Towards an accurate combined periodic/embedded cluster protocol for modeling adsorption on metal-oxide surfaces

PIETRO MARIA CURZIETTI[1] and NICOLA TASINATO[1]

[1]*Scuola Normale Superiore, Pisa, 56126, Italy*
pietro.curzietti@sns.it

ABSTRACT

In this study, we explore the interaction between the H_2O molecule and the anatase-TiO_2 {101} surface, using a combined periodic/ cluster approach within the framework of density functional theory (DFT). To accurately describe molecular adsorption and surface-mediated reactivity,[1] two fundamental tasks are undertaken: (1) constructing a quantum-mechanical region to accurately capture the local environment-adsorbate interactions and (2) embedding the cluster within a low-level region that ensures a correct description of the electronic structure, to capture the long-range electrostatic effect of the surface and to achieve convergence of the computed properties towards the bulk limit. Current approaches often encounter challenges in simultaneously taking into account[2]: small cluster size, consistency criteria in cluster extraction, automation of the procedure connecting periodic structures with the corresponding molecular clusters, accurate description of energetics and electronic structures. We developed and validated a computational protocol within the above described periodic/cluster framework against the periodic reference simultaneously considering water adsorption on anatase. We developed an electrostatic embedding scheme that exploits frozen Mulliken charges and pseudopotentials to capture bulk electrostatic interactions and to saturate the dangling bonds of the cluster, reducing charge accumulation at the edges. We characterized the embedding models with density of states (DOS) diagrams and with an in-house version of the charge displacement analysis.[3] Future developments involve the investigation of the interaction between co-adsorbed molecules, the modeling of reactivity in the framework of water-splitting on embedded clusters and the study of the excited states.

References

[1] Bandura, A. V., et al. «Adsorption of Water on the TiO 2 (Rutile) (110) Surface: A Comparison of Periodic and Embedded Cluster Calculations». The Journal of Physical Chemistry B, vol. 108, fasc. 23, **2004**, pp. 7844–53

[2] Shi, Benjamin X., et al. «General Embedded Cluster Protocol for Accurate Modeling of Oxygen Vacancies in Metal-Oxides». The Journal of Chemical Physics, vol. 156, fasc. 12, **2022**, p. 124704.

[3] Bistoni, Giovanni, et al. «Advances in Charge Displacement Analysis». Journal of Chemical Theory and Computation, vol. 12, fasc. 3, **2016**, pp. 1236–44.