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

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The redox properties of Cu(n) 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 (S1, SII, SIII) affects the reduction process dramatically. Cu(n) 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(n) 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(n) depends strongly on the simultaneous presence of Cu(0) and on its ability to activate hydrogen and induce an autocatalytic reduction mechanism. While Cu(n) species in the large cavities are easily reduced to the metal, tending to segregate from the zeolite lattice, Cu(n) 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.

Introduction

The extensive attention for copper-modified zeolites as catalysts for environmental and other reactions of technical interest has induced a variety of investigations into the reduction behaviour of Cu(n) species in microporous aluminosilicate matrices.1–8 Temperature-programmed reduction (TPR) was the most frequently used tool in these studies,1–8 but investigations by XAFS and photoemission techniques are known as well.4,5,7,8 As opposed to bulk CuO, Cu(n) in microporous aluminosilicate matrices is reduced in two steps, which have been attributed to the reduction steps Cu(n) → Cu(I) and Cu(I) → Cu(0). The stabilisation of cations in the intrinsic electrostatic field of the zeolite matrix provides a convenient explanation for this observation. For the Y zeolite, it is known that the second reduction step proceeds only at very high temperatures,6 which may be attributed to a particular stabilisation exerted on the cations at the remote sites in the hexagonal prisms (Sl) or in the sodalite cages (SII, SIII).

We have previously demonstrated that the two-step reduction scheme is not particular for aluminosilicate zeolites but occurs in siliceous MFI (silicalite-1) as well.9 Moreover, during the reduction of Cu(n) oxide clusters deposited into silicalite-1, Cu(0) nuclei were present already after the first reduction step without triggering an accelerated (autocatalytic) reduction of the remaining Cu(n) ions upon a temperature increase of almost 100 K. Together with related observations in the course of Cu(n) reduction in ZSM-5 and in MCM-48 (of different Cu content) this result gave rise to the conclusion that Cu metal nuclei are unable to activate hydrogen below a critical particle size.

During the work with the MFI matrices, a significant stabilisation of Cu ions that might be attributed to the intra-zeolite electrostatic potential was not observed. A more pronounced influence can be expected in zeolites with higher Al content, e.g. Y. With the FAU structure, the influence of the remote cation sites on the course of the reduction is an additional interesting feature. We report here studies on the reduction of Cu(n) in dealuminated as well as in aluminosilicate FAU. The influence of the remote sites has been traced by starting from Cu-Y samples in calcined or in uncalcined initial state. Additionally, the influence of Zn ions on the reduction of Cu(n) ions has been investigated for siliceous and aluminosilicate FAU. Cu- and Zn-exchanged zeolites have been described as catalysts for the water gas shift reaction.10 The present context is an effort to create model methanol synthesis.