Hydrogen storage on Palladium doped nanoporous carbons

María J. López[1], Iván Cabria[1], Cecilia Bores[1], Silvia Fraile[2], Julio A. Alonso[1]

1 Dpto. de Física Teórica, Universidad de Valladolid, 47011 Valladolid, Spain
2 Dpto. de Física Aplicada-LATUV, Universidad de Valladolid, 47011 Valladolid, Spain
maria.lopez@fta.uva.es

Abstract

Nanoporous carbons are among the best candidates for hydrogen storage. Recently we have revealed the structure of nanoporous carbons derived from carbides [1]. A structure of open pores emerges and the carbon network forming the pore walls consists in one atom thick graphene layers interconnected among them and exhibiting exposed graphene edges. The storage of hydrogen is driven by the adsorption of molecular hydrogen on the pore walls of the material. However the performance of these materials at room temperature and moderate pressures is quite limited. Some promising experiments suggest that Palladium nanoparticles might enhance the storage of hydrogen in porous carbons by surface reactions [2], although the mechanism is not well known. To gain some insight on the role played by palladium in the storage of hydrogen, we have investigated the adsorption and formation of small palladium clusters on a graphene surface, and the adsorption and dissociation of molecular hydrogen on the adsorbed palladium clusters. Density functional calculations show that Pd atoms have a strong tendency to form clusters [3]. Supported three-dimensional clusters are more stable than planar ones, and the transition from planar to three-dimensional structure occurs early as a function of cluster size, namely at Pd_4. This feature is a consequence of the strong Pd-Pd interaction. We have also investigated the adsorption and the dissociation of molecular hydrogen on the deposited Pd clusters as a function of cluster size, from a single Pd adatom to the Pd_6 cluster. The mechanisms for the molecular adsorption of the hydrogen molecule and for the possible subsequent dissociation are discussed, as well as the activation barriers for dissociation. According to the present simulations, a single adsorbed Pd atom does not dissociate the hydrogen molecule. Starting with deposited Pd_2, the clusters dissociate the molecule with no barriers or with small barriers (see Fig. 1).

The dissociation and adsorption of molecular hydrogen on the edges of graphene nanoribbons is also investigated to gain insight on the contribution of the exposed graphene edges of the nanoporous carbons to the reversible hydrogen storage capacity of these materials. Our Density functional calculations show that molecular hydrogen dissociates and adsorbs atomically at the ribbon edges without activation barrier. The adsorption energies are quite large, between 2.5 and 5.7 eV, what indicates that the ribbon edges are very reactive and will be saturated with hydrogen whenever available. However, under mild conditions of pressure and temperature hydrogen cannot be desorbed from the edges and, therefore, the edges do not contribute to the reversible storage capacity of the material.

References

[1] M.J. López, I. Cabria, and J.A. Alonso, J. Chem. Phys., **135** (2011) 104706.
[2] C.I. Contescu, et al., J. Phys. Chem. C **113** (2009) 5886; A. Lueking and R.T. Yang, Appl. Catal. A **265** (2004) 259.
[3] I. Cabria, M.J. López, and J.A. Alonso, Phys. Rev. B **81** (2010) 035403.

Figures

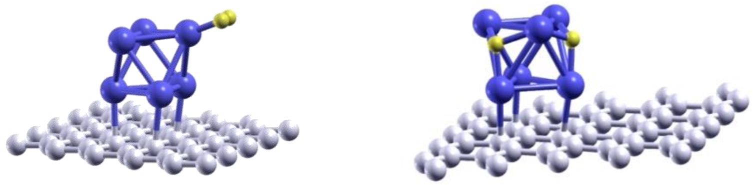

Figure 1: Adsorbed (left) and dissociated (right) hydrogen molecule on an octahedral Pd_6 cluster supported on a graphene surface.