Key ingredients for the screening of single atom catalysts for the hydrogen evolution reaction: the case of titanium nitride

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Single Atom Catalysts (SACs) are considered a new frontier in the field since they establish a bridge between homogeneous and heterogeneous catalysis. Computational chemistry allows to access the atomistic details of catalytic processes, and it is extremely helpful to rationalize of even predict the properties of systems. A lot of attention has been dedicated to the reactions of evolution and conversion of molecular hydrogen and oxygen from or to liquid water [1]. The Computational Hydrogen Electrode (CHE) approach is well established to predict the activity of catalytic materials and was originally developed to study reactions on extended surfaces. In this approach the free energy of key intermediates adsorbed is used to explain the catalytic activity, or even to predict new potential candidates. In recent years, this framework was directly transferred and apply to SACs, although their reactivity differs from extended systems. In this speech we discuss a computational screening of Single Atom Catalysts (SACs) bound to titanium nitride (TiN), an emerging supporting matrix. The catalysts were tested against the Hydrogen Evolution Reaction (HER), based on density functional theory (DFT). We show the role of fundamental ingredients to consider for a reliable screening of SACs, that are typically neglected. Namely, the formation of H_2-complexes [2] besides the classical H* one has an important impact on the predicted HER activity. Also, the results indicate that one needs to adopt self-interaction corrected functionals [3]. Once unconventional intermediates in a self-interaction corrected scheme, the number of potential good catalysts for HER is strongly reduced, since the formation of unconventional intermediates lead to thermodynamic barriers. This study highlights the importance of including the key ingredients for the prediction of new systems, as the formation of unconventional intermediates and the adoption of self-interaction corrected functionals. Also, this study highlights some interesting candidate deserving more dedicate work.

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[2] Di Liberto, Giovanni, Luis A. Cipriano, and Gianfranco Pacchioni. JACS 143.48 (2021) 20431-20441
[3] I. Barlocco, L.A. Cipriano, G. Di Liberto, G. Pacchioni. Adv. Theo. & Simul. 6, 2200513 (2023)