

Structure, stability and reactivity of bimetallic overlayer and supported cluster systems studied from first principles

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The systematic modification of the reactivity of metal surfaces is of strong current interest since it might lead to the design of better catalysts in heterogeneous and electro-catalysis. In particular, bimetallic surfaces are well-suited for tailoring the reactivity since they offer the possibility to prepare specific surface compositions and structures.

The structure, stability and reactivity of bimetallic overlayer and supported cluster systems has been studied theoretically from first principles within the framework of density functional theory (DFT). Several bimetallic systems such as PtRu [1], PdAu [2, 3] and PdCu [4] will be discussed. We will address the initial stages of the electrodeposition by analysing the metal-metal interaction. While for example Pd and Au are only relatively weakly interacting, Pd and Cu exhibit a strong interaction. Therefore the PdCu system tends to form surface alloys rather than overlayer systems. This is demonstrated in Fig. 1, where the surface energies of different Pd_xCu_y structures on Cu(111) are plotted. The tendency towards surface alloy formation is, however, also triggered by the large lattice mismatch between Pd and Cu.

The intermetallic interaction together with the lattice mismatch is also crucial for the reactivity of the studied bimetallic systems which have been analysed in terms of the d -band model [5]. According to the DFT calculations, both electronic and geometric factors modify the interaction of the overlayer systems with adsorbates by roughly the same amount for the PdAu and the PtCu systems. Furthermore, the local reactivity of small Pd_n cluster with $n=3, 7$ and 10 supported by Au(111) has been studied by calculating atomic hydrogen and CO adsorption energies as a microscopic probe. The Pd clusters turn out to interact less strongly with adsorbates than corresponding pseudomorphic Pd overlayers on Au which is a consequence of the reduced atomic distances in the clusters together with the cluster-support interaction. The electronic structure of the supported clusters is analysed in detail in order to address the unusual electrochemical stability of nanofabricated supported metal clusters [6, 7].

Finally, the influence of a water bilayer on the adsorption energies has been studied. Fig. 2 shows the minimum energy structure of CO on a Pd/Au(111) surface covered with a water bilayer structure. We found that the adsorption energies are reduced by less than 10% by the presence of water. This indicates that theoretical adsorption studies at the solid-vacuum interface might also be relevant for the solid-liquid interface.

Figures

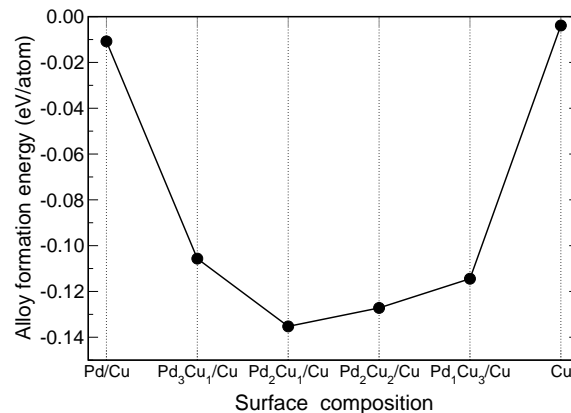


Fig. 1 Calculated surface energy in eV/atom for different surface compositions of PdCu alloys on Cu(111). The energy zero corresponds to a Cu layer on Cu(111), i.e., to a pure Cu(111) surface [4].

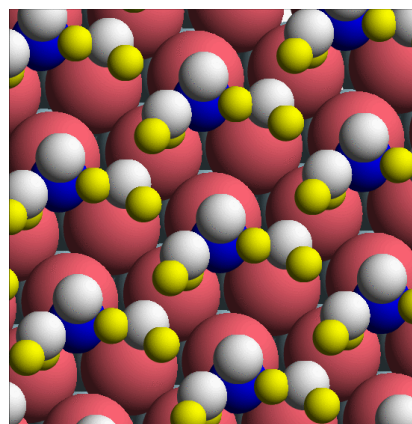


Fig. 2 Minimum energy structure of CO and a water bilayer on a Pd/Au(111) overlayer system. The CO molecules which are adsorbed much closer to the surface than the water molecules are located in the middle of a H_2O hexagon.

References

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