

Reduction of Copper in Porous Matrixes. Stepwise and Autocatalytic Reduction Routes

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The reduction of Cu(II) oxide species in siliceous matrixes of different porosity (MFI, FAU, MCM-48) and in aluminosilicate MFI was studied by temperature-programmed reduction in hydrogen (TPR), by X-ray absorption fine structure (after stationary hydrogen treatments), and by transmission electron microscopy. It was found that the reduction may proceed in one or in two reduction steps. The two-step scheme known for zeolites was observed also for Cu(II) in siliceous microporous matrixes, with similar temperature of Cu(II) reduction onset as for the aluminosilicate MFI. Therefore, the two-step scheme cannot be explained by the stabilization of Cu ions by intra-zeolite electrical fields. CuOx clusters in MCM-48 were reduced in a one-step scheme (similar to bulk CuO) at high Cu content (6 wt %) but in a two-step scheme at low Cu content (1 wt %). The two reduction steps observed with most samples cannot be identified with the transitions of all Cu(II) to Cu(I) and of Cu(I) to Cu(0). Instead, Cu(0) nuclei were observed already at low reduction temperatures and were found to coexist with Cu ions over temperature ranges of different extension. This coexistence range was narrow in materials that favor aggregation of the Cu nuclei into particles: Cu-MCM-48 of low Cu content and Cu-ZSM-5. In the latter, metal segregation from the pore system was found to be accompanied by an autocatalytic initiation of the second reduction step. In the siliceous microporous matrixes, the Cu(0) nuclei were observed to coexist with Cu ions over wide temperature ranges (100 K for MFI) at temperatures far above that of Cu reduction in the bulk oxide. These observations suggest that oligomeric Cu metal nuclei which may have been formed, e.g., at the intersections of the MFI channel system, may be unable to activate hydrogen, which would be required for rapid reduction of the coexisting Cu ions.