

Oxidative dehydrogenation of a terminal water at the rutile TiO₂(110)-water interface

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Oxidative dehydrogenation (ODH) of a H₂O molecule is enormously costly, taking 2.7 eV. Deprotonation requires 0.8 eV. The difference is still large enough to give the hydroxyl radical a daunting oxidative power of 1.9 V *vs* SHE. Will adsorption on a transition metal oxide surface bring the ODH energy down? If so, will this not also decrease the reduction potential of the adsorbed OH radical product? We have investigated this question using a combination of density functional theory based molecular dynamics (DFTMD) and free energy perturbation methods. The model metal oxide system is the much studied rutile TiO₂(110)-water interface. Using PBE, the surface ODH energy was indeed found to be lower than in solution. Resolving in a deprotonation and oxidation free energy, revealed that the increase in acidity of a terminal H₂O relative to solution[1] is an important factor in the H₂O activation. The oxidation potential of the OH radical was found, somewhat surprisingly, to be almost the same. The surface ODH energy is not directly available from experiment. We can however use the solution data mentioned above as validation. Unfortunately our reduction potential of the aqueous OH radical is too small by as much as 0.6 V[2]. This effect is now generally understood to be the result of the tendency of the generalized gradient approximation (GGA) to delocalize holes in O2p orbitals. For the same reason the GGA pushes the valence band maximum in TiO₂ up by 0.8 eV[3]. For the surface ODH reaction the delocalization error even leads to the formation of the wrong species, namely an adsorbed hydroxide anion plus delocalized hole in the valence band, rather than an hydroxyl radical. These observations cast serious doubt on the PBE results. Only recently we were able to make progress thanks to the development of efficient methods for the implementation of exact exchange under periodic boundary conditions[4]. DFTMD simulation using the HSE screened hybrid functional, indeed traps the hole with localization energies of 0.5 eV or more. This talk will be a brief review of our DFTMD methodology together with the presentation of some of the latest results obtained with HSE.

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