

1 **The reduction of copper in porous matrices—the role of electrostatic stabilisation** 1

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The redox properties of Cu(II) species in FAU matrices have been studied by temperature programmed reduction (TPR) in hydrogen and by XAFS analysis of the products obtained after (stationary) reduction treatments at various temperatures. The influence of the matrix polarity was investigated by comparing aluminosilicate FAU (Y zeolite) with siliceous FAU. In addition, the influence of Zn ions on the reduction process was studied. It was found that both the matrix composition and the presence of zinc ions exert a significant influence on the course of the reduction. In Y zeolite, heat treatment which is known to transfer Cu(II) ions to remote sites (S_I, S_{I'}, S_{II'}) affects the reduction process dramatically. Cu(II) is most easily reduced in siliceous FAU, but the reduction proceeds in two clearly separated steps. Between these steps, small Cu(0) nuclei coexist with Cu(I) species, apparently unable to activate hydrogen for the autocatalytic reduction of the remaining Cu ions. The polarity of the matrix causes an upshift of the Cu(II) reduction temperature (in TPR by *ca.* 80 K for sites in the large cavity, by *ca.* 105 K for the remote sites), but the reduction of Cu(I) depends strongly on the simultaneous presence of Cu(0) and on its ability to activate hydrogen and induce an autocatalytic reduction mechanism. While Cu(I) species in the large cavities are easily reduced to the metal, tending to segregate from the zeolite lattice, Cu(I) ions in remote sites are strongly stabilized towards further reduction and even traces of Cu metal form only at very high temperatures. In the presence of zinc ions, the Cu metal particles formed were found to be smaller than in zinc-free samples. 15 20 25 30

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