Electron Spin Resonance Investigation of the Catalytic Activity of Copper-Exchanged X-type Zeolites

By I. R. LEITH, C. KEMBALL, and H. F. LEACH*

(*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh* EH9 3JJ)

Summary Changes in the e.s.r. spectrum of a copper-exchanged zeolite after treatment with but-1-ene indicate the preferential reactivity of copper ions in one particular environment and their subsequent migration.

REPLACEMENT of sodium ions in an X-type zeolite by copper(II) ions has been shown[1] to have a profound effect on its catalytic activity for the isomerization of n-butenes. In order to understand the function of the copper ions in the catalytic process knowledge of their distribution in the zeolite framework is desirable. Using e.s.r. techniques we have now obtained direct evidence that the copper ions in partially dehydrated copper-exchanged X-type zeolites are distributed among several different crystallographic locations. The copper ions in one of these positions were shown to be accessible to, and to react readily with, but-1-ene.

The e.s.r. spectrum obtained when a sample of Linde 13X-type zeolite containing approximately four copper(II) ions per unit cell was dehydrated in a pressure of *ca.* $1·3 \times 10^{-3}$ N m^{-2} for 12 h at 673 K is shown in Figure (1a).† The low-field part of this spectrum, associated with $g_{\|}$, is shown on an expanded scale in Figure (2a). Two sets of four equidistant peaks are clearly shown, with an overlap occurring with the first peak of each set. This double set of peaks arises from the hyperfine interaction of the unpaired electron with copper(II) ions ($I = 3/2$) located in two crystallographically distinct environments. For the first group of peaks the value of $g_{\|}$ is 2·380 ± 0·005 with a parallel hyperfine splitting $A_{\|}$ of 12·9 mT; for the second group the corresponding values are $g_{\|} = 2·349 \pm 0·005$ and $A_{\|} = 14·8$ mT.

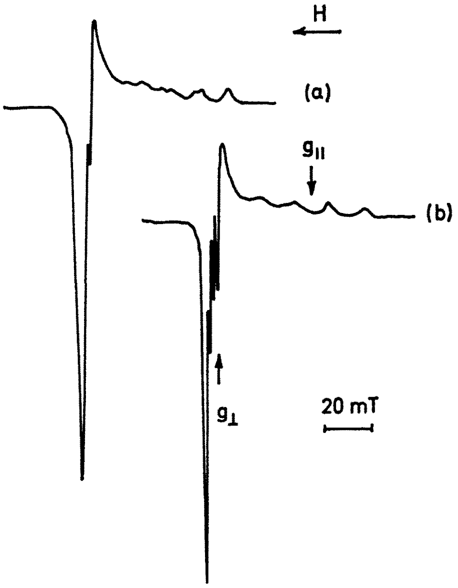

FIGURE (1) (a) *E.s.r. spectrum of copper*(II) *ions in copper X-zeolite dehydrated at* 673 K *for* 12 h, (b) *as* (a), *after treatment at* 473 *K for* 3 *h with but*-1-*ene.*

TABLE. *E.s.r. parameters for the low field spectra of the copper X-zeolite*

	Pretreatment	$g_{\|}$ 1	$g_{\|}$ 2	$g_{\|}$ 3	$A_{\|}$/mT 1	$A_{\|}$/mT 2	$A_{\|}$/mT 3
a	Dehydrated at 673 K for 112 h	2·380	2·349	—	12·9	14·8	—
b	As *a*, heated in but-1-ene at 473 K for 3 h	—	2·347	—	—	14·2	—
c	As *b*, heated in oxygen at 473 K for 1 h	—	2·348	2·287	—	14·2	16·8

The general line shape shown in Figure (1) is similar to that obtained by several workers[2] for copper(II) dispersed in a polycrystalline matrix, and is typical of the spectrum expected for a paramagnetic species possessing an axially symmetric *g*-tensor. Similar spectra have been reported recently by Slot and Verbeek[3] for low percentage copper-exchanged Y-type zeolites in which the sodium had previously been replaced by either magnesium or zinc, and also by Tikhomirova and Nikolaeva[4] for copper-exchanged A-type zeolites.

The reaction of but-1-ene at 473 K over a sample of the copper-exchanged zeolite, dehydrated as before at 673 K, caused a gradual reduction in the total intensity of the e.s.r. spectrum. Figure (2b) shows the low-field side of the spectrum following treatment of the catalyst with but-1-ene at 473 K for 3 h. Strikingly, the set of peaks associated with a $g_{\|}$ value of 2·380 is completely removed. The copper ions corresponding to this environment are therefore much more accessible and reactive towards but-1-ene than those associated with a $g_{\perp}$ value of 2·349. The but-1-ene treatment also caused an appreciable narrowing of the hyperfine lines associated with $g_{\|}$ on the high field side of the spectrum with the four individual components becoming clearly visible [Figure (1b)]. This reduction in the dipolar broadening effects observed for the dehydrated catalyst [Figure (1a)] indicates a decrease in the concentration of copper(II) species—presumably a reduction process.

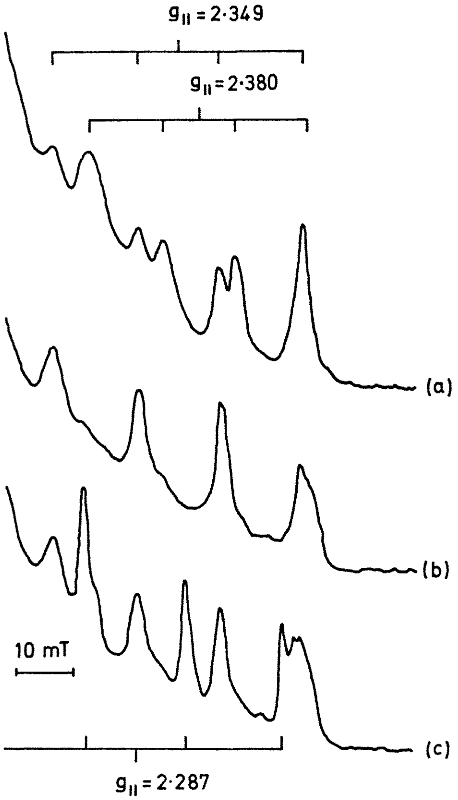

FIGURE (2) *Expanded low field spectrum of copper*(II) *ions in copper X-zeolite.* (a) *As in* 1(a), (b) *as in* 1(b), (c) *after removal of but*-1-*ene, followed by oxygen treatment at* 473 *K for* 1 *h.*

When the catalyst, treated with but-1-ene, was re-oxidised by heating in oxygen for 1 h at 473 K the original

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† All e.s.r. spectra were recorded at 77 K using a Hilger Watts 'Microspin' spectrometer operating at 9330 MHz with a magnetic field modulation of 100 kHz.

spectral intensity was restored. The low-field side of the spectrum now included a third set of four peaks centred on a $g_{\parallel}$ value of 2·287 ± 0·005 [Figure (2c)], the fourth peak of the new group being masked by the high field portion of the spectrum. The values of $g_{\parallel}$ and $A_{\parallel}$ obtained after various catalyst pretreatments are summarised in the Table.

The third group of peaks, indicative of copper(II) ions in a new environment, suggests that a migration of copper ions may have taken place during the but-1-ene treatment. The fact that the spectrum is not altered if the dehydrated catalyst is heated in oxygen without any prior but-1-ene treatment accords with this view.

The oxygen treatment also produces changes in the high field portion of the e.s.r. spectrum. This is at present being examined in more detail and, together with a study of the effect of extent of copper exchange, will be reported elsewhere.

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