 s for both patterns. In both cases the value of d_{min} was 1.13 Å, corresponding to 444 reflections. A starting model for the framework structure was taken from the work of Vaughan,[11] and the structure was analysed by Rietveld profile refinement,[16] using the GSAS suite of programs.[17] Refined lattice parameters were a = 18.751(2), b = 14.802(1), c = 7.4119(5) Å, in space group *Immm*. Restraints were applied to the T–O bond lengths (T = tetrahedral atom). The model converged to R_{wp} = 0.096 (*a*), 0.054 (*b*), and R_p = 0.054 (*a*), 0.036 (*b*), and showed clear discrepancies between the observed and calculated patterns. A difference map clearly revealed the location of three sorption sites. Inclusion of Kr atoms at these sites, with fixed U_{iso} (0.1 Å^2) but variable occupancy led to final agreement factors of R_{wp} = 0.068 (*a*), 0.034 (*b*) and R_p = 0.038 (*a*) and 0.026 (*b*) for 48 least-squares parameters. Fig. 1 shows observed, calculated and difference profiles for Kr-loaded ferrierite at 0.8663 Å.

The changes in the intensities for the on- and off-edge data sets are only sensitive to the anomalously scattering atoms and does not depend upon the Bragg angle. The value of f' changes from approximately −6.489 (0.8663 Å) to −0.321 (0.6483 Å) electrons for the two wavelengths selected. The use of both patterns in the refinement enables us to improve the precision of the structural parameters of these atoms. The occupancies of the 3 sites are 1.94(3) (i), 1.31(3) (ii) and 0.77(3) (iii) per unit cell. The locations of these sites are illustrated in Figs. 2–4, respectively. The site with the highest occupancy (i) is situated in the eight-membered ring. There are a total of six contacts between Kr and oxygen atoms of the window ranging between 2.90(2) and 3.23(2) Å. In site (ii) the Kr atom is displaced away

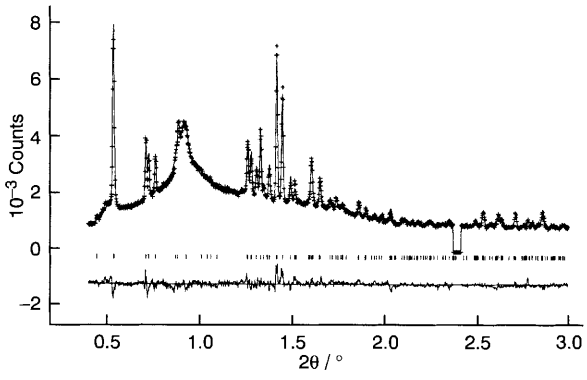

Fig. 1 Observed (+), calculated (—) and difference (lower trace) profiles for Kr-loaded ferrierite at 0.8663 Å. The tick marks show the position of allowed reflections.

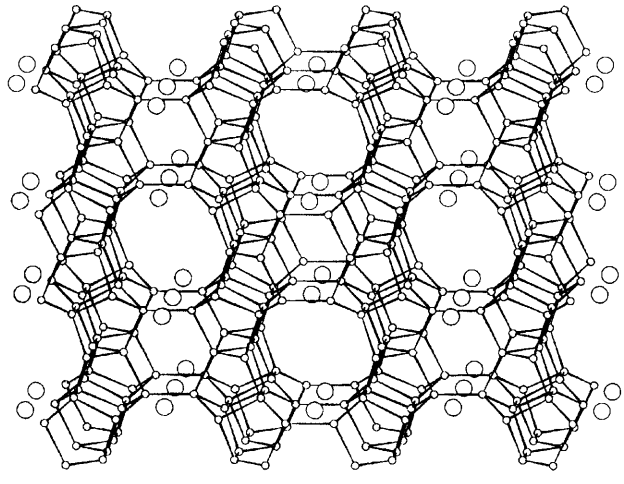

Fig. 2 View approximately along [001]. Large circles represent Kr site (i), small circles the tetrahedral framework sites. O atoms have been omitted for clarity.

from the centre of the large cages towards the ten-membered ring and makes four contacts of 3.60(3) Å with O atoms in this ring. The site with the lowest occupancy (iii) has the Kr atom displaced away from its idealised position at the centre of the ten-membered ring, with five contacts < 3.65 Å to O atoms. The plausibility of our model is supported by the observation that the site with the highest occupancy has the Kr atom making the shortest van der Waals contacts with the O atoms of the framework. We are currently investigating the stability of these sites using computational methods. The location of the krypton atoms may serve as suitable starting points for modelling studies of hydrocarbon molecules within ferrierite.

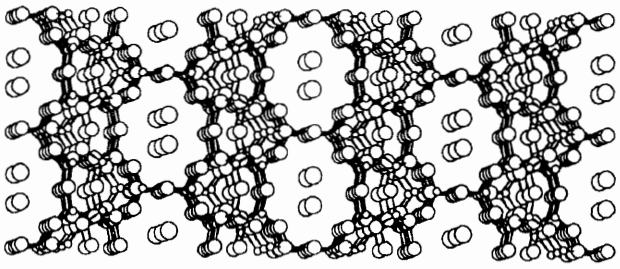

Fig. 3 View approximately along [010]. Largest circles represent Kr site (ii), medium circles O atoms, smallest circles tetrahedral framework sites.

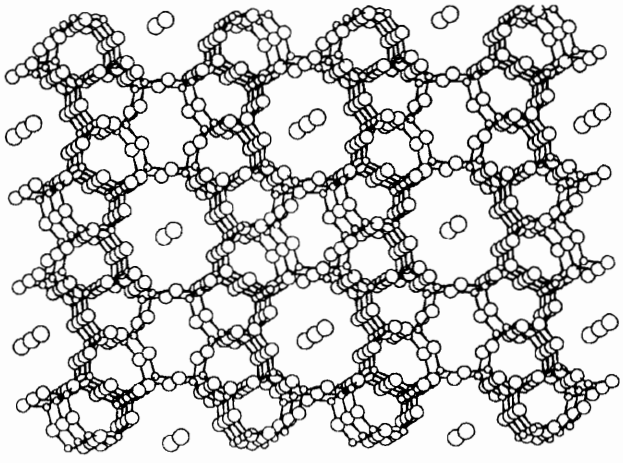

Fig. 4 View approximately along [001]. Largest circles represent idealised Kr site (iii), medium circles O atoms, smallest circles tetrahedral framework sites.

We thank the SERC for provision of beam time and facilities, and use of the ICSD database at Daresbury Laboratory, Dr J. W. Couves for his interest in the project, BP plc for donation of the zeolite samples and Dr G.Bushnell-Wye for his assistance in collecting the data on station 9.1.

Received, 28th November 1994; Com. 4/07265K

References

1 J. M. Thomas, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1673.
2 A. N. Fitch, H. Jobic and A. Renouprez, *J. Phys. Chem.*, 1986, **90**, 1311.
3 P. A. Wright, J. M. Thomas, A. K. Cheetham and A. K. Nowak, *Nature*, 1985, **318**, 611.
4 P. A. Wright, J. M. Thomas, S. Ramdas and A. K. Cheetham, *J. Chem. Soc., Chem. Commun.*, 1984, 1338.
5 I. Gameson, T. Rayment, J. M. Thomas and P. A. Wright, *J. Phys. Chem.*, 1988, **92**, 988.
6 Z. A. Kaszkur, R. H. Jones, J. W. Couves, D. Waller, C. R. A. Catlow and J. M. Thomas, *J. Phys. Chem. Solids*, 1991, **52**, 1219.
7 Z. A. Kaszkur, R. H. Jones, D. Waller, C. R. A. Catlow and J. M. Thomas, *J. Phys. Chem.*, 1993, **97**, 426.
8 E. Dooryhee, G. N. Greaves, A. T. Steel, R. P. Townsend, S. W. Carr, J. M. Thomas and C. R. A. Catlow, *Faraday Discuss. R. Soc. Chem.*, 1990, **89**, 119.
9 J. B. Parise, J. A. Hriljac, D. E. Cox, D. R. Corbin and V. Ramamurthy, *J. Chem. Soc., Chem. Commun.*, 1993, 226.
10 A. P. Wilkinson, A. K. Cheetham, S. C. Tang and W. J. Reppart, *J. Chem. Soc., Chem. Commun.*, 1992, 1485.
11 P. A. Vaughan, *Acta Crystallogr.*, 1966, **21**, 983.
12 H. H. Moolweer, K. P. de Jong, B. Kraushaar-Czarnetzki, W. H. J. Stork and B. C. H. Krutzen, *Studies in Surface Science and Catalysis, Zeolites and Related Microporous Materials State of the Art*, Elsevier, 1994, vol. 84, p. 2327.
13 A. J. T. Hope, C. A. Leng and C. R. A. Catlow, *Proc. R. Soc. London, A Math. Phys. Sci.*, 1989, **424**, 57.
14 P. J. Barrie and J. Klinowski, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1992, **24**, 2.
15 T. Takaishi, K. Nonaka and T. Okada, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 3317.
16 H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65.
17 A. Larson and R. B. Von Dreele, GSAS Manual, Los Alamos report No. LA-UR-86-748, 1986.