Change of Reducibility of Cupric Ions in Y Zeolites with Reduction–Reoxidation Cycles

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Summary Of the two peaks in the temperature-programmed reduction spectra of copper(II)-exchanged Y-type zeolites, the low-temperature peak increased while the high-temperature peak decreased upon successive treatments with H_2–O_2, which indicates the rearrangement of Cu^{II} ions in the zeolite framework.

RECENTLY, Jacobs and Beyer have reported an increase in reduction rates of cupric ions when copper-exchanged Y zeolites are subjected to several CO–O_2 redox treatments.[1] However, the effect of successive redox treatment on the two reduction processes which have been observed in temperature-programmed reduction (t.p.r.) experiments[2–4] were not considered. We have observed changes in the t.p.r. spectra of Cu^{II}-exchanged Y zeolites (CuNaY) upon successive H_2–O_2 redox treatments. The results presented herein have allowed the experimental characterisation of the behaviour of cupric ions in zeolites.

Samples of CuNaY-*m* (*m* represents the exchange level of cupric ions) and the apparatus used were essentially the same as those previously reported.[4-6] The sample was mounted in the t.p.r. cell and then pretreated at 773 K as follows: evacuation for 1 h, exposure to oxygen (13·3 kPa) for 1 h, and re-evacuation for 30 min. After preparation, the sample was exposed to oxygen (13·3 kPa) at 773 K, cooled to 298 K in the presence of oxygen, and evacuated for 15 min before the temperature-programmed reduction (5 K min^{-1}.). In all experiments, a mixture of hydrogen (1·3%) and nitrogen (98·7%) was used as the reductant. The mixed gas was passed through the sample and was then introduced, first, into a cold trap (195 K) to remove any water vapour formed in the reaction of hydrogen with zeolite oxygen and, secondly, into a thermal conductivity detector to measure the hydrogen uptake (t.p.r. spectra).

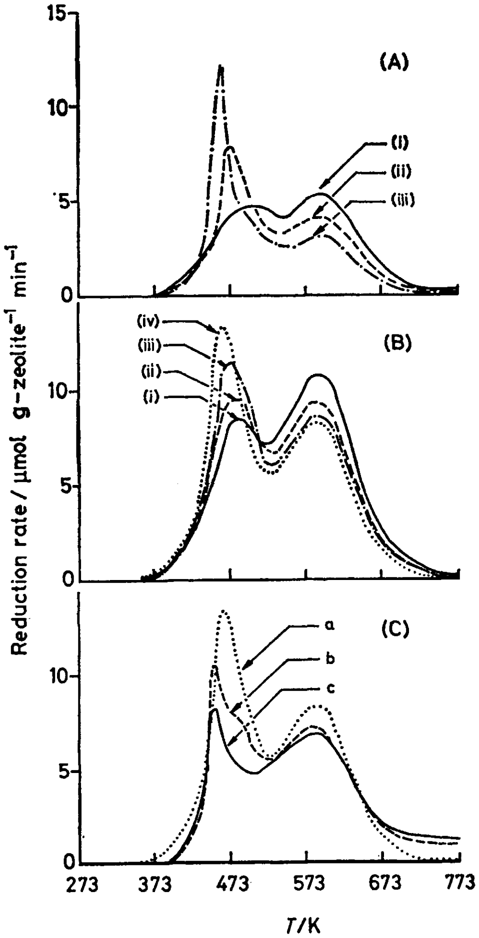

FIGURE. The t.p.r. spectra of cupric ions: A, CuNaY-25 and B, CuNaY-52, (i) after 1 t.p.r. cycle, (ii) after 2 t.p.r. cycles, (iii) after 3 t.p.r. cycles, (iv) after 5 t.p.r. cycles; and C, stabilized CuNaY-52, (a) without evacuation at 773 K, (b) with evacuation for 10 min, and (c) for 60 min at 773 K prior to the t.p.r. procedure.

Typical t.p.r. spectra are shown in the Figure, (A) and (B). Each spectrum consists of two peaks separated by *ca.* 100 K, in good agreement with the results of other workers.[2,3] In the CuNaY-25 and -52 samples, the t.p.r. spectra underwent significant changes with repetition of the reduction (t.p.r.)–reoxidation (sample preparation) cycles; the low-temperature reduction process (α) increased as the high-temperature reduction process (β) decreased. These spectra were substantially stabilized after the fifth cycle. The total hydrogen consumptions per mol of Cu^{II} ion in the sample was *ca.* 0·5, regardless of the exchange levels of Cu^{II} ions, and remained essentially unchanged throughout repetition of the redox cycles; for example, the values for CuNaY-25 were 0·56, 0·51, 0·48, 0·54, and 0·53 for the 1st, 2nd, 3rd, 4th, and 5th t.p.r. experiments, respectively. Consideration of previous[4] and these results indicates firstly that the reduction from Cu^{II} to Cu^{I} occurs in all positions of the zeolite framework, secondly that the redox cycles change the reducibility of the Cu^{II} ions, and thirdly that the increments in the α process cause an increase in the reduction rates, akin to that reported by Jacobs and Beyer.[1]

After stabilization of the t.p.r. spectrum, activation energies for the α and β reductions were measured for CuNaY-52 by the method of Gentry *et al.*[3] and were 70† and 81 kJ mol^{-1}, respectively. These may be compared with values of 70 and 111 kJ mol^{-1}, which have been obtained from an isothermal kinetic study,[7] and of 64 ± 10 and 84 ± 13 kJ mol^{-1}, measured by Gentry *et al.*[3] In addition, these values are greater than that (49 ± 7 kJ mol^{-1}) obtained for the reduction of cupric oxide to metallic copper on X zeolites and the redox cycles observed in this work did not give any peaks in the *X*-ray diffraction patterns which could be attributed to metallic copper or cupric (or cuprous) oxide particles.‡ It is thus concluded that successive H_2–O_2 treatments do not give rise to the formation of copper oxides and that the increments in the α process are not due to the reduction of such oxides.

To characterize further this behaviour, the influence of evacuation at high temperatures, prior to the reduction procedure, on the t.p.r. spectra was examined on CuNaY-52. Curves (b) and (c) of C in the Figure were obtained after the *stabilized* samples were evacuated at 773 K subsequent to the sample preparation and prior to t.p.r. It is evident that the α reduction consists of two reduction processes; a component at *ca.* 493 K (termed α_2) was gradually eliminated upon the evacuation at 773 K, while another component at *ca.* 453 K (termed α_1) remained. This is very different from the phenomenon observed in the *fresh* CuNaY-52 sample in which most of the α process disappeared upon evacuation at 773 K and no peak appeared at *ca.* 453 K.[4] Thus, we conclude that successive redox cycles cause the rearrangement of the Cu^{II} ions which produce the β process so that they produce the α_1 process. These results, along with those of the previous paper,[4] and with the suggested[1] formation of Cu–O–Cu species, probably in supercages in successive redox treatments indicate that

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† This value is an average of the activation energies of the two reduction processes, subdivided in a later section of this communication.

‡ Cupric (or cuprous) oxide particles have been reported to be formed in X zeolites with ease (ref. 3) or in Y zeolites under more severe reduction conditions with hydrogen (see R. G. Herman, J. H. Lunsford, H. K. Beyer, P. A. Jacobs, and J. B. Uytterhoeven, *J. Phys. Chem.*, 1975, **79**, 2388).

the α_1, α_2, and β processes are, respectively, the reduction of the Cu–O–Cu species located in the supercage, the reduction of the unpaired Cu^{II} ions in all positions of the zeolite framework, and the reduction of the Cu–O–Cu species sited in the sodalite cages.

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