Bonding and reactivity at catalytic interfaces: Modelling novel electrodes from ideal to realistic reaction environments

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Platinum-group metals (PGM) supported and dispersed on highly reducible oxides are common active catalysts for the industrial synthesis of chemical products and for renewable-energy applications such as fuel cells or artificial photosynthesis. Due to the high price of PGM, the sustainable development of these technologies requires new materials that reduces the content of precious metal without affecting the device efficiency.
I will discuss the challenges opened by these systems to electronic-structure simulations and will present case studies in the context of electrodes for solar energy [1-3] and fuel cells applications [4-7].
We combine DFT simulations with ab-initio molecular dynamics, atomistic thermodynamics, metadynamics, and other enhanced-sampling methods to reveal the new surface chemistry opened by these systems. The calculations are used to characterise the chemical bonding and the reactivity at the electrode active sites in a wide range of compositions and environments, ranging from model surfaces at T=0K in vacuum conditions to realistic wet electrodes at finite temperatures, i.e. chemical reactions at complex solid-liquid interfaces comprising nano-structured surfaces in contact with a solution.

The calculated results allow for rationalising the available experimental data and identify correlations among the reaction mechanisms, thermodynamic efficiency, and local structure of the active sites, thus shedding light on the origins of the amplified reactivity and stability of novel electrodes.

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