Mechanism of Surface Reactions: Insights from First Principles Calculations

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Although surface reactions are ubiquitous in chemical processes, their mechanisms are far from being understood. Commonly, the experimental chemist faces too many variables and possibilities to propose and asses a given mechanism, making it almost impossible to go further that a reasonable hint. The knowledge of the reaction sites as well as the involved species brings details that when mixed together with the experimental data allows a deeper view of the elementary steps that usually are related with a surface chemical transformation. Computer simulations based on reliable quantum mechanics methods have been used for long in the study of molecular reactivity, whilst their use in surface reactions modeling, *i.e*. large systems modeling, is high time computer demanding and has been scarce; in particular, ab initio molecular dynamics simulations have been considered prohibitive. However, the development of modern fast computers has allowed carrying out astonishing studies. In this talk two different scenarios of chemical reactivity are described. The first one concerns the atomic layer deposition (ALD) of hafnium oxide using Cl_4Hf and water as precursors. This process has been shown a remarkable procedure to deposit films of a high-*k* dielectric in a controlled way. We find that the adsorption energy and the preferred site of adsorption of the metal precursor are strong functions of the water coverage. As water coverage increases, the metal precursor preferentially interacts with multiple surface adsorption sites. During the water pulse the removal of Cl^- is facilitated through a micro-solvation. The second mechanism is that involved in the water gas shift reaction that has attracted a lot of interest as a source of clean hydrogen. The impact of the key step, the water dissociation, is found to be dissimilar when different catalysts (Cu, Cu/TiO_2, Au/TiO_2) are used.

References:

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