Locating the Sites of Adsorbed Species in Heterogeneous Catalysts: a Rietveld Neutron Powder Profile Study of Xenon in Zeolite-rho

Paul A. Wright,[a] John M. Thomas,*[a] Subramaniam Ramdas,[a] and Anthony K. Cheetham[b]

[a] *Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EP, U.K.*
[b] *Chemical Crystallography Laboratory, University of Oxford, 9 Parks Road, Oxford OX1 3PD, U.K.*

As well as yielding the atomic structure of the aluminosilicate host, neutron diffraction reveals the preferential location of adsorbed Xe to be at the central site in the octagonal prism in D^+-rho zeolite, both at 5 and at 210 K: 'atom–atom' calculations also show this to be the preferred site.

The symmetries and intensities of low energy electron diffraction (LEED) patterns can disclose where adsorbate species are located on single crystal surfaces, and so also, under favourable circumstances, can the techniques of electron energy loss spectroscopy (EELS) and secondary ion mass spectrometry (SIMS). However, heterogeneous catalysts of the type used industrially seldom, if ever, occur in single-crystal form: they are almost invariably high-area powders that need to be able to withstand a range of pre- and post-treatments such as exposure to air and to promoters, high-temperature outgassing, thermal activation, and regeneration. Moreover, even model-studies with single-crystal analogues of the real-life catalyst probed under high-vacua are generally precluded because most commercially important catalysts cannot readily be prepared in single-crystal form (good examples are Co/MoS_2 or Ni/WS_2 for hydrodesulphuration, or the various zeolitic catalysts for cracking and isomerization).

Powder diffraction, especially with neutrons, offers attractive prospects, especially for zeolitic catalysts (which are often difficult to obtain as single crystals), of quantitatively pinpointing the structural features of sorbent–sorbate complexes. It is already well-established[1—3] that, for those zeolites where the crystallographic asymmetric units are relatively simple, the atomic structure of the high-area solids can be reliably extracted from powder profile (Rietveld)† refinements.[4,5] The siting and co-ordination of certain exchangeable cations and the (Brønsted) acid sites on the aluminosilicate framework can be evaluated in this fashion.

This work illustrates that the neutron Rietveld technique constitutes a powerful method of locating an occluded guest species within the accessible cavities and tunnels of zeolitic catalysts. To establish the feasibility of this approach we have selected a 'non-reactive' system, Xe in zeolite-rho, which serves as a realistic model system for commercial analogues (*e.g.* methanol in ZSM-5). The structures of the various

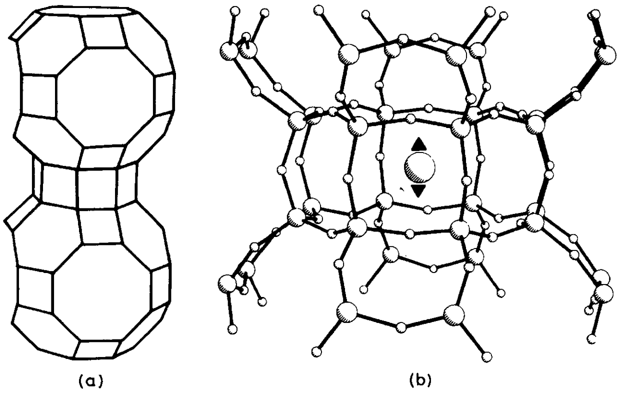

Figure 1. (a) Schematic polyhedral drawing of framework structure of zeolite-rho. Each vertex represents a tetrahedral (T) site (occupied either by Si^{4+} or Al^{3+} ions). The lines connecting vertices are T–O–T links which, for simplicity, are drawn straight. (b) Segment of structure (to scale) of adsorbate–adsorbent complex at 5 K determined in this work. Note the preferential location of Xe at centre of octagonal prism. Arrows signify directions along which Xe oscillates with increasing temperature.

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† The Rietveld procedure sets out to arrive at a final refinement, $R_{pr.}$, for the profile of the neutron powder diffraction pattern in which all the peaks are gaussian; y_i(obs.) and y_i(calc.) are the observed and calculated intensities, respectively, at the *i*th position on the profile, and *c* is the scale factor. (See refs. 1—5 and 7 for further details).

$$R_{pr.} = \Sigma|y_i(\text{obs.}) - \frac{1}{c}\, y_i\,(\text{calc.})|/\Sigma|y_i(\text{obs.})|$$

cation-exchanged forms of zeolite-rho have been previously determined by integrated intensity and profile refinement of powder patterns. Zeolite-rho has a flexible framework consisting of two interpenetrating but unconnected three-dimensional channel systems, which have topologically different absorption volumes [octagonal prisms and supercages, Figure 1(a)] within one or each of which xenon may be bound. Access to, and space within, these internal channels is maximized when the zeolite has protons as the exchangeable cation.

Zeolite-rho was prepared according to established procedures,[6] and *X*-ray diffraction, as well as ^{29}Si and ^{27}Al magic-angle spinning n.m.r., analytical electron microscopy, and i.r. studies confirmed that it was highly crystalline and phase pure.[7] The material was exchanged with NH_4^+ ions and heated (to drive off NH_3) thereby producing the H^+-form which was then converted into the D^+-form by prolonged exposure to D_2O. Xe was sorbed from the gas phase, and approx. 6 Xe atoms were retained per unit cell. The neutron powder profiles, obtained on the D1A instrument at Institut Laue Langevin, Grenoble, were recorded with the sample at 5 and at 210 K. Standard refinement procedures yielded the atomic co-ordinates of the adsorbent–adsorbate complex shown in Figure 1(b).

At 5 K, all the Xe (like the Cs^+ ion which has a radius comparable to that of Xe) resides within 0.2 Å of the centre of the octagonal prism. At 210 K the degree of occupancy of this site drops to *ca.* 70% of its former value, and additional sites in the supercage just outside the octagonal prism (Figure 1) become partially occupied.

Atom–atom, pairwise evaluation procedures akin to those used extensively in organic solid-state chemistry,[8,9] with $Xe \cdots O$ potentials[10] written as shown in equation (1) (energy in kJ mol^{-1}, distances in Å) provide separate evidence

$$U_{Xe\cdots O} = \Sigma \quad [-1.06 \times 10^{-4}/r_{ij}^6 + 9.25 \times 10^{-5} \exp(-3.6 r_{ij})] \quad (1)$$

that there is a deeper potential well for adsorption at the centre of the octagonal prism, with accessible minima, where the adsorption energy is 29.7 kJmol^{-1} (*cf.* experimental value[11] of 29.5 kJmol^{-1}). See Figure 2.

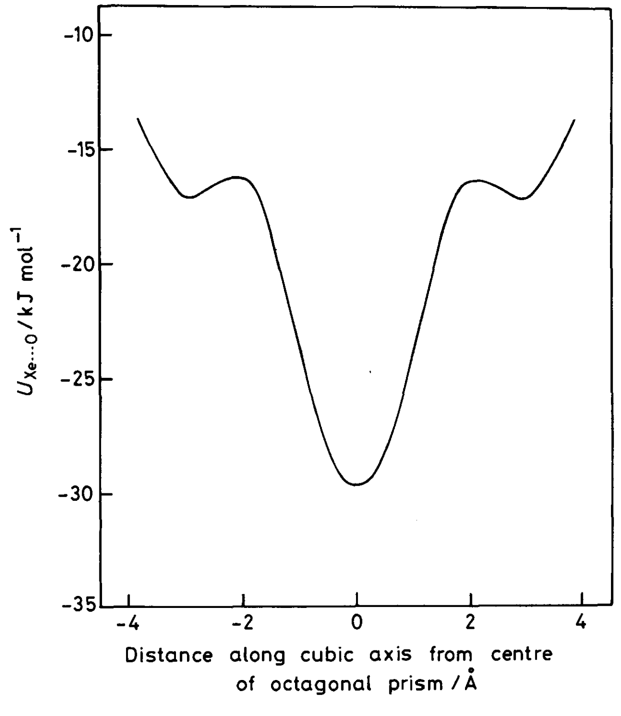

Figure 2. Results of 'atom–atom' computation [see equation (1)] of the binding energy $U_{Xe\cdots O}$ of Xe in zeolite-rho. The deepest minimum corresponds to the site at the centre of the octagonal prism, and the shallower minima to sites just outside the 8-membered windows of this prism.

The implications of this feasibility study are clear. Given adequate neutron flux (and beam time!) and a variable-temperature, variable-pressure cell,[12] *in situ* studies[13] of the location, movement and fragmentation of molecules occluded within zeolitic catalysts ought also to be possible, thereby affording greater information than hitherto available about the dynamics of catalytic changes under reactor conditions. In particular, the structure of the catalyst, the nature of the active sites and the preferred siting of reactants are all experimentally accessible. It is also noteworthy that early *X*-ray work on chabazite[14] and on Xe and SO_2 sorbed in zeolite A[15] yielded promising results relevant to this study and its future extensions.

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