Cu on ZnO: alternating Cu charge states and accurate adsorption energy calculations upon charge transfer

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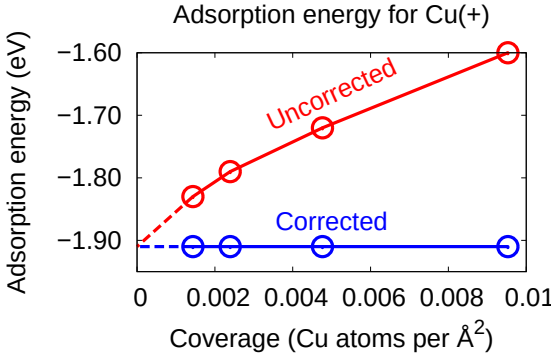
Cu/ZnO catalysts are used in industry to catalyze methanol synthesis and the water-gas shift reaction. It has been suggested that the morphology of the Cu particles influences the catalytic activity. For this reason, understanding and possibly controlling the growth of Cu particles on ZnO is of great interest.

This contribution has two messages: (i) as Cu adatoms diffuse across the ZnO($10\bar{1}0$) surface, their oxidation state repeatedly switches, and (ii) in order to accurately model the adsorption of the positively charged Cu species in a supercell, a "band-filling correction" is needed.

We recently studied the migration of two Cu atoms on the ZnO($10\bar{1}0$) surface and the formation of a Cu dimer using hybrid density functional theory [1]. We found that, depending on the adsorption site, Cu atoms adsorb with either oxidation state 0 or +1. In the latter case, the Cu atom has donated an electron to the ZnO conduction band. Single Cu atoms diffuse across the ZnO($10\bar{1}0$) surface with small migration barriers (0.3-0.4 eV), *repeatedly switching their oxidation states*. The formation of a Cu dimer from two adsorbed Cu atoms is energetically favorable with two competing structures of similar stability, both being charge neutral.

We have subsequently studied the coverage dependence of the Cu/ZnO adsorption energy (E_{ads}) in detail, and found that due to the charge transfer between Cu and ZnO it is necessary to invoke a correction scheme to calculate accurate E_{ads} values in the low-coverage limit. *The calculated adsorption energy of the Cu(+) species is highly coverage dependent*, which could possibly be attributed to electrostatic repulsion between the positively charged Cu species, but also to the "filling-up" of the ZnO conduction band that occurs as a result of the charge transfer from Cu to ZnO. We propose a simple method, the *band-filling correction*, to calculate E_{ads} in the low-coverage limit from calculations performed for finite coverage [2].



[1] Hellström, M., Spångberg, D., Hermansson, K., Broqvist, P. *Phys. Rev. B*, 86:235302, 2012.

[2] Hellström, M., Spångberg, D., Hermansson, K., Broqvist, P. *submitted*.