

Structure-reactivity relationship and elementary reaction steps in electrocatalysis

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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 electrocatalysis. This requires a detailed knowledge of the fundamental factors that determine the reactivity. We have addressed this issue by performing periodic density functional theory (DFT) calculations of simple molecules interacting with typical electrode metal surfaces. We have in particular focused on bimetallic surfaces since they are well-suited for tailoring the reactivity by preparing specific surface compositions and structures.

Bimetallic systems can show chemical properties that either correspond to an average over both constituents or they exhibit properties that are beyond those of the single constituents [1]. We have studied the local reactivity by determining the adsorption energies of probe molecules such as CO. Besides the effect of strain we have focused on the ligand effect caused by the electronic interaction between the components of a bimetallic system and the ensemble effect related to the availability of higher coordinated adsorption sites. In PtAu [2] and PdCu [3] systems, both effects can show opposite trends as a function of the composition. In addition, we have addressed the influence of the presence of water and of an external electric field on the chemisorption properties [4].

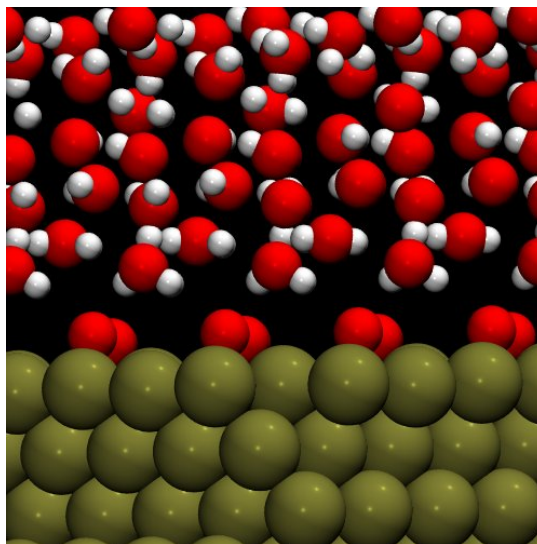


Fig. 1 Adsorption geometry of O₂ on Pt(111) in the presence of water and one Zundel ion, considered as an initial step in the oxygen reduction reaction.

Furthermore, first results will be reported with respect to the determination of the elementary reaction steps in electrocatalysis such as the oxygen reduction reaction on Pt(111) (see Fig. 1).

References:

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