Novel Cation Sited in a Dehydrated Divalent Copper-exchanged Zeolite

By I. E. Maxwell* and J. J. de Boer

[*Koninklijke/Shell-Laboratorium, Amsterdam* (*Shell Research B.V.*)]

Summary Single-crystal *X*-ray analysis has shown that in dehydrated divalent copper-exchanged faujasite the so-called site III-type cations are located at the pore entrances to the supercage and are effectively bonded to only one framework oxygen, thus being present in a highly unsaturated co-ordination geometry.

In recent years there has been considerable speculation[1] about the location of the so-called site-III cations in faujasite-type zeolites. These cations are presumed to be sited inside the large cages and are of interest since they are accessible to adsorbate molecules. We now report the results of a single-crystal *X*-ray analysis of dehydrated divalent copper-exchanged faujasite in which site III-type cations have been located.

Crystals of $Cu_{28}(AlO_2)_{56}(SiO_2)_{136}$ (assuming complete exchange of a sample of natural faujasite, dehydrated at 150° C for 20 h under a vacuum of 10^{-5} Torr) were confirmed to have space group $Fd3m$, $a = 24{\cdot}643(5)$ Å. Intensity data were collected using a Nonius three-circle automatic diffractometer and Cu-K_{α} *X*-radiation. Six equivalent data sets were obtained and averaged to yield 212 unique reflections. Full-matrix least-squares refinement resulted in a final conventional *R* factor of 0·050.

Divalent copper cations were located at sites† I (1·5), I′ (14·2), II′ (0·8), II (5·3) and III (3·3).‡ The siting of 90% of the expected total number of copper ions has been established and in the present structure site-III cations are located in the supercage at the edges of the four-membered oxygen rings (Figure 1). These cations have a highly

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† The site nomenclature is as follows: site I, centre of hexagonal prism; site II, six-membered ring face of sodalite cage on the supercage side; site I′ and II′ lie on the other sides of the six-membered rings, opposite sites I and II, respectively, inside the sodalite cage.

‡ Numbers in parentheses indicate the occupancy factors for each site in cations per unit cell.

unusual co-ordination geometry, being strongly bound to only one framework oxygen atom [distance to O(1) = 2·18(7)Å] and very weakly to another [distance to O(4) = 2·77(7)Å]. The short distance to O(1) also indicates that these species are indeed copper cations (*cf.* $r_{Cu^{2+}} + r_{O^{2-}} = 2\cdot10$; ref. 2) and not water molecules or the parent cations (K^+ in this case), for which the shortest possible distances to the zeolite framework would be approximately 2·8 and 2·7Å, respectively. In addition, this short distance indicates that there is no strong interaction of residual water molecules with site-III type Cu^{2+} ions.

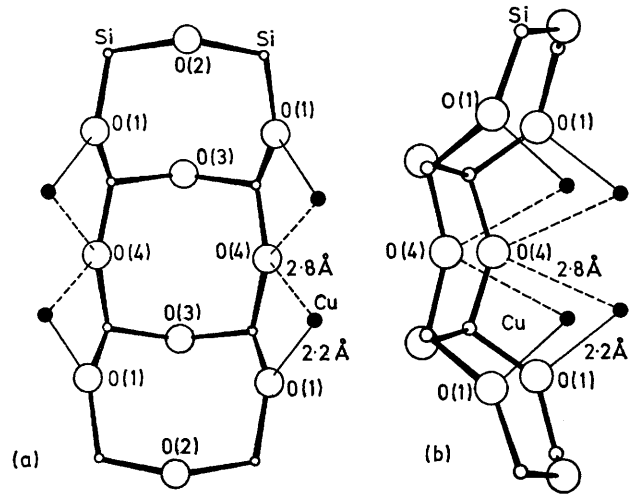

FIGURE 1. Perspective views showing symmetry-related site-III Cu ions co-ordinated at the edges of the four-membered oxygen rings inside the supercage. (a) Front view (b) side view.

The oxygen atoms O(1) bridge the hexagonal prisms and form the entrances to the supercage, with the copper ions protruding into the pore opening (Figure 2). Such cations are clearly very favourably sited for interaction with adsorbate molecules, particularly in comparison with site II-type cations (also located in the supercage), which are significantly shielded from substrate molecules by the surrounding six-membered ring of framework oxygen atoms. Moreover, the highly unsaturated co-ordination geometry would also further facilitate interaction with adsorbed species. The structural results therefore provide strong support that site-III cations play a major rôle in the known catalytic (e.g. oxidation,[3] cracking[4] and isomerization,[5]) properties of divalent-copper faujasite.

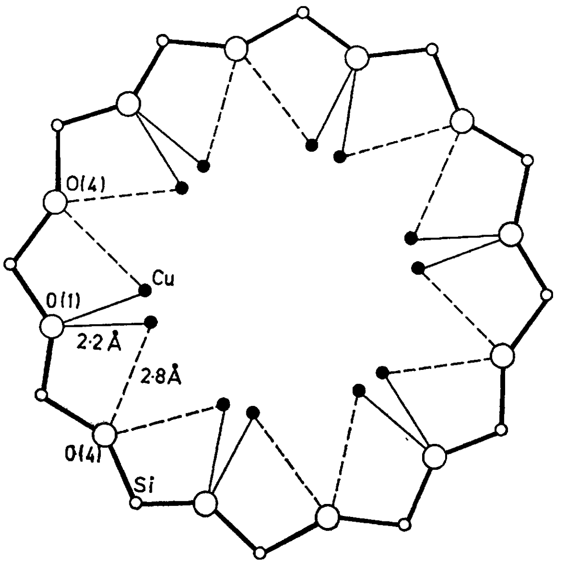

FIGURE 2. Perspective view showing symmetry-related site-III Cu ions which protrude into the supercage pore entrance. Owing to the low occupancy factor (3·3 per unit cell) approximately only one in every five pore entrances (16 per unit cell) will contain a site-III Cu ion.

The observed location of site-III copper ions is contrary to previous predictions, which placed the metal ions at the centres of the four-membered rings.[1a,b] Further studies will be necessary to determine whether the position found for the site-III Cu^{2+} ions is generally occupied by other cations. Interestingly, this site corresponds very closely to that proposed for the most reactive protons in hydrogen faujasite.[6]

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