

Oxidation of Cu(100) through dissociative CO₂ adsorption

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We use density functional theory (DFT) calculations to investigate the dissociative adsorption of CO₂ on the pristine and oxygen covered Cu(100). Surface stability with respect to oxygen coverage is calculated together with O 1s core level shifts. The results are compared to (AP)XPS experiments. A reaction mechanism for CO₂ dissociation at Cu(100) is proposed. As a structural model for monoatomic steps on Cu(100) we use Cu(611).

We find that CO₂ adsorption and dissociation on Cu (100) and Cu(611) occurs via CO₂ adsorption in a bent CO₂^{δ-} mode over a hollow position. On the pristine surfaces, adsorption to the CO₂^{δ-} mode is associated with a barrier of 0.55 eV and 0.60 eV for Cu(100) and Cu(611) respectively. The corresponding barrier for dissociation from the adsorbed state is 0.83 eV and 0.57 eV. Only the first barrier is affected by the presence of co-adsorbed oxygen. However, the stability of adsorbed CO₂ on the surface is critically dependent on the position of co-adsorbed oxygen atoms.

Oxidation of Cu(100) is found to occur via the formation of a p(2x2) overlayer (0.25 ML) followed by a reconstructed (2√2x√2)R45° -O missing (MR) structure (0.50 ML). A c(4x6) structure with a 0.3 ML coverage is, however, close in stability for intermediate oxygen chemical potentials. We find that tensile strain (+2%) stabilizes the c(4x6) surface structure with respect to the p(2x2). The calculated shifts in the O 1s binding energy are in good agreement with the measured evolution of the binding energy. The shift to higher O 1s binding energies with increasing oxygen coverage is found to correlate with the charge on neighboring copper atoms. The work suggest a path for oxidation of Cu(100) where CO₂ adsorbs dissociatively on areas of the surface with low oxygen coverage. Oxygen diffusion and clustering initiates surface reconstruction which eventually leads to growth of MR-patches. The results are in good agreement with experimental observations of the evolution of the O 1s core level shift as a function of oxygen coverage upon CO₂ exposure.

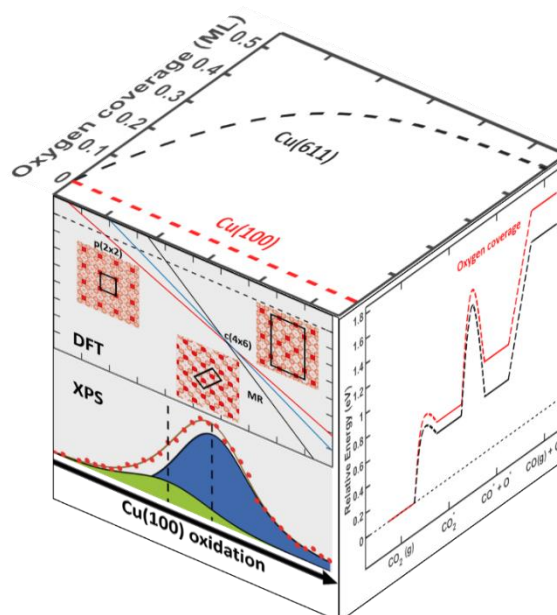


Figure 1. Schematic representation of surface stability diagram, potential energy diagram for CO₂ dissociative adsorption and oxygen coverage evolution in time.