

ACCELERATED FIRST-PRINCIPLES MOLECULAR DYNAMICS TO STUDY HYDROGEN INTERACTION WITH TRANSITION METAL DOPED CARBON MATERIALS

Samir H. Mushrif,^{*,†} Gilles H. Peslherbe[†] and Alejandro D. Rey^{*}

^{*}Department of Chemical Engineering, McGill University, 3610 University Street, Montreal, QC, H3A 2B2, Canada
[†]Centre for Research in Molecular Modeling and Department of Chemistry and Biochemistry, Concordia University, 7141 Sherbrooke West, Montreal, QC, H4B 1R6, Canada

Introduction

Hydrogen is involved in a large number of catalytic reactions and a significantly important class of catalytic material in hydrogen involving reactions consists of transition metal clusters anchored on a support, particularly a carbon based support. After (i) the sp^2 type carbon based materials like nanotubes, activated carbon and activated carbon fibers have been recognized as potential hydrogen storage materials and (ii) transition metal doping has demonstrated an increase in the hydrogen storage capacities of such materials, the interaction of hydrogen with these materials has become the focus of interest for hydrogen storage. The nature of hydrogen bonding (physisorption or chemisorption) and the possibility of its dissociation and migration on the catalyst material are the key factors governing the functionality of these materials¹⁻³. Though of great importance, the interaction mechanism of hydrogen with metal-doped carbon materials is mostly studied by interpreting experimental data for a combination of sequential steps in the entire catalysis process and the deficiency of isolated studies of hydrogen interaction with these materials has left some doubts about its mechanism and dynamics, the existence of spillover, the energetics of the process and the process of desorption of monoatomic hydrogen in the form of diatomic hydrogen molecule. In the present paper, for the first time, we have attempted to model simultaneously the finite temperature dynamics and energetics of the interaction of hydrogen with a carbon supported Pd cluster.

Simulation Details

A cubic simulation cell is used with a system of coronene molecule (as a model carbon support), a Pd₄ cluster and a hydrogen molecule, as shown in Fig. 1. All the calculations are performed using the CPMD software, version 3.13.2, which provides an implementation of the first-principles Car-Parrinello molecular dynamics scheme⁴. The first-principles calculations are performed using the planewave pseudopotential implementation of the Kohn-Sham density functional theory. The Goedecker pseudopotential⁵ with the local density approximation, which has been validated in our previous work⁶, is used. All the simulations are performed at 300 K. The Car-Parrinello scheme, even after reducing the computational cost of ab initio molecular

dynamics, may not access time scales of more than a few picoseconds in practically available computer time and resources. Believing the existence of energy barriers associated with the course of interaction of hydrogen with metal-doped carbon supported materials, we implement the metadynamics technique to accelerate the dynamics and to reconstruct the energy surface as a function of the coordinates of interest (*cf.* Fig. 1), during the course of the interaction. The metadynamics technique, as described by Laio and Gervasio⁷, is based on the principle of filling up the energy well with potentials, to help the system overcome the energy barriers. In metadynamics, the potentials dropped to fill the energy well are tracked and the energy surface is then reconstructed using these potentials. The metadynamics technique is implemented by extending the Car-Parrinello Lagrangian as⁸

$$\mathfrak{L}_{MTD} = \mathfrak{L}_{CP} + \sum_{cv} m_{cv} \dot{\mathfrak{s}}_{cv} - \frac{1}{2} \sum_{cv} k_{cv} \left[\mathfrak{s}_{cv}(\vec{R}_{cv}) - \mathfrak{s}_{cv} \right]^2 + \nu_{cv}(t, \mathfrak{s}) \quad (1)$$

where \mathfrak{L}_{CP} is the Car-Parrinello Lagrangian and \mathfrak{s} is a vector of the collective variables (coordinates of interest) that form the energy well to be filled or that form the energy surface of interest. The first term is the kinetic energy of the collective variables, the second term is the harmonic restraining potential and the last term is the Gaussian-type potential that fills the energy surface. It is given as⁷

$$\nu_{cv}(t, \mathfrak{s}) = \sum_{t_i < t} H_{MTD}(t_i) \exp \left[- \frac{\left\{ (\mathfrak{s}^t - \mathfrak{s}^{t_i}) \right\}^2}{2 \left[\mathbf{w}(t_i) \delta \mathfrak{s}(t_i) \right]^2} \right] \quad (2)$$

where the parameter $H(t_i)$ represents the height of the added potential and $\delta \mathfrak{s}(t_i)$ and $\mathbf{w}(t_i)$, together, represent the width of the Gaussian potential. The reader is referred to the recent paper by Laio and Gervasio⁷ for further mathematical and conceptual details.

Results and Discussion

A regular Car-Parrinello molecular dynamics simulation (without implementing metadynamics) at 300 K is initially performed on the system shown in Fig. 1. It is observed that the adsorption of hydrogen on the Pd₄ cluster tip is simultaneously accompanied by the dissociation of the H-H bond. The process is associated with a negligible energy barrier and the Kohn-Sham energy variation along the molecular dynamics trajectory shows that the adsorption energy is approximately 50 KJ/mol. To accelerate the dynamics of the process of further migration of the adsorbed H atoms and to compute the associated energy barriers, metadynamics is then implemented.

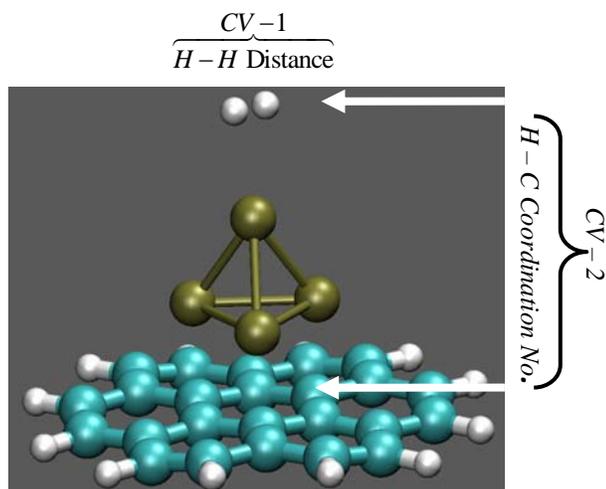


Fig. 1: Coronene supported Pd_4 cluster and the interacting H_2 molecule. The collective variables for the metadynamics simulation are also shown. Carbon atoms are shown in blue, palladium atoms in brown and hydrogen atoms in white.

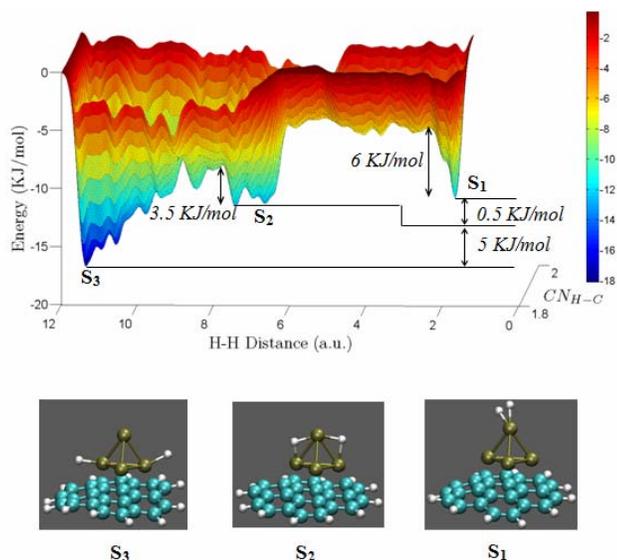


Fig. 3: The three dimensional free energy surface reconstructed from the metadynamics simulation of the system with fixed Pd coordinates. S_1 , S_2 , and S_3 indicate the key minima in the free energy surface and the images displayed below the plot are the snapshots of the system at corresponding values of the collective variables. The color coding of the atoms is the same as that of Fig.1.

The collective variables (CV) for metadynamics are shown in Fig. 1. The starting point for the metadynamics simulation is two H atoms dissociatively chemisorbed on the tip of the coronene supported Pd_4 cluster. Figure 2 shows the reconstructed free energy surface as a function of the collective variables. The simulation system snapshots at the key landmarks in the energy surface are also shown. Analysis of the energy surface calculated from metadynamics reveals

that the system has to cross energy barriers of ~ 6 KJ/mol and ~ 3.5 KJ/mol to come out of the local minima states S_1 and S_2 , respectively. After crossing these barriers, H atoms gradually move towards the carbon support, thus taking the system to an energy state which is 5 KJ/mol lower than that of the H atoms attached to the edges of the cluster. The state S_3 is the lowest energy level state of the system.

Metadynamics simulations are also performed to study (i) the migration of H atoms from the Pd cluster to the carbon support and (ii) the associative desorption of the H atoms from the Pd cluster. Those results will be presented at the Carbon 2010 conference.

Conclusions

To the best of our knowledge, the dynamics and energetics of the chemisorption and subsequent migration of hydrogen on a carbon supported Pd_4 cluster at room temperature are computed for the first time using first-principles molecular dynamics and metadynamics. The initial dissociative chemisorption is shown to be a barrierless process, however, the subsequent migration of H atoms is associated with small energy barriers less than 10 KJ/mol. The migration of H atoms from the tip of the cluster towards the carbon support is an energetically favorable process. It is also suggested that the migration of H atoms from the cluster to the carbon support is associated with a relatively high energy barrier.

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