# The Location of Adsorbed Pyridine in Sodium-Y Zeolite

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Pyridine adsorbed at low coverage in sodium-Y zeolite has been located by powder neutron diffraction in the twelve-ring window between supercages.

The presence of acid sites in zeolites is crucial to their role as catalysts in a number of important chemical processes.[1] These acid sites may be of a Brønsted or Lewis nature and have been investigated by a range of experimental[2—9] and theoretical[10] techniques. Spectroscopic studies have used basic probe molecules, such as pyridine,[2—4] ammonia,[8] and trimethylphosphine,[7] for which there is a clear distinction between the protonated cation and the neutral molecule, to explore the nature of the acid sites. Hence, IR studies[2] on pyridine sorbed on hydrogen-Y and sodium-Y zeolites show the formation of pyridinium ions and, therefore, the dominance of Brønsted sites in the former, and suggest adsorption at a Lewis site in the latter. Similar indications obtained from the measurement of the chemical shifts by $^{15}$N NMR spectroscopy[4] have supported this conclusion. Direct evidence for the nature of the Brønsted-acid sites in zeolites has come from powder neutron diffraction studies,[11] which have also been successful in locating a number of hydrocarbon molecules in zeolites, such as benzene in sodium-Y,[12,13] benzene[14] and pyridine[15] in zeolite-L. Presented here are the results of a powder neutron

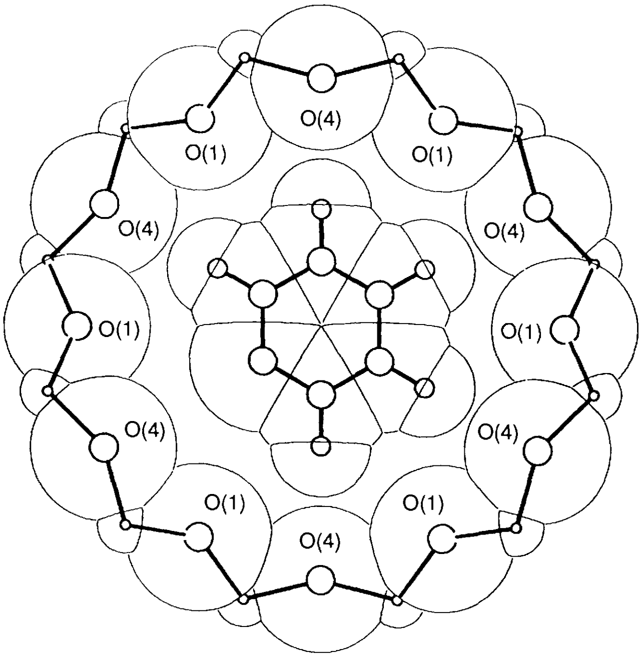

**Figure 1.** View of the pyridine molecule in the twelve-ring window between the supercages.

diffraction study of sodium-Y zeolite showing the structural arrangement of pyridine in its sorption site and its possible interactions with the framework.

Sodium-Y zeolite, of composition $Na_{56}Si_{136}Al_{56}O_{384}$, was loaded with a nominal coverage of one molecule of deuteriated pyridine per supercage and was contained in a thin-walled vanadium sample can. Powder neutron diffraction data covering the angular range 5—160° in 2θ were obtained for the bare and loaded zeolites on the diffractometer D2B at the ILL, Grenoble, at a wavelength of 1.595 Å over a period of 12 h at room temperature and 4 K. The diffraction patterns were analysed by the Rietveld method.[16]

The final $R$ factors for refinement of the bare zeolite[13] in space group $Fd\bar{3}m$ [$a$ = 24.8187(2) Å] were $R_{wp} = 11.4\%$, $R_I = 7.9\%$ and $R_{exp} = 4.4\%$. This was used as the starting model for the refinement of the pyridine-loaded zeolite and gave $R_{wp} = 33.2\%$ when the pyridine was excluded. Inclusion of the pyridine molecules at the two positions discovered for benzene in sodium-Y zeolite[12,13] showed the site in the twelve-ring window to be the sole adsorption site at this coverage. No significant occupancy of the site attached to the SII sodium ion in the supercage or any other position in the cavities of the zeolite was observed. The final $R$ factors were $R_{wp} = 11.5\%$, $R_I = 8.5\%$ and $R_{exp} = 6.0\%$ at room temperature. The pyridine molecules lie perpendicular to the [111] axis and are centred on the site 16d (1/2, 1/2, 1/2) which has point symmetry $\bar{3}m$, so that crystallographically the molecules have sixfold orientational disorder about the cube diagonal, with the nitrogen, carbon, and deuterium atoms directed towards the six O(4) atoms in the twelve-ring window, Figure 1.

The pyridine ring is centred on a site of $\bar{3}m$ symmetry and the refinements indicate that there is no significant displacement from this position. Application of the $\bar{3}m$ site symmetry generates six equivalent orientations of the molecule, enabling the scattering density in the window to be described by an average molecule with hexagonal symmetry. The molecule was, therefore, constrained to perfect hexagonal geometry, with C/N–C/N and C–D bond lengths of 1.40 and 1.08 Å, respectively.

The preferential adsorption of pyridine at the window site indicates an interaction between the molecule and the framework. This differs from benzene in sodium-Y zeolite where the molecules are preferentially located in the supercage bound to the SII sodium ions *via* their π-electron density.[12,13] Occupation of this site stabilises the neighbouring window site which consequently shows proportionately higher occupancy with increasing benzene coverage,[13] with the eventual formation of benzene clusters.[17—19]

The IR[2] and $^{15}N$ NMR[4] spectroscopic studies show that in sodium-Y zeolite, pyridine is adsorbed at a Lewis-acid site, which may be associated with the charge-balancing cations[3] or the aluminium atoms in the framework.[1] In the window site the pyridine molecule exhibits no direct co-ordination to the sodium ions, either *via* its π-electron system or the lone pair of the nitrogen atom. This also appears true for the framework and is illustrated by the reluctance of the nitrogen atom to approach the framework by displacement of the molecule from the $\bar{3}m$ centre. Thus, the average N/C–O(4) and N/C–O(1) distances are 3.840(3) and 3.829(3) Å, respectively. This is too great a separation for there to be charge transfer from the pyridine ring to the framework. Stabilisation of this position is, therefore, likely to be due to interaction of the dipole of the molecule with charge distribution around the window associated with the arrangement of the aluminium atoms.

Each supercage has four twelve-ring windows shared with the neighbouring supercages. Hence, at a pyridine coverage greater than two molecules per supercage the window sites will be full and a second site for pyridine will be necessary in this structure. This is currently under investigation.

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