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 materials. 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 Pd$_4$ 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 scheme. The first-principles calculations are performed using the plane-wave pseudopotential implementation of the Kohn-Sham density functional theory. The Goedecker pseudopotential is used with the local density approximation, which has been validated in our previous work, 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, during the course of the interaction. The metadynamics technique, as described by Laio and Gervasio, 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 as

$$\mathcal{L}_{MD} = \mathcal{L}_{CP} + \sum_{cv} m_{cv} \dot{\mathbf{s}}_{cv}^2 - \frac{1}{2} \sum_{cv} k_{cv} \left( \mathbf{S}_{cv} \left( \mathbf{R}_{cv} \right) - \mathbf{s}_{cv} \right)^2 + V_{cv} \left( t, \mathbf{s} \right)$$

where $\mathcal{L}_{CP}$ is the Car-Parrinello Lagrangian and $\mathbf{s}$ 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 as

$$V_{cv} \left( t, \mathbf{s} \right) = \sum_{t \in T} H_{MD} \left( t \right) \exp \left[ - \frac{\left( \mathbf{s} - \mathbf{s}^t \right)^2}{2 \left( w \left( t \right) \delta \mathbf{s} \left( t \right) \right)^2} \right]$$

where the parameter $H \left( t \right)$ represents the height of the added potential and $\delta \mathbf{s} \left( t \right)$ and $w \left( t \right)$, together, represent the width of the Gaussian potential. The reader is referred to the recent paper by Laio and Gervasio 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 Pd$_4$ 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.
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 S1 and S2,
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 S3 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 Pd4 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.

Acknowledgments. Financial support to this work was
provided by the National Science Foundation under the award
number EEC-9731689 and the Petroleum Research Fund (ADR) and
the Natural Sciences and Engineering Research Council (NSERC) of
Canada (GHP and SHM). Computational resources were provided by
the Réseau québécois de calcul de haute performance (RQCHP).

References
[2] Pajonk GM. Contribution of spillover effects to heterogeneous
Schlogl R, Milroy D, Jackson SD, Torres D, Sautet P. Understanding
Palladium Hydrogenation Catalysts: When the Nature of the Reactive
Molecule Controls the Nature of the Catalyst Active Phase.
55(22):2471-2474.
[5] Hartwigsen C, Goedecker S, Hutter J. Relativistic separable dual-
space Gaussian pseudopotentials from H to Rn. Physical Review B
of the palladium(II) acetylacetonate crystal structure. Chemical
events and reconstruct the free energy in biophysics, chemistry and
material science. Reports on Progress in Physics 2008; 71(12):
126601.
[8] Iannuzzi M, Laio A, Parrinello M. Efficient exploration of
reactive potential energy surfaces using Car-Parrinello molecular