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An ab initio study of the adsorption of CO on a Zn_4O_4 cluster with wurtzite-like structure

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Abstract

The adsorption of CO on a free Zn_4O_4 cluster with a wurtzite-like structure is studied by means of quantum-chemical ab initio methods at the Hartree–Fock level and with inclusion of electron correlation effects. The Zn_4O_4 cluster contains twofold and threefold coordinated Zn and O atoms and can therefore serve as a model substrate for the adsorption of CO on different adsorption sites at terraces, step edges, and corners of various ZnO surface planes. The calculations show that CO binds most strongly to the twofold and the threefold coordinated Zn atoms; the calculated binding energies are 0.52 and 0.33 eV, respectively. The preferred adsorption geometries are "end-on", with the C atom towards Zn and linear Zn–C–O configurations. The bonding of CO to the oxygen atoms of the Zn_4O_4 cluster, on the other hand, is very weak; the binding energies are less than 0.1 eV and the "side-on" adsorption geometries are more favourable. The mechanism of the bonding between CO and the Zn_4O_4 cluster as well as the differences in the bonding properties of the various adsorption sites are explained by means of a constrained space orbital variation (CSOV) analysis. A comparison with the bonding of CO to an isolated Zn^{2+} ion is also included.