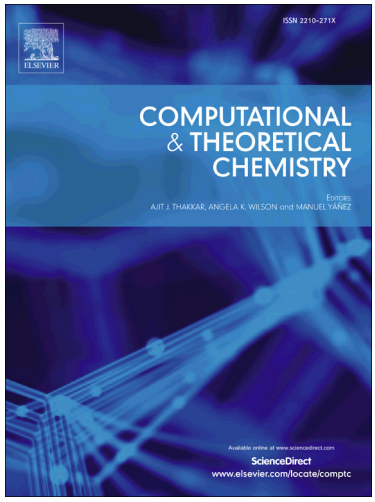

Steric and chemical effects on the hydrogen adsorption and dissociation on free and graphene–supported palladium clusters

Alejandra Granja-DelRío, Julio A. Alonso, María J. López

PII: S2210-271X(16)30484-4
DOI: http://dx.doi.org/10.1016/j.comptc.2016.11.029
Reference: COMPTC 2315

To appear in: *Computational & Theoretical Chemistry*

Please cite this article as: A. Granja-DelRío, J.A. Alonso, M.J. López, Steric and chemical effects on the hydrogen adsorption and dissociation on free and graphene–supported palladium clusters, *Computational & Theoretical Chemistry* (2016), doi: http://dx.doi.org/10.1016/j.comptc.2016.11.029

Steric and chemical effects on the hydrogen adsorption and dissociation on free and graphene–supported palladium clusters.

Alejandra Granja-DelRío, Julio A. Alonso, and María J. López*

Departamento de Física Teórica, Atómica y Óptica, Universidad de Valladolid, 47011, Valladolid, Spain.

Abstract

Palladium doping enhances the hydrogen storage capacity of nanoporous carbons. The purpose of this work is to asses the effect of the carbonaceous support on the adsorption of hydrogen on Pd clusters. Hydrogen adsorbs on Pd clusters following two channels: molecular adsorption and dissociative chemisorption. These two adsorption channels are investigated on free Pd clusters and Pd clusters supported on pristine and defective (with vacancies) graphene using the Density Functional Formalism. Pd_6 is taken as case study. Free Pd_6 can adsorb twelve hydrogen molecules in the molecular form, a number higher than the nine and eight molecules that can be adsorbed on the cluster supported on pristine graphene and on a graphene vacancy, respectively. However the most stable adsorption channel is, in all cases, the dissociative chemisorption of hydrogen. As the cluster is being loaded with hydrogen, there is a competition between the two adsorption channels. Pd_6 supported on a graphene vacancy is able to dissociate three hydrogen molecules, whereas the free cluster can dissociate up to seven molecules. In both cases, six additional molecules can be adsorbed in the molecular form. The higher saturation limit obtained for the free clusters is explained in terms of the steric and chemical effects of the supporting layer. These effects are of primarily importance to asses the role of the Pd dopant on the adsorption and storage of hydrogen on nanoporous carbons.

*Corresponding author: maria.lopez@fta.uva.es