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Role of Dihydride and Dihydrogen Complexes in Hydrogen Evolution Reaction on Single-Atom Catalysts

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Abstract

The hydrogen evolution reaction (HER) has a key role in electrochemical water splitting. Recently a lot of attention has been dedicated to HER from Single Atom Catalysts (SAC).[1] The activity of SACs in HER is usually rationalized or predicted using the seminal model proposed by Nørskov and co-workers in 2005,[2] where the free energy of an H atom adsorbed on an extended metal surface M (formation of a MH intermediate) is used to explain the trends in the exchange current for HER. SACs differ substantially from metal surfaces, and can be considered analogs of coordination compounds. In coordination chemistry, at variance with metal surfaces, stable dihydride or dihydrogen complexes (HMH) can form.[3,4] We show that the same can occur on SACs and that the formation of stable HMH intermediates, in addition to the MH one, may change the kinetics of the process. Extending the original kinetic model to the case of two intermediates (MH and HMH) one obtains a three- dimensional volcano plot for the HER on SACs. DFT numerical simulations on 55 models demonstrate that the new kinetic model may lead to different conclusions about the activity of SACs in HER. The results are validated against selected experimental cases. The work provides an example of the important analogies between the chemistry of SACs and that of coordination compounds.

References

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