

First Principles Investigations of Properties of Low Dimensional Systems and Their Role in Selective Hydrogenation

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in partial fulfillment of the requirements for the degree of

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by

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2017

CERTIFICATE

Certified that the work incorporated in the thesis entitled **First Principles Investigations of Properties of Low Dimensional Systems and Their Role in Selective Hydrogenation** submitted by **Indu Kaul** was carried out by the candidate, under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other University or institution.

Date:

(Dr. Prasenjit Ghosh)
Supervisor

Declaration

I declare that this written submission represents my ideas in my own words and where others ideas have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that violation of the above will be cause for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

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List of Publications

List of publications resulting from work presented in this thesis

1. **Indu Kaul**, Niharika Joshi, Nirmalya Ballav and Prasenjit Ghosh, Hydrogenation of ferrimagnetic graphene on Co surface: Significant enhancement of spin moment by C-H functionality *J. Phys. Chem. Lett.*, **2012**, 3, 2582-2587.
2. Niharika Joshi, **Indu Kaul**, Nirmalya Ballav and Prasenjit Ghosh, Spin enhancement and band gap opening of ferrimagnetic graphene on fcc-Co(111) upon hydrogenation, *AIP Conf. Proc.*, **2013**, 1512, 694-695.
3. **Indu Kaul** and Prasenjit Ghosh, First Principles Investigations of Small Bimetallic PdGa Clusters as Catalysts for Hydrogen Dissociation (manuscript accepted for publication in Chemical Physics)
4. **Indu Kaul** and Prasenjit Ghosh, Selective hydrogenation of acetylene on Pd_xGa_y clusters- DFT study (manuscript under preparation).
5. **Indu Kaul**, Souvik Chakraborty, Sudip Roy and Prasenjit Ghosh, Adsorption of cyclododecene on different Pd surfaces: A first Principles Study (manuscript under preparation).

List of publications from other work

1. Sumit Kumar, **Indu Kaul**, Partha Biswas and Alope Das, Structure of 7-Azaindole2-Fluoropyridine Dimer in a Supersonic Jet: Competition between N-HN and N-HF Interactions *J. Phys. Chem. A*, **2011**, 115, 1029910308.
2. Sumit Kumar, Partha Biswas, **Indu Kaul** and Alope Das, Competition between Hydrogen Bonding and Dispersion Interactions in the IndolePyridine Dimer and (Indole)₂ Pyridine Trimer Studied in a Supersonic Jet *J. Phys. Chem. A*, **2011**, 115, 7461-7472.

Synopsis

The work presented in this thesis comprises of theoretical investigations of properties of some low dimensional systems and the plausibility to use them as catalysts for selective hydrogenation. The thesis is divided in two parts. In the first part (chapter-3) of this thesis, we present our results on the novel properties induced in graphene sheet, a two dimensional material when it forms an interface with a ferromagnetic metal surface. Moreover, we also predict novel ways to tune these properties by chemical modification of the graphene sheet. The second part of this thesis (chapter:4-6) contains the studies of heterogeneous catalysis (primarily selective hydrogenation reactions) on model catalysts made of Pd and PdGa intermetallic compounds (IMCs). While for Pd we have investigated both surfaces and clusters, for PdGa we have studied small bimetallic clusters. We note that while Pd is known to be a very good catalyst, the results on PdGa clusters are theoretical predictions. Density functional theory (DFT) based calculations have been used as the primary theoretical tool in these studies.

The thesis is divided into six chapters.

In chapter-1 we discuss why low dimensional systems are interesting.

Chapter-2 describes the basics of DFT and density functional perturbation theory (DFPT). DFT calculations are performed to determine the ground state structures and electronic properties of a given system. DFPT is used to calculate the vibrational frequencies of some of the systems studied in this thesis to ascertain their dynamic stability.

Graphene, a two dimensional sheet of sp^2 hybridized C atoms, exhibits many interesting properties. However, for practical applications it needs to be placed on a substrate. The graphene/ferromagnetic transition metal interfaces are widely studied as probable candidates for spintronics. Chapter-3 contains the results of our theoretical predictions

that graphene supported on Co substrate becomes weakly ferrimagnetic. Further, we also show that hydrogenating the graphene sheet is a possible way to not only tune the magnetic interactions but also to induce a band gap in the graphene sheet. We find that there is a six-fold increase in the average magnetic moment of the hydrogenated graphene sheet. Moreover, there is also a large band gap opening.

Over the last few years, PdGa IMCs are being intensively studied as efficient catalysts for the hydrogen adsorption/dissociation and for the selective hydrogenation of acetylene to ethylene. In chapter-4 of this thesis, we present our efforts to explore the plausibility of using the sub-nanometer sized (*zero-dimensional*) bimetallic PdGa clusters (dimers, trimers and tetramers) as catalysts for hydrogen dissociation. Since these clusters have not yet been synthesised experimentally we have investigated the thermodynamic stability of these clusters in gas phase and as well as on support (MgO(001) surface in our case). Our calculations predict that both in the gas phase as well as on support, for a given cluster size, all the bimetallic clusters are more stable than the pure Pd and Ga clusters. The clusters having equimolar ratio of Pd and Ga atoms are most stable. Our studies of hydrogen dissociation reaction on these clusters show that Pd atoms are the active sites in these model catalysts and the dissociation takes place through Kubas mechanism. Our calculation predict that Pd₃Ga is the most reactive catalyst in gas phase. However, its reactivity decreases and is comparable to that of Pd₄ when put on MgO support.

Encouraged by the results of hydrogen dissociation on the bimetallic clusters in the previous chapter and experimental reports on using PdGa surfaces as catalyst for selective hydrogenation of acetylene to ethylene, in chapter-5, we explored the plausibility of using the bimetallic clusters as catalysts for the above reaction. We note that this is an industrially important reaction and the challenge to the scientific community is to design a catalyst with high reactivity and selectivity. Though Pd is used as a catalyst for this reaction, it exhibits poor selectivity. Amongst all the clusters considered in this study, Pd₃Ga has the lowest barrier for ethylene formation. However, the stoichiometric Pd₂Ga₂ cluster shows better selectivity. Further, we find that the hydrogenation mechanism is based on the Horiuti-Polanyi scheme where hydrogenation is preceded by coadsorption of the reactants (hydrogen and alkene/alkyne molecules).

Cyclo-dodecadiene (CDD) is an important intermediate obtained in the selective hydro-

genation of 1,5,9-c,t,t-cyclo-dodecatriene (CDT) to cyclododecene (CDE). This reaction is an important step in the synthesis of lauric acid, that is used in the production of Nylon-12. Though Pd is used as a catalyst for this reaction, it exhibits poor selectivity. As a first step to understand the reason for the poor selectivity exhibited by the Pd catalysts we have studied in chapter-6 the effect of the local coordination of the active atoms in the Pd catalyst on the adsorption of cyclo-dodecadiene (CDD). To achieve this we have considered flat Pd(100) surface, a stepped surface and an adatom on the Pd(100) surface. As we move from the flat surface to the adatom, there is a reduction in the coordination number of the Pd atoms interacting with the molecule. Our results show that the stability of different isomers is sensitive to the local coordination of the reactive ensemble. Further we have also investigated the influence of pre-adsorbed hydrogen on the molecular adsorption.

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Chapter 1

Introduction

In this thesis we present results of theoretical investigations of properties of low dimensional systems (mainly zero and two-dimensional) and explored the possibility of using them as catalysts for selective hydrogenation. Low dimensional systems usually have properties that are very different (and sometimes novel) compared to the corresponding three dimensional bulk material. Hence these systems are important both from fundamental and technological point of view. Further due to the modified properties of these systems, it is also expected that chemical processes taking place on these materials will be highly affected. For example, in the field of heterogeneous catalysis, that comprises a significant part of this thesis, it is observed that not only the reaction barriers but also the reaction mechanisms differs significantly when the catalysts are in the form of a thin film (two-dimensional) or a cluster (zero-dimensional).

1.1 Low dimensional systems

Systems whose properties are significantly changed due to the fact that they are finite along at least in one of the three dimensions are known as low dimensional systems. They can be classified as follows:

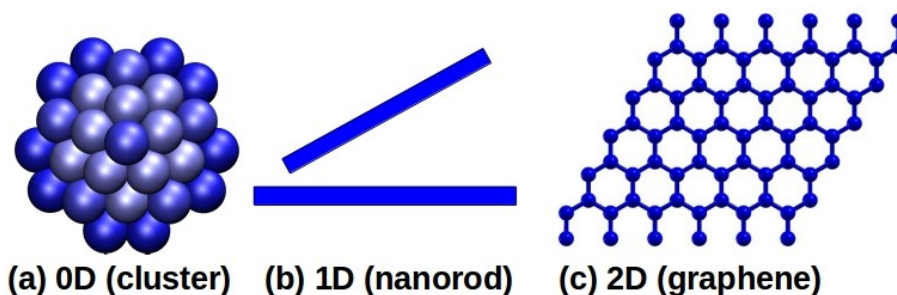


Figure 1.1: Examples of low dimensional materials: (a) 0D, (b) 1D and (c) 2D.

Zero dimensional (0D), where the system is finite along all the three dimensions. Examples of such systems are clusters, quantum dots, fullerenes, etc. (Figure-1.1(a)).

One dimensional (1D), where the system is finite along two dimensions and infinite along the third dimension. Nanowires, nanorods, nanotubes etc. (Figure-1.1(b)) are examples of 1D systems.

Two dimensional (2D), where the system is finite along one dimension and is infinite along the other two dimensions. Graphene sheet (Figure-1.1(c)) is an example of a 2D system.

The reduced dimensionality usually results in a reduction of the atomic coordination number. This gives rise to properties and functionalities that are sometime drastically different from that of the bulk.

In this thesis, we have investigated properties of novel low-dimensional systems. We have focussed primarily on 0D and 2D systems. We have investigated properties of graphene-ferromagnetic metal interfaces. Moreover, we have also studied reaction mechanisms on metallic and intermetallic clusters (0D) and metallic surfaces (2D).

1.2 Theoretical tools

Several theoretical tools (both classical and quantum mechanical) are available to study different phenomena depending on the length and time scales involved. In this thesis we have used quantum mechanical (density functional theory based) tools. The chemical processes studied in this thesis requires sophisticated theoretical treatment because it involves breaking and formation of chemical bonds. Hence use of classical potential is not enough. Density functional theory (DFT) developed by W. Kohn, P. Hohnberg and L. J. Sham is probably the most sophisticated and computationally less expensive tool to study

these systems *ab initio*. In this thesis we have made use of DFT as well as its extension in the form of density functional perturbation theory (DFPT). Both these theories have been implemented in several commercial and freely available softwares. The results presented in this thesis have been obtained using the open source Quantum ESPRESSO software.

1.3 Outline of the thesis

The rest of the thesis is divided into five chapters.

Chapter-2 gives the detailed description of the density functional theory (DFT) and the practical aspects related to its plane-wave implementation. We have also described density functional perturbation theory (DFPT) that we have used to calculate the vibrational properties of some of the systems studied in this thesis.

In **Chapter-3**, we have presented the results for the graphene-transition metal interfaces. We have studied the adsorption of pristine graphene on Co(0001) and Co(111) surfaces. The studies involve examining the electronic and magnetic properties of graphene. We find induced magnetism in the graphene sheet. The supported graphene sheet becomes ferrimagnetic. We also predict that semihydrogenation of graphene can significantly alter its properties. Not only it results in a six-fold enhancement in the magnetic moment but also results in a band gap opening at the K-point of the Brillouin Zone.

Hydrogen activation by Pd and Pd based materials is not only a primary reaction in fuel cells but also is the first reaction step to various industrially important chemical reactions or catalytic processes. In **Chapter-4**, we have presented the detailed studies of hydrogen dissociation on small Pd_xGa_y tetramers in the gas phase as well as on MgO(100) surface.

Chapter-5 contains the results of our efforts to explore the plausibility of using the above mentioned bimetallic clusters as catalysts for selective hydrogenation of acetylene to ethylene, which is used to purify the ethylene feed. Ethylene is used as a starting material in many polymerization reactions.

Cyclo-dodecadiene (CDD) is an important intermediate obtained during the selective hydrogenation of 1,3,5-cyclo-dodecatriene (CDT) to cyclo-dodecdecene (CDE). In **Chapter-**

6, we have studied the adsorption of cyclo-dodecadiene (CDD) on Pd(100) surfaces, step edges and kinks at varying hydrogen coverage to understand the role of reduced atomic coordination number and hydrogen concentration on the adsorption of the above molecule on these surfaces.

Chapter 2

Computational methods

2.1 Density Functional Theory

2.1.1 Introduction

Matter can be viewed as a system consisting of interacting positively charged nuclei and negatively charged electrons, sometimes under the influence of external field. This ensemble of particles can be in gas phase or in condensed phase. The Hamiltonian (H) for such a system can be written as:

$$H = - \sum_{I=1}^N \frac{\hbar^2}{2M_I} \nabla_I^2 - \frac{\hbar^2}{2m} \sum_{j=1}^n \nabla_j^2 + \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} + \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{I,j} \frac{Z_I e^2}{|\mathbf{r}_j - \mathbf{R}_I|}, \quad (2.1)$$

where $\hbar = h/2\pi$, h being the Planck's constant. M_I and m are the masses of the I^{th} nucleus and electron respectively. e is the charge of an electron and Z_I is the atomic number of the I^{th} nuclei. The summation indices for the electrons are denoted by lower case subscripts while those on the nuclei are denoted by upper case subscript. In principle all the properties of the system can be derived by solving the time-independent Schrödinger equation (SE):

$$H\Psi_n(\mathbf{R}, \mathbf{r}) = \epsilon_n \Psi_n(\mathbf{R}, \mathbf{r}), \quad (2.2)$$

where ϵ_n are the energy eigenvalues and $\Psi_n(\mathbf{R}, \mathbf{r})$ are the corresponding eigenfunctions of the total system.

However, the total number of particles constituting a matter is very large (of the order of

Avogadro's number). This results in large number of degrees of freedom. For example if there are N nuclei and n electrons then the system has $3(N + n)$ degrees of freedom. Further the fact that electrons are Fermions and their wave function needs to be antisymmetric makes it more complicated. Additionally, the Coulomb interaction prevents separation of the electronic and nuclear degrees of freedom. For the above mentioned reasons, it is impossible to solve Eqn. 2.2 within a full quantum mechanical framework. Hence several approximations needs to be made to solve the above equation.

2.1.2 Adiabatic or Born-Oppenheimer approximation

Born and Oppenheimer observed that electrons, being much lighter than the nuclei, move much faster compared to the nuclei present in matter [1]. Hence the time scale associated with the motion of nuclei is much slower than that of the electrons. Therefore, it can be assumed that electrons instantaneously follow the nuclear motion while remaining in the same stationary state of the electronic Hamiltonian. Keeping this in mind, the first term in the Hamiltonian described in Eqn. 2.1 can be treated as a perturbation to H . This allows one to define the eigenfunctions of H in such a way that they depend parametrically on the nuclear positions $\mathbf{R}$. The eigenfunctions of the complete system can be written as:

$$\Psi(\mathbf{R}, \mathbf{r}) = \sum_n \chi_n(\mathbf{R}) \psi_n(\mathbf{R}; \mathbf{r}) \quad (2.3)$$

where $\psi_n(\mathbf{R}; \mathbf{r})$ defines a complete set of states for the electrons at each $\mathbf{R}$ and $\chi_n(\mathbf{R})$ are the coefficients of the electronic states. Using the above equation, the SE can be written as two coupled differential equations:

$$\left(-\frac{\hbar^2}{2m} \sum_{j=1}^n \nabla_j^2 + \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i \neq J} \frac{Z_J^2}{|\mathbf{r}_i - \mathbf{R}_J|} + \sum_{I \neq J} \frac{Z_I Z_J e^2}{|R_I - R_J|} \right) \psi_n(\mathbf{R}; r) = E_n(\mathbf{R}) \psi_n(\mathbf{R}; \mathbf{r}) \quad (2.4)$$

$$\left(-\sum_{I=1}^N \frac{\hbar^2}{2M_I} \nabla_I^2 + E_n(\mathbf{R}) \right) \chi_n(\mathbf{R}) = \epsilon \chi_n(\mathbf{R}) \quad (2.5)$$

Thus within the BO approximation the nuclei are subject to an effective potential $E_n(\mathbf{R})$ that is determined by the solution of the electronic problem. This results in decoupling of the vibrational DOF from the electronic DOF. $E_n(\mathbf{R})$ is also called the BO potential

energy surface.

Once $E_n(\mathbf{R})$ is known, Eqn. 2.5 is easily solvable. However, in Eqn. 2.4 still the two-body Coulomb potential is present. Hence these are still not solvable within a full quantum mechanical framework. Therefore further approximations are necessary.

2.1.3 Hohenberg-Kohn Theorems

In an effort to provide an exact theory for a system of interacting particles Hohenberg and Kohn proposed two theorems in 1964 [2]. They are ([3]):

Theorem 1: For any system of interacting particles in an external potential $V_{ext}(\mathbf{r})$, the potential $V_{ext}(\mathbf{r})$ is determined uniquely, except for a constant, by the ground state particle density $n_0(\mathbf{r})$.

Theorem 2: A *universal functional* for the energy $E[n]$ in terms of the density $n(\mathbf{r})$ can be defined, valid for any external potential $V_{ext}(\mathbf{r})$. For any particular $V_{ext}(\mathbf{r})$, the exact ground state energy of the system is the global minimum value of this functional, and the density $n(\mathbf{r})$ that minimizes the functional is the exact ground state density $n_0(\mathbf{r})$.

These theorems suggest that if $n(\mathbf{r})$ is specified all properties (e.g. kinetic energy, etc.) can be uniquely determined and hence each such properties, including the total energy, can be viewed as a functional of density. For a given external potential $V_{ext}(\mathbf{r})$, this energy functional [also known as HK functional (E_{HK})] is given by:

$$E_{HK}[n] = F[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}, \quad (2.6)$$

where the functional $F[n]$ contains the kinetic energy ($T[n]$) of the electrons and the electron-electron interaction (E_{e-e}). Thus, $F[n]$ can be written as:

$$F[n] = T[n] + E_{e-e}. \quad (2.7)$$

The Hohenberg-Kohn functional is minimized with respect to the ground state charge density corresponding to the external potential subject to the constraint that the integral of $n(\mathbf{r})$ equals the total number of electrons. Thus the HK theorem replaces the traditional description based on wavefunctions (which depend on $3N$ independent variables, N being the number of electrons) with a much more tractable description in terms of the charge density which depends only on three variables. This results in enormous simplification of

the quantum mechanical problem of searching for the ground-state properties of a system of interacting particles. However the functional form of $F[n]$ is not known. The HK theorem proves that it exists, but does not give its form.

2.1.4 Kohn and Sham Ansatz

Kohn and Sham came up with a functional form of the Kohn-Sham functional in 1965 ([4]). They mapped the complex many body problem of a system of interacting electrons to an auxiliary system that can be solved easily. The Kohn-Sham ansatz rests on two assumptions [3]:

1. The exact ground state density can be represented by the ground state density of an auxiliary system of non-interacting particles.
2. The auxiliary Hamiltonian is chosen to have the usual kinetic operator and an effective local potential $V_{\text{eff}}(\mathbf{r})$ acting on an electron at point $\mathbf{r}$.

Using these two ansatz, the Kohn-Sham approach is to rewrite the Hohenberg-Kohn functional as:

$$F_{KS}[n] = T_0[n] + E_H[n] + E_{xc}[n], \quad (2.8)$$

where $T_0[n]$ is the ground state kinetic energy of a system of non-interacting electrons as a function of its ground state charge density distribution. $E_H[n]$, which is given by

$$E_H[n] = \frac{e^2}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}', \quad (2.9)$$

is the Hartree energy and $E_{xc}[n]$ is the exchange- correlation energy. Therefore the KS total energy functional, $E_{KS}[n]$, is given by:

$$E_{KS}[n] = F_{KS}[n] + \int n(\mathbf{r})V_{\text{eff}}(\mathbf{r})d\mathbf{r}. \quad (2.10)$$

The variation of $E_{KS}[n]$ with the constraint that the total number of electrons is kept fixed, leads to the same equation as would hold for a system of non-interacting electrons subject to an effective potential $V_{scf}(\mathbf{r})$, whose form is

$$V_{scf}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}), \quad (2.11)$$

where

$$v_{xc}(\mathbf{r}) \equiv \frac{\delta E_{xc}}{\delta n(\mathbf{r})}, \quad (2.12)$$

is the functional derivative of the exchange-correlation energy.

Thus if V_{scf} is known one needs to solve only the one electron Schrödinger equation:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{scf}(\mathbf{r})\right)\psi_n(\mathbf{r}) = \epsilon_n\psi_n(\mathbf{r}). \quad (2.13)$$

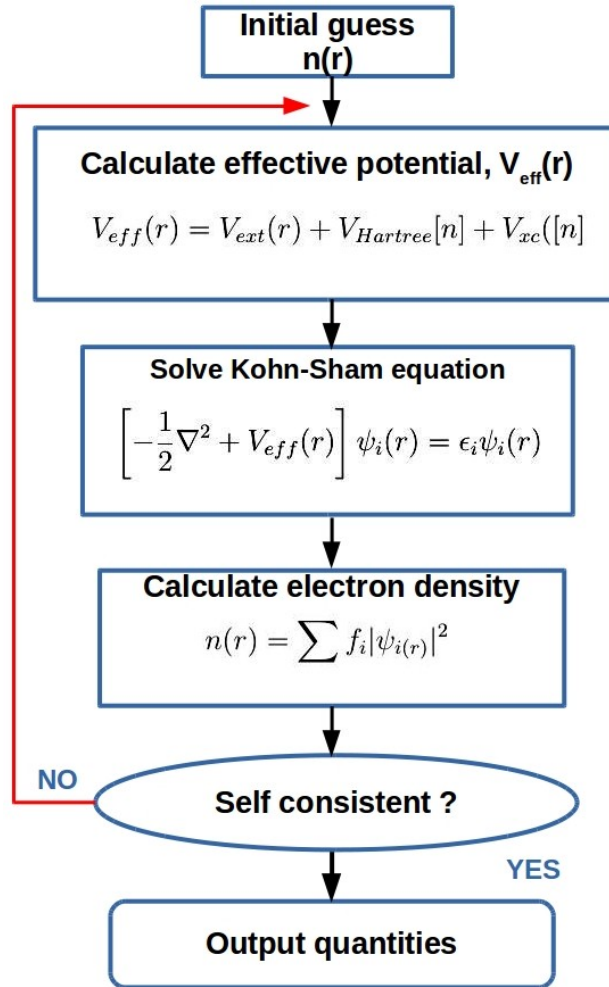


Figure 2.1: Flow chart showing the self consistent loop used to solve the KS equations.

$\psi_n(\mathbf{r})$ are the auxiliary Kohn-Sham orbitals. The charge density $n(\mathbf{r})$ is given by:

$$n(\mathbf{r}) = \sum_{n=1}^N |\psi_n(\mathbf{r})|^2. \quad (2.14)$$

The total energy can be obtained by solving the effective one particle equation. Eqn. 2.13 can be solved in a self consistent way and the procedure to do so is schematically shown in Figure 2.1

2.1.5 Exchange correlation

The many body effects of a system of N particles are incorporated through the calculation of the exchange correlation functional. Since the functional form of the exchange correlation energy in terms of electron density is not known, it is usually approximated. The Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA) of the exchange correlation functional are the most widely used ones.

The LDA of the exchange correlation energy is an integral over space where it is approximated that the exchange correlation energy at each point is same as that of a homogeneous electron gas with the density of the system of interacting electrons at that point. It is given by:

$$E_{xc}^{LDA} = \int n(\mathbf{r}) \epsilon_{xc}^{hom}(n(\mathbf{r})) d^3\mathbf{r}, \quad (2.15)$$

where $\epsilon_{xc}^{hom}(n(\mathbf{r}))$ is the exchange correlation density of a homogeneous electron gas at $\mathbf{r}$ with a density $n(\mathbf{r})$. The exchange-correlation potential (v_{xc}^{LDA}) is given by:

$$v_{xc}^{LDA}(\mathbf{r}) = \frac{\delta E_{xc}^{LDA}[n]}{\delta n(\mathbf{r})}. \quad (2.16)$$

Approximate forms of ϵ_{xc}^{hom} have been obtained from Quantum Monte Carlo calculations by Ceperley and Alder [5], which were later parametrized by Perdew and Zunger [6] using a simple analytical form.

Although the LDA approximation adequately describe properties of weakly correlated systems like semiconductors and simple metals, it fails while trying to compute electronic and structural properties of strongly correlated systems such as transition metal oxides. To overcome these failures of the LDA, the exchange-correlation energy is evaluated with an

approximation that at each point in space it is not only a functional of $n(\mathbf{r})$ but also of its gradient and higher derivatives. This is known as the Generalized Gradient Approximation (GGA). Within the GGA, the exchange-correlation energy (E_{xc}^{GGA}) is given by:

$$E_{xc}^{GGA} = \int n(\mathbf{r}) \epsilon_{xc}^{hom}(n(\mathbf{r}), |\nabla n(\mathbf{r})|, |\nabla^2 n(\mathbf{r})| d\mathbf{r}, \dots). \quad (2.17)$$

There are many flavours of the GGA exchange correlation functional. Some of the most widely used ones are those developed by Becke (B88) [7], Perdew and Wang (PW91) [8] and Perdew, Burke and Ernzerhof (PBE) [9]. For finite or semi-infinite systems GGAs are usually describe the electron correlations reasonably well. However they are still unable to provide a proper description of strongly correlated infinite solids.

2.1.6 Total energy calculation

Using the eigenvalues obtained from the self consistent solution of the KS equations, the total energy of a system of N electrons is obtained using the following equation:

$$E_{tot}[n] = \sum_{i=1}^N \varepsilon_i - \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r} + E_{xc}[n] - \int n(\mathbf{r})V_{xc}(\mathbf{r})d\mathbf{r} + E_{Ewald}. \quad (2.18)$$

Because of the double counting of electrons in the calculation of energy eigenvalues, we subtract half of the Hartree energy. The contribution to ε_i from exchange-correlation interaction ($\langle \psi_i | V_{xc} | \psi_i \rangle$) is not equal to E_{xc} . Hence in order to calculate E_{tot} we will subtract $\langle \psi_i | V_{xc} | \psi_i \rangle$ and add E_{xc} . E_{Ewald} is the energy of the nuclear-nuclear interaction for a particular ionic configuration $\mathbf{R}$, evaluated using Ewald summation method [10–12].

2.1.7 Basis

The KS equations are solved by expanding the wavefunctions in a basis. Typically there are many types of basis sets that can be used to expand the wave function. For example one can use Gaussian functions, plane waves, atomic orbitals or a mixture of two or more types of basis set. All the DFT calculations presented in this thesis were done using a plane wave basis set $e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$, where $\mathbf{k}$ is the wavevector at which the K-S equations are solved and $\mathbf{G}$ is a reciprocal lattice vector. The plane waves become discrete only when periodic boundary conditions are used. The number of plane waves (i.e. size of the basis

set) in a basis set is determined by an energy parameter E_{cut} using the following equation:

$$\frac{\hbar |\mathbf{k} + \mathbf{G}|^2}{2m_e} < E_{cut}. \quad (2.19)$$

E_{cut} is determined by checking the convergence of the quantity of interest with E_{cut} .

The advantages of using a plane wave basis set are: (i) Pulay forces [13] being absent, as the basis is independent of atomic position, it is easy to evaluate forces using the Hellmann-Feynman theorem [14, 15], (ii) the quality of the basis is controlled by a single parameter and (iii) it is easy to implement while coding.

However, while using a plane wave basis, a large number of plane waves are required to expand the wavefunctions in the core region, where the core electrons' wavefunctions are highly peaked, and valence electron wavefunctions have several oscillations. This problem can be removed by using pseudopotentials as described below.

2.1.8 Pseudopotentials

The effective potential experienced by the valence electrons when the core electrons are frozen is called the pseudopotential. It is obtained by pseudizing the wavefunction of the valence electrons, i.e., the oscillations of the wavefunctions of the valence electrons in the core region are removed by replacing it with a smooth function. The pseudo and all-electron wavefunction match each other beyond a particular value of radial distance from the centre of the nucleus r_c . r_c is chosen such that the last node of the all electron wave function lies within it. If the same pseudopotential can be used in different environments of the atom, the pseudopotential is said to be transferable. As r_c increases, the number of plane waves required to represent a pseudo wavefunction generally decreases, but the transferability also decreases. There are many types of pseudopotentials like norm-conserving, ultrasoft etc.

In norm-conserving pseudopotentials, in the core region, the norm of the pseudo-wavefunction is equal to the norm of the all electron wavefunction thereby ensuring the transferability of the pseudopotential.

Relaxation of the norm-conservation condition leads to Vanderbilt's ultrasoft potential [16] which allows one to use a very low energy cut-off. However, upon doing so the or-

thonormality requirements of the atomic orbitals and the norm conservation is lost. The issue of the orthonormality requirements can be solved by considering a generalised eigenvalue problem, where a generalised orthogonality constraint is expressed in terms of an overlap operator. The second problem is solved by adding to the system's charge an augmentation charge that is localised within the core regions.

2.1.9 k-point sampling and smearing

Numerical integrations over the Brillouin zone are computed by summing over a finite mesh of k-points. Generally the most widely used k-point mesh is the Monkhorst-Pack [17] grid. For metals this approximation is extremely delicate because the abrupt change in occupancy near the Fermi surface can make the sampling inadequate. Moreover, in order to capture the finite features of band crossing, one needs quite a fine k-point mesh for metals, making the calculations computationally expensive.

The use of the number of k-points for metals can be reduced by slightly broadening the energy levels. Many broadening schemes are available; for example Gaussian broadening [18], Methfessel-Paxton smearing [19], Marzari-Vanderbilt cold smearing [20], etc.

2.1.10 Calculation of forces and stresses

To determine the ground state structure of a system one needs to minimise the forces and stresses. Hence it is necessary to calculate the forces acting on the individual atoms and the stresses acting on the unit cell, so as to optimize the atomic positions and lattice vectors of the unit cell. When the forces acting on the atoms are zero, it signifies that the atomic coordinates are relaxed. Zero stress implies that the unit cell lattice vectors have been optimized.

The forces are calculated using the Hellmann-Feynman theorem [14, 15] that is expressed as:

$$F_I = -\frac{\delta E(\mathbf{R})}{\delta \mathbf{R}_I} = -\langle \Psi(\mathbf{R}) | \frac{\delta E(\mathbf{R})}{\delta \mathbf{R}_I} | \Psi(\mathbf{R}) \rangle, \quad (2.20)$$

where $\Psi(\mathbf{R})$ are the electronic eigenstates of H_{BO} for a given configuration $\mathbf{R}$, F_I is the force acting on the I^{th} atom.

The advantage of this method is that we do not need to calculate the energies of the system at many configurations and can extract the information of the force constants for the bonds easily. There should be an additional term to Eqn. 2.20, which is the derivative of the basis set with respect to the position of the ion. This term, which is called the Pulay force, vanishes if we use a complete basis set and the Hellmann-Feynman forces become exactly equal to the derivative of the total energy with respect to the position of the ions. However, we usually use an incomplete basis set. As a result the Pulay force does not vanish, introducing an error in the calculated Hellmann-Feynman forces. Using a plane wave basis set one can easily get rid of these forces.

Stresses are calculated using the “stress theorem” proposed by Nielsen and Martin [21,22]. The stress tensor, $\sigma_{\alpha\beta}^s$, is the derivative of total energy with respect to the strain tensor, $\epsilon_{\alpha\beta}^s$:

$$\sigma_{\alpha\beta}^s = -\frac{1}{\Omega} \frac{\delta E_{tot}}{\epsilon_{\alpha\beta}^s}, \quad (2.21)$$

where α and β are the Cartesian indices and Ω is the volume of the unit cell.

2.2 Phonons from density functional perturbation theory

The lattice-dynamical behaviour of solids and vibrational properties of molecules probed through infrared, Raman and neutron diffraction spectra acts as fingerprints of these material. Moreover there are other properties of solids like specific heat, thermal expansion, etc., that depend on their lattice-dynamical behaviour. The basic theory of lattice vibrations was first developed by Born and Huang [23]. Over the last few years, the development of DFT and density functional perturbation theory (DFPT) [24–26] (based on linear response theory), made it possible to perform a large number of *ab initio* calculations [27,28] of lattice vibrations.

2.2.1 Lattice dynamics from electronic-structure theory

We have seen before that the adiabatic approximation enables us to decouple the vibrational DOF from the electronic DOF.

The vibrational frequencies ω are determined by the eigenvalues of the Hessian matrix of

the Born-Oppenheimer energy (also called the matrix of the interatomic force constants), scaled by their nuclear masses:

$$\det \left| \frac{1}{\sqrt{M_I M_J}} \frac{\partial^2 E(\mathbf{R})}{\partial \mathbf{R}_I \partial \mathbf{R}_J} - \omega^2 \right| = 0. \quad (2.22)$$

As mentioned in the Section 2.1.10, the forces are given by the Hellmann-Feynman theorem. The Hamiltonian depends on $\mathbf{R}$ via the electron-ion interaction that couples to the electronic degrees of freedom only through the electron charge density. The force acting on I^{th} nucleus is given by:

$$\mathbf{F}_I = - \int n_{\mathbf{R}}(\mathbf{r}) \frac{\partial V_{\mathbf{R}}(\mathbf{r})}{\partial \mathbf{R}_I} d\mathbf{r} - \frac{\partial E_{\text{Ewald}}(\mathbf{R})}{\partial \mathbf{R}_I}, \quad (2.23)$$

where $V_{\mathbf{R}}(\mathbf{r})$ is the electron-nucleus interaction,

$$V_{\mathbf{R}}(\mathbf{r}) = - \sum_I \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R}_I|}. \quad (2.24)$$

The Hessian of the B-O energy surface appearing in Eqn. 2.22 is given by:

$$\frac{\partial^2 E(\mathbf{R})}{\partial \mathbf{R}_I \partial \mathbf{R}_J} \equiv - \frac{\partial \mathbf{F}_I}{\partial \mathbf{R}_J} = \int \frac{\partial n_{\mathbf{R}}(\mathbf{r})}{\partial \mathbf{R}_J} \frac{\partial V_{\mathbf{R}}(\mathbf{r})}{\partial \mathbf{R}_I} d\mathbf{r} + \int n_{\mathbf{R}}(\mathbf{r}) \frac{\partial^2 V_{\mathbf{R}}(\mathbf{r})}{\partial \mathbf{R}_I \partial \mathbf{R}_J} d\mathbf{r} + \frac{\partial^2 E_N(\mathbf{R})}{\partial \mathbf{R}_I \partial \mathbf{R}_J}.$$

Eqn. 2.25 states that in order to calculate the Hessian of the BO surface one needs to calculate $n_{\mathbf{R}}(\mathbf{r})$ and its linear response to a distortion of the nuclear geometry $\partial n_{\mathbf{R}}(\mathbf{r})/\partial \mathbf{R}_I$. While $n_{\mathbf{R}}(\mathbf{r})$ can be evaluated using DFT, DFPT is used to evaluate $n_{\mathbf{R}}(\mathbf{r})$.

2.2.2 Density-functional linear response

The electron response ($\partial n_{\mathbf{R}}/\partial \mathbf{R}$) appearing in Eqn. 2.25 can be obtained within the framework of DFPT. This is achieved by linearizing Eqns. 2.11, 2.13 and 2.14. Linearization of Eqn. 2.14 leads to

$$\Delta n(\mathbf{r}) = 2\text{Re} \sum_{n=1}^N \psi_n^*(\mathbf{r}) \Delta \psi_n(\mathbf{r}). \quad (2.25)$$

Variation of KS orbitals $\Delta \psi_n(\mathbf{r})$ is obtained by standard first-order perturbation theory:

$$(H_{SCF} - \epsilon_n) | \Delta\psi_n \rangle = -(\Delta V_{SCF} - \Delta\epsilon_n) | \psi_n \rangle, \quad (2.26)$$

where H_{SCF} is the unperturbed KS Hamiltonian and $\Delta\epsilon_n = \langle \psi_n | \Delta V_{SCF} | \psi_n \rangle$ is the first order variation of the KS eigenvalues. The first order correction to the self consistent potential ΔV_{SCF} is given by:

$$\Delta V_{SCF}(\mathbf{r}) = \Delta V(\mathbf{r}) + e^2 \int \frac{\Delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{dv_{XC}(n)}{dn}|_{n=n(r)} \Delta n(\mathbf{r}). \quad (2.27)$$

Eqns. 2.25, 2.26 and 2.27 form a set of self-consistent equations for the perturbed system, completely analogous to the KS equation in the unperturbed case, with the KS eigenvalue equation being replaced by the solution of a linear system. The value of $\partial n_{\mathbf{R}}(\mathbf{r})/\partial \mathbf{R}_I$ is then fed back to Eq. 2.25 to get the dynamical matrix.

Usually the first order correction to a given eigenfunction of the Schrödinger equation is given by:

$$\Delta\psi_n(\mathbf{r}) = \sum_{m \neq n} \psi_m(\mathbf{r}) \frac{\langle \psi_m | \Delta V_{SCF} | \psi_n \rangle}{\epsilon_n - \epsilon_m}, \quad (2.28)$$

the summation running over all the states of the system, occupied or empty. Thus in order to explicitly compute the $\Delta\psi_n(\mathbf{r})$ from Eqn. 2.28 we need to know the full spectrum of the KS Hamiltonian. Moreover extensive summations over conduction bands is needed. Both these factors will make the calculations computationally expensive. Instead, if we evaluate $\Delta\psi_n(\mathbf{r})$ using Eqn. 2.26, only knowledge of the occupied manifold of the system is necessary. Additionally one can also exploit the availability of many efficient algorithms to numerically solve for the linear system. Therefore, in this way the computational cost of determining the density response to a single perturbation is of the same order as that needed to calculate the unperturbed ground state density.

The method discussed so far holds good for systems with band gaps. However, for metals one needs to take into account the presence of finite density of states at the Fermi level and the change in orbital occupation number that may occur when an infinitesimal perturbation is applied.

Chapter 3

Effects of hydrogenation on electronic and magnetic properties of graphene supported on Co surfaces

3.1 Introduction

Magnetism in materials has usually been associated with systems containing unpaired localized d or f electrons. Over the last decade there has been a lot of debate regarding magnetism in carbon (C) based materials where there are s and p electrons. [29, 30]. Recently magnetism has been found in different C based materials. For example, Ohldag *et al.* [31] have shown that proton-irradiated graphite is magnetic where the cause for the magnetism has been attributed to the presence of defects due to irradiation. [32] In lower dimension systems, for example, zigzag edged graphene nanoflakes have also been predicted to be magnetic. [33] In addition to the intriguing fact that magnetism is observed (or predicted) in different forms of graphene, its unique electronic structure gives rise to exceptional transport and spin-filtering properties, making it a promising candidate for applications in graphene based electronic devices. [34] However, graphene is a semi-metal with the conduction and valence band forming the Dirac cone at the K point of the Brillouin Zone (BZ).

To use graphene as materials for semiconductor spintronics, it is not only desirable to make graphene magnetic but also to open up the band gap. It has been recently shown that covalent functionalization of graphene [35] or non-covalent stacking with aromatic molecules through π - π interactions can be used to open the band gap. [36, 37] Moreover, for any device application of graphene, making contacts with metals is necessary.

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In particular, growth of graphene on Ni(111) and Co surfaces are particularly interesting because of the almost perfect lattice matching between the substrate (Ni or Co surfaces) and the graphene sheet. The lattice matching enables growth of stable epitaxial overlays without the formation of complex superstructures which are the results of large lattice mismatch. Recent studies of the electronic and magnetic properties of graphene supported on Ni(111) surface by Weser *et al.* [38] have shown that there is a *weak* induced magnetic moment ($0.01 \mu_B$) in the graphene sheet. In order to use the induced magnetic properties of graphene for device applications, it is desirable to increase the magnitude of the induced magnetic moment. On intercalating an Fe monolayer in between Ni(111) surface and graphene, one can *slightly* increase the induced magnetic moments. While the magnetic moments of the two inequivalent C atoms in absence of Fe are 0.031 and $-0.019 \mu_B$, upon intercalating Fe, the magnetic moments increase to -0.050 and $0.039 \mu_B$. [39]

Although there have been many studies (both experimental and theoretical) on Ni(111)/graphene interfaces, graphene on Co surfaces is almost unexplored. [40] Compared to Ni (bulk magnetic moment of $0.62 \mu_B$ per Ni atom), the magnetic moment of Co atoms (bulk magnetic moment of $1.69 \mu_B$ per Co atom) are much higher. Therefore one might expect that the magnitude of the induced magnetic moments on graphene supported on Co(0001) might be much higher than those on Ni(111) surface. In this work, we have discussed our detailed investigations of the electronic and magnetic properties of graphene supported on Co(0001) surface. We also propose an effective way (through chemical functionalization) to (i) *significantly* enhance the induced magnetic moment in the graphene sheet supported on Co surface and (ii) opening up of the band gap at the K -point of the Brillouin zone (BZ), which is experimentally achievable.

3.2 Computational details

The calculations are performed using Quantum Espresso software [41]. Electron-ion interactions are described using ultrasoft pseudo potentials. [42] We have used a kinetic energy cut off of 30 Ry and 300 Ry for wavefunctions and charge density respectively. The electron-electron exchange and correlation are described using Perdew, Burke, and Ernzerhof parameterization based generalized gradient approximation (GGA-PBE) [9]. Brillouin zone integrations have been done with a $(34 \times 34 \times 1)$ Monkhorst-Pack k -point mesh. [17] In order to speed up the convergence we have used Marzari-Vanderbilt smear-

ing [20] with a smearing width of 0.01 Ry. For bulk Co we obtain a lattice parameter of 2.50 Å, a c/a ratio of 1.55 and a magnetic moment of $1.69 \mu_B$ per Co atom, which are in good agreement with the previous reports. [43,44] The lattice parameter of graphene (2.46 Å) obtained from our calculations is also in excellent agreement with earlier calculations and experimental measurements. [45]

The Co(0001) surface is modeled with an asymmetric slab consisting of seven layers of Co, where the bottom three layers are kept fixed at the bulk interplanar separation and the remaining four layers are relaxed. The fixed bottom layer is passivated with Cu atoms to quench the *spurious magnetization*. In order to avoid the interaction between the periodic images, a vacuum of about 10 Å is used. In practice when graphene is grown on a substrate, the graphene sheet is strained by the substrate potential. The amount of strain depends on the degree of lattice mismatch. In the case of Co(0001) surface, there is an almost perfect lattice matching with graphene. Hence the graphene sheet is expected to grow pseudomorphically on the Co substrate. Therefore to study the interactions of graphene sheet with the Co substrate, both the graphene and Co substrate are kept at the Co(0001) lattice parameter of 2.50 Å. Dispersive interactions play an important role in graphene-transition metal interfaces which is not taken into account by conventional PBE exchange correlation functional. Therefore we have included an empirical vdW (van der Waals) correction to account for the dispersive interactions. [46, 47] However, we note that this is an empirical correction to the total energy and it does not affect the magnetic couplings of the system.

3.3 Results and discussion

3.3.1 Pristine graphene on Co surface

We considered three possible configurations, namely *top-fcc*, *top-hcp* and *hcp-fcc*. In *top-fcc* (Figure-3.1 (a) and (d)), one of the C atoms is directly above the Co atom of the topmost layer and the second C atom is at the void fcc site. For the *top-hcp* configuration (Figure-3.1(b) and (e)) one of the C atoms is situated above the Co atoms of the first layer (top site) while the other is on the top of the Co atom in the second layer (hcp site).

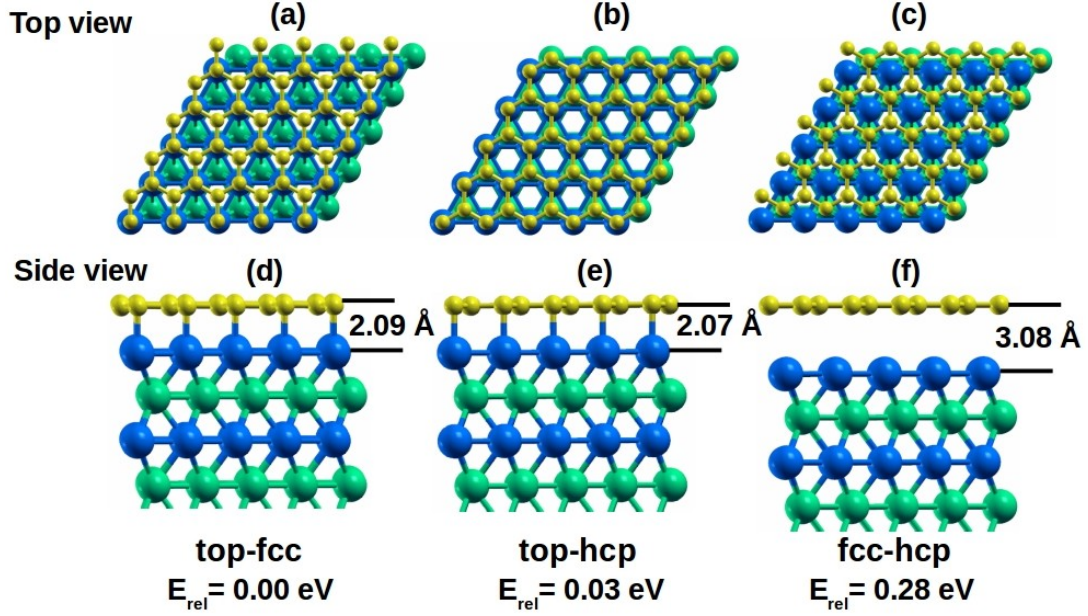


Figure 3.1: Top and side view of graphene on Co(0001) in *top-fcc* (a and d), *top-hcp* (b and e) and *hcp-fcc* (c and f) configurations. The numbers given below each configuration shows the relative energy difference between the different configurations w.r.t the most stable configuration (*top-fcc*). Reprinted (adapted) with permission from *J. Phys. Chem. Lett.*, **2012**, 3, 2582-2587. Copyright©2012 American Chemical Society.

In *hcp-fcc* (Figure-3.1(c) and (f)), the two C atoms are placed on hcp and fcc sites respectively. Our calculations show that graphene show strongest binding with the Co substrate in the *top-fcc* configuration, the binding energy of the graphene sheet being -0.22 eV/C atom. A comparison of the binding energy with and without including van der Waals interaction shows that the contribution of van der Waals interaction to the binding energy is -0.20 eV/C atom, suggesting that the binding of the graphene sheet with Co is predominantly due to van der Waals interaction. The Co-C distance is 2.09 Å and we do not observe any buckling of the graphene sheet. Our results are in excellent agreement with earlier reported results. [48,49] However, the energy difference between the *top-fcc* and *top-hcp* configuration is quite small. Therefore it is not possible to say conclusively whether graphene would be in the *top-fcc* or the *top-hcp* configuration. We note that the STM measurements of graphene on Co(0001) by Eom *et al.* also could not conclusively show whether graphene would prefer to be on the *top-fcc* or the *top-hcp* configuration. [40] Further experiments and calculations which can capture the effects of the local coordination (for eg. C-1s core level X-ray absorption spectra) are needed to conclusively decide which of the two configurations are preferred or whether both of them co-exist. Since

from our calculations the top-fcc configuration is lowest in energy, we have used this configuration for the hydrogenation study.

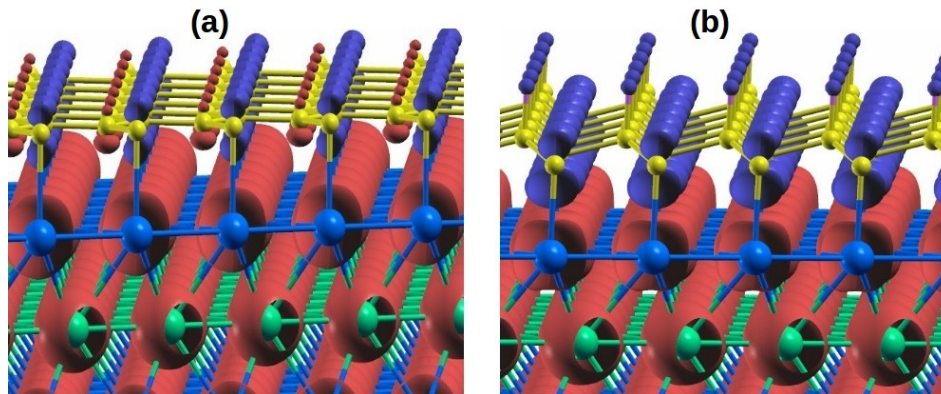


Figure 3.2: Magnetization density isosurfaces of the pristine graphene and hydrogenated graphene on Co(0001). Red (blue) isosurfaces denote spin-up (down) magnetization density. Reprinted (adapted) with permission from *J. Phys. Chem. Lett.*, **2012**, 3, 2582-2587. Copyright©2012 American Chemical Society.

Figure-3.2(a) shows the calculated magnetization density plot for the *top-fcc* configuration. The free standing graphene sheet is non-magnetic, however we find that there is an induced magnetic moment in the graphene sheet when it is placed on the Co substrate. The top-C atoms have a magnetic moment of $-0.083 \mu_B$ which are aligned anti-parallel to those on the Co atoms. The C atoms on the fcc sites have a magnetic moment of $0.059 \mu_B$ and are aligned parallel to the Co atoms. Hence graphene turns ferrimagnetic with an average magnetic moment of $-0.024 \mu_B$. The magnetic moment of Co top layer is quenched from $1.78 \mu_B$ per surface Co atom for the clean surface to $1.54 \mu_B$.

To understand the origin of the induced magnetic moment, we calculated the projected density of states (PDOS) and the k -point resolved PDOS (KPDOS). The contour plots of the KPDOS along the high symmetry directions of the BZ gives the contribution from each atom to the band structure. The PDOS (Figure-3.3) shows strong hybridization of the C-2*p* states of graphene and Co-3*d* states which lead to splitting of spin-up and spin-down states of the C atoms. Mainly the hybridization occurs between the C- p_z orbitals lying perpendicular to the plane of the graphene sheet and the Co- d_{z^2} orbitals due to symmetry matching. This is also evident from the KPDOS for the spin-up and spin-down channels as shown in Figure-3.4.

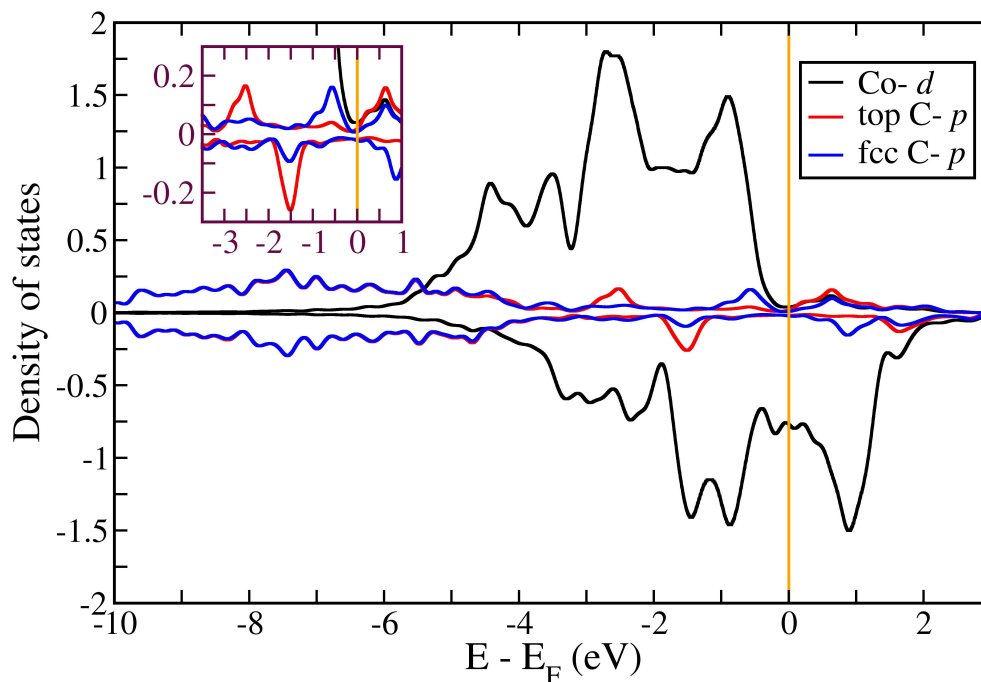


Figure 3.3: Projected density of states plot (PDOS) of the top-fcc configuration of graphene on Co(0001) surface. Reprinted (adapted) with permission from *J. Phys. Chem. Lett.*, **2012**, 3, 2582-2587. Copyright©2012 American Chemical Society.

Due to the interaction between the substrate and graphene, the Dirac cone at the K point of the BZ (which is a characteristic feature of the electronic structure of graphene) is destroyed, resulting in a slight opening of the band gap at the K-point (0.38 eV for spin-up and 0.24 eV for spin-down). For the spin-up channel, at the K-point of the BZ, the states at 0.10 eV and -2.45 eV (Figure-3.4) results from the interaction of top-C- p_z states with the Co- d_{z^2} states. Since the fcc-C atom occupies the hollow site formed by the three surface Co atoms, the p_z states of the fcc-C interact more strongly with the Co d_{zx} , d_{zy} , $d_{x^2-y^2}$ and d_{xy} states. These interactions give rise to new states at -0.27 eV (primarily from interaction primarily with the Co d_{zx} , d_{zy} states), -1.00 eV, -1.40 eV and -1.72 eV (these states are due to interactions primarily with the Co $d_{x^2-y^2}$ and d_{xy} states) as shown in Figure-3.4. Similar features are also observed for the spin-down channel as shown in Figure-3.4. However, in this case the states are moved much higher in energy.

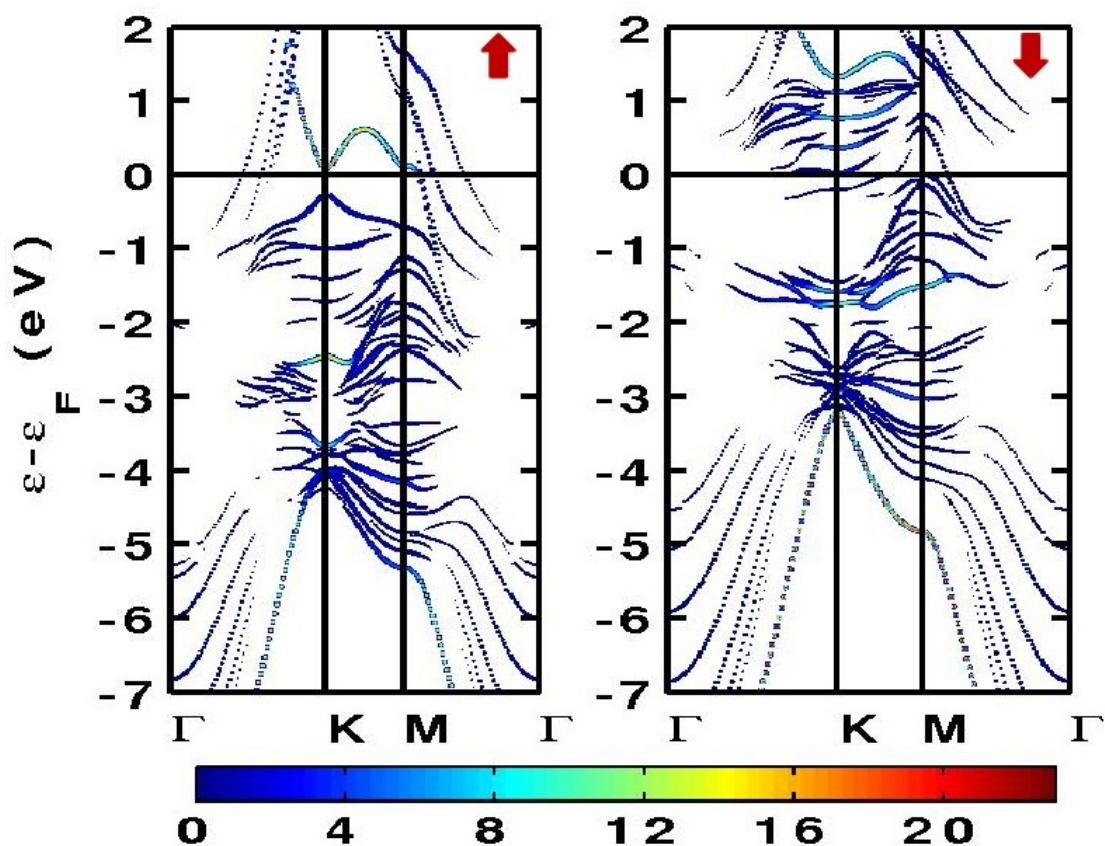


Figure 3.4: Contour plots of the contribution of the top and fcc C- p_z orbitals to the total density of states for spin-up and spin-down respectively, along the high-symmetry directions of the BZ. Reprinted (adapted) with permission from *J. Phys. Chem. Lett.*, **2012**, 3, 2582-2587. Copyright©2012 American Chemical Society.

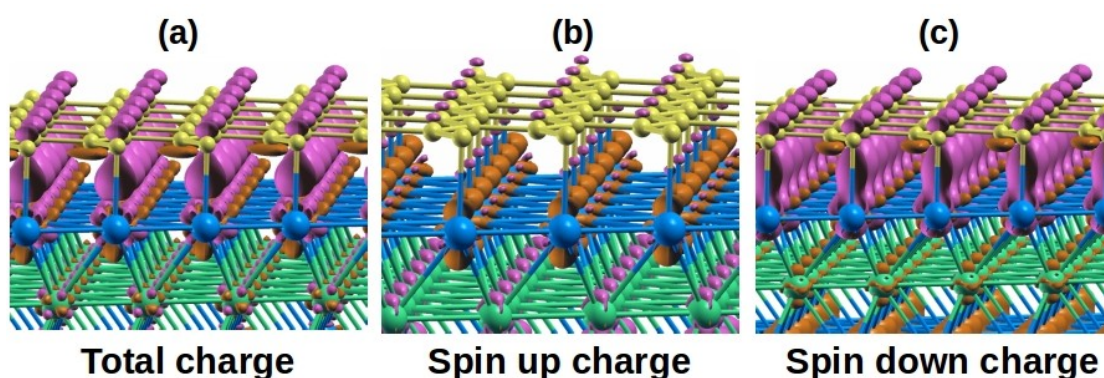


Figure 3.5: Isosurfaces corresponding to spin resolved (total (a), for spin-up (b) and spin-down (c)) charge transfer between graphene and Co(0001) surface. Pink (brown) lobes denotes the charge accumulation (depletion). Reprinted (adapted) with permission from *J. Phys. Chem. Lett.*, **2012**, 3, 2582-2587. Copyright©2012 American Chemical Society.

This pd hybridization at the Co/graphene interface also results in charge transfer between the Co atoms and the graphene sheet. Figure-3.5 shows spin-resolved charge transfer isosurfaces for graphene-Co(0001) interface. For the clean Co surface, the $3d$ spin-up (spin-down) states are completely (partially) filled. Therefore when graphene interacts with Co, there is a transfer of spin-up electrons from the Co d states to the p states of the fcc-C atoms. There is also slight accumulation of spin-up charge in between the top-C atoms of graphene and the surface Co atoms (Figure-3.5(b)). For the spin-down electrons, there is both donation and back-donation of electrons between the graphene sheet and the Co substrate (Figure-3.5(c)). The net effect of this spin resolved charge redistribution is that the majority of the electrons accumulated on the fcc-C (top-C) atoms are predominantly spin-up (down), resulting in the net magnetic moment on the fcc-C (top-C) atom to be aligned parallel (anti-parallel) to those on the Co atoms. Moreover, Figure-3.5(a) also shows that the fcc-C atoms are electron deficient sites while the top-C atoms are electron rich sites.

3.3.2 Hydrogenated graphene on Co surface

Upon hydrogenating the graphene supported on the Co surface with 0.50 ML of hydrogen (where 1 ML means one H atom per graphene C atom), H can bind either on the top or on the fcc-C atoms. Both the geometries are shown in the Figure-3.6. We find that H prefers to bind to the fcc-C atom with a binding energy of -2.04 eV/H atom. This is 0.10 eV stronger than the binding of the H atom to the top-C atoms. H forms strong covalent bonds with the fcc-C atoms, which, as mentioned in the previous paragraph are the electron deficient sites, and therefore the more preferred sites.

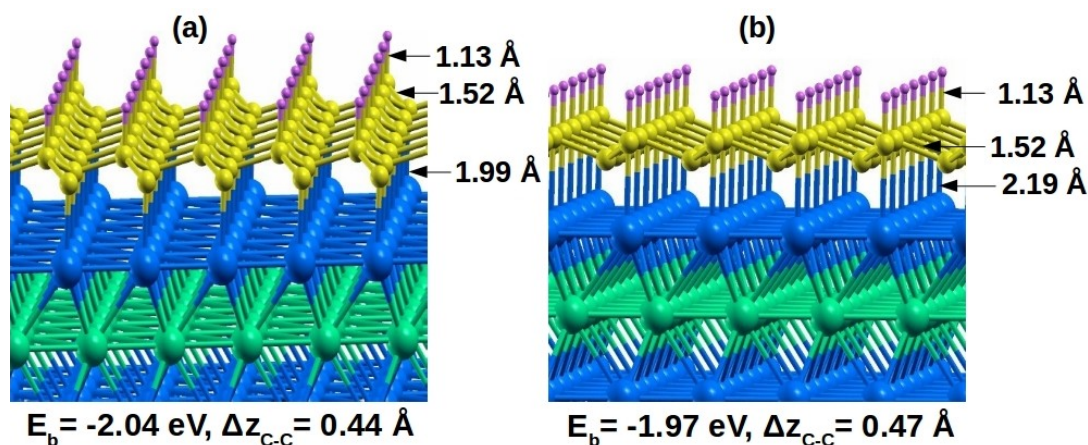


Figure 3.6: Configurations of hydrogenation of graphene on both top-C and fcc-C atoms on Co(0001). Reprinted (adapted) with permission from *J. Phys. Chem. Lett.*, **2012**, 3, 2582-2587. Copyright©2012 American Chemical Society.

To estimate the stability of the semi-hydrogenated graphene sheet, we have calculated its binding energy with and without van der Waals interaction. The binding energies are about -1.80 and -1.16 eV/(1×1) unit cell respectively. Thus for semi hydrogenated graphene van der Waals interaction is not as dominant as for the pristine graphene. The contribution of van der Waals interaction to the binding energy is -0.64 eV/(1×1) unit cell. In order to accommodate the H atoms, the graphene lattice tend to undergo an expansion, [50] which, in the present case is not possible as graphene is constrained by the substrate potential. As a result, hydrogenation results in strong buckling of the graphene sheet. The fcc-C atoms move away from the substrate while the top-C atoms move towards the surface. The C-C interplanar separation is 0.44 Å and the C-H bond distance is 1.13 Å.

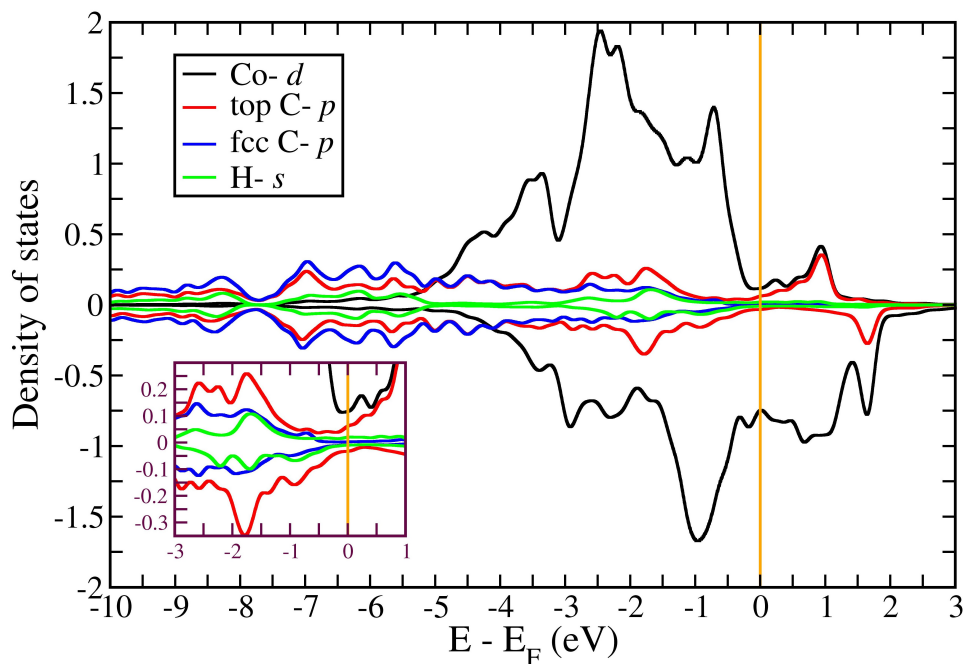


Figure 3.7: Projected density of states plot (PDOS) of hydrogenated graphene on Co(0001) surface. Reprinted (adapted) with permission from *J. Phys. Chem. Lett.*, **2012**, 3, 2582-2587. Copyright©2012 American Chemical Society.

The PDOS and magnetization density of the graphene sheet on Co(0001) after hydrogenation are shown in Figure-3.7 and 3.2(b) respectively. Hydrogenation of the graphene sheet results in the following two effects. Firstly, the H-atom forms strong σ -bonds with the fcc-C atoms of graphene, resulting in significant quenching of the magnetic moment of the fcc-C atom (from $0.059 \mu_B$ to $0.01 \mu_B$). We also observe slight magnetic moment on the H atom ($0.03 \mu_B$). Secondly, due to the formation of the σ -bonds between the fcc-C atoms and H, the π electron cloud on the top-C atom is further localized. This results in increase in the magnetic moment on the top-C atom from $-0.083 \mu_B$ to $-0.15 \mu_B$. However, unlike graphone (free standing semi hydrogenated graphene), the electrons in the unhydrogenated top-C atoms of the graphene sheet supported on Co(0001) surface are not completely localized due to the interaction with the Co substrate. This results in smaller magnitude of the magnetic moment compared to free standing graphone. The magnetic moment of Co top layer is quenched from $1.54 \mu_B$ per surface Co atom to $1.19 \mu_B$ upon hydrogenating graphene. Like the supported graphene sheet, the hydrogenated graphene sheet becomes ferrimagnetic, but now with an average magnetic moment of $-0.14 \mu_B$, aligned anti-parallelly with respect to Co. Thus chemical modification of the graphene sheet through hydrogenation results in **six-fold** increase in magnetic moment

of the graphene sheet. Note that for graphene and hydrogenated graphene supported on fcc-Co(111) surface, we have found similar results which are presented in the Appendix A. The pristine graphene when placed on the Co(111) surface also turns ferrimagnetic having a net magnetic moment of $-0.021 \mu_B$. Upon the semi-hydrogenation of graphene on Co(111), the graphene remains the ferrimagnetic with an increased magnetic moment of $-0.13 \mu_B$ (**six-fold** increase).

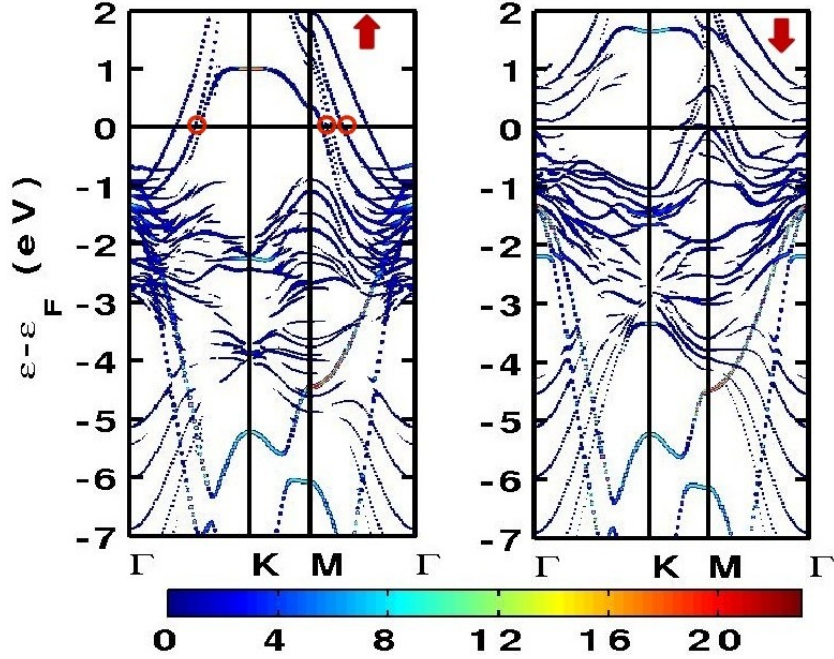


Figure 3.8: Contour plots of the contribution of the top and fcc C- p_z orbitals to the total DOS for spin-up and spin-down channels, along the high-symmetry directions of the BZ of hydrogenated graphene on Co(0001). The red circles denote the states that have a p character. Reprinted (adapted) with permission from *J. Phys. Chem. Lett.*, **2012**, 3, 2582-2587. Copyright©2012 American Chemical Society.

Figure-3.8 show the KPDOS of the hydrogenated graphene along the high symmetry directions of the BZ. In addition to the increase in the magnitude of the magnetic moment, hydrogenation of the supported graphene sheet results in further opening up of the band gap at the K-point of the BZ. For the spin-up states, the band gap at the K-point is about 3.19 eV while for the spin-down states it is about 2.64 eV. Moreover, unlike free standing graphene, the electronic states for both the spin-up and spin-down electrons crosses the Fermi energy at other points of the BZ. This is due to the strong $sp-d$ hybridization. We analyzed the wavefunctions corresponding to these states. While for the spin-up channel there are three states (marked by red circles in Figure-3.8 which has significant p character

coming from the C atoms of graphene, for the spin-down channels, all the states crossing the Fermi energy have a predominantly Co-*d* character. Thus, when using this interface in a device, while the spin-up channel of the supported hydrogenated graphene sheet will be conducting, the spin-down channel may be insulating. This might enable more efficient spin filtering when these interfaces will be used in spintronic devices.

3.4 Outlook and summary

As for the experimental feasibility, single layer graphene can be easily prepared on a metallic thin film Co substrate [51] and subsequent basal-plane hydrogenation (at saturated coverage) can be performed either by low-pressure dc plasma discharge of a hydrogen-argon mixture [52] or by a commercially available Omicron EFM H source. [51] Considering the reactivity of active hydrogen atoms (radicals) one would expect equal probability of the covalent attachment to both the top and the fcc C atoms as far as the kinetic factor dominates. However, hydrogenation predominantly on the fcc-C atoms, which is thermodynamically favorable as suggested by our calculations, can be achieved by controlling reaction parameters like temperature, partial pressure (hydrogen dosage) and time. Furthermore, dehydrogenation could be achieved upon simple annealing of the sample at 450°C in inert atmosphere. [52] Thereby, our presented approach of tuning the interfacial magnetochemical effect in ferrimagnetic graphene is apparently reversible. We also note that, the induced magnetic moment in graphene on ferromagnetic Ni surface, even though very small (in the order of 0.05-0.10 μ_B), was successfully estimated by employing X-ray magnetic circular dichroism (XMCD) spectroscopy [38, 39] and spin-resolved photoemission spectroscopy (PES). [53] Here the proposed **six-fold** enhancement in the magnetic moment in graphene on ferromagnetic Co surface by hydrogenation is also anticipated to be measured by similar surface-sensitive spectroscopic techniques (XMCD and/or PES).

In conclusion we have studied in details the electronic and magnetic properties of graphene supported on Co(0001) surface. Our calculations show that there is an induced magnetic moment in the graphene sheet whose origin we attribute to the different charge transfer of the spin-up and the spin-down electrons. The graphene sheet becomes ferrimagnetic with an average magnetic moment of -0.024 μ_B , aligned antiparallel with respect to that of the Co substrate. Upon hydrogenating the graphene sheet at saturation coverage, there is a **six-fold** increase in the average magnetic moment of the graphene sheet. Considering

the feasibility, we hope our results might motivate experimental studies on the proposed system.

Chapter 4

Small Bimetallic PdGa Clusters as Catalysts for Hydrogen Dissociation

4.1 Introduction

Adsorption (uptake), dissociation (activation), diffusion and desorption (release) of hydrogen are important in several industrial processes. For example in the polymerisation industry dissociated hydrogen is necessary for the selective hydrogenation of acetylene (present as an impurity in the feed stock) to ethylene. [54, 55]. In proton conducting fuel cells, where hydrogen is used as a fuel, oxidation of hydrogen gas takes place at the anode resulting in formation of electrons and protons, the latter then diffuses to the cathode. [56, 57] For the case of hydrogen storage, the challenge is to find materials that can provide reversible storage at room temperature i.e. moderate binding energies of hydrogen. Further, if hydrogen is stored and transmitted in dissociated form, then the hydrogen dissociation barriers should be low. Hydrogen dissociation is also an important reaction step in synthesis of hydrogen peroxide (H_2O_2).

An important requirement that an efficient heterogeneous catalyst should satisfy is that the uptake, activation and release of hydrogen should happen easily. Usually transition metals like Pt, Pd, etc. are used as catalysts for the above mentioned processes. However, these properties are mutually exclusive, i.e. a low activation barrier is associated with strong binding of the adsorbates and intermediate species. As a result most of these catalysts are inefficient for many industrial processes. For eg. though Pd acts as a highly reactive catalyst for the selective hydrogenation of acetylene, it exhibits poor selectivity. [58–60] Moreover the noble metal catalysts are also expensive. Hence efforts are on to search for alternative catalysts that are cheaper and more efficient than the existing ones. Recently

Armbrüster *et al.* showed that PdGa acts as a catalyst with high selectivity for selective hydrogenation of acetylene to ethylene. [61] With a combination of experiments and density functional theory (DFT) based calculations Prinz *et al.* have elucidated the complete reaction mechanism on PdGa(111) surface. [62] Additionally there have been many DFT based studies on other PdGa surfaces. [63–66]. In contrast to Pd surfaces where hydrogen undergoes dissociative adsorption, the hydrogen dissociation and diffusion barriers are quite high on the PdGa surfaces (0.51 - 0.97 eV).

Metal clusters not only show size dependent variations in their properties but also they exhibit novel properties that are not found in their bulk or surface forms. Further, bimetallic clusters provide additional opportunity to tune their properties, and thereby their functionalities, through a variation in their composition. [67] In the context of heterogeneous catalysis most of the bimetallic clusters that have been studied have transition metal elements as both their components. [67–69] However there are few studies on the reactivity of bimetallic clusters made from a combination of *d* and *p* block elements, [70] even though there are several intermetallic compounds where one of the components is a transition metal and the other is a *p* block metal and their surfaces act as efficient catalysts. For example PdGa [61] and Al₁₃Fe₄ [71] acts as good catalysts for selective hydrogenation of acetylene to ethylene. It would be interesting to study how the catalytic properties of clusters of these materials are compared to that of the bulk.

Moreover for all practical applications, the clusters are dispersed on a support. Usually metal oxides materials (eg. Al₂O₃, TiO₂, SiO₂, MgO etc) or carbides (TiC, Mo₂C etc.) are used as prime supports. The interaction between the metallic clusters with the support perturbs the electronic properties of the clusters which in turn affect their reactivity.

In this work we have studied in details the thermodynamic stability, and structural, electronic and magnetic properties of small bimetallic PdGa clusters (from dimers to tetramers) in gas phase as a function of their size and chemical composition. Further to explore the possibility of using them as catalysts we studied adsorption of molecular hydrogen on all the clusters and dissociation of molecular hydrogen on the tetramers. In order to understand how the reactivity of the clusters change in the presence of an oxide support we have studied H₂ dissociation on the tetramers supported on a commonly used oxide, namely MgO.

The rest of the chapter is divided as follows. In Section 4.2 we provide the computational details. The geometry and electronic properties of the bare clusters in gas phase and on MgO support are described in Section 4.3.1 and 4.3.2. This is followed by the results of H₂ adsorption on these clusters in Section 4.3.3.1 and 4.3.3.2 followed by the reaction mechanism of hydrogen dissociation described in Section 4.3.4. Finally we conclude in Section 4.4.

4.2 Computational details

We have performed spin polarized DFT based calculations using the Quantum Espresso software. [41] Electron-ion interactions are described using ultrasoft pseudo potentials. [42] The electron-electron exchange-correlation potential is approximated with the Perdew, Burke, and Ernzerhof (PBE) parametrization of the generalized gradient approximation (GGA). [9] In order to check the robustness of our results on the choice of exchange correlation functional, we have computed the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the dimers in gas phase (at PBE geometry) using the Perdew-Zunger parametrization of the LSDA exchange correlation functional [72] and the rev-PBE functional [73]. The results are presented in Figure-B2 of Appendix B. We find that the HOMO and LUMO are qualitatively similar to that obtained using the PBE functional, suggesting that our results are qualitatively independent of the choice of functionals.

We have used kinetic energy cut offs of 35 Ry and 400 Ry for wavefunctions and charge density respectively. To speed up convergence we have used Marzari-Vanderbilt [20] and Gaussian smearing [18] with a width of 0.002 Ry. For each case we have ensured that the contribution to the total energy from smearing is zero, thereby guaranteeing that the total energies are independent of the choice of the smearing scheme. The clusters are placed in an orthogonal unit cell. To minimise spurious interactions between the periodic images we have ensured that there is a vacuum of at least 10 Å between them along each direction of the box. Brillouin zone integrations have been done using the gamma point. Structural stability of the gas phase clusters was verified by determining the vibrational frequencies of the system using density functional perturbation theory (DFPT); the absence of imaginary frequencies in the vibrational spectrum confirms that the geometries determined by

us correspond to true minima in the potential energy landscape. [25]

For the latter case (tetramers on MgO support), we have used an asymmetric slab of four layers of MgO where the bottom two layers are kept fixed at bulk MgO interplanar distances while the upper two layers have been relaxed. The tetramers are placed on the top layer of the MgO(100) surface where the periodic images are separated by a vacuum of at least 12 Å along the z-direction. We have obtained a bulk lattice parameter of 4.25 Å for MgO which has an excellent matching with the experimental value of 4.21 Å. [74]

The stability of the pure bare clusters in gas phase is determined by calculating their binding energy (E_b) that is given by:

$$E_b = (E_{M_N} - NE_M)/N, \quad (4.1)$$

where E_{M_N} is the total energy of the Pd/Ga cluster of size N , and E_M represents the total energy of single Pd/Ga atom in gas phase. Further, we have also calculated the zero point energy (ZPE) corrected formation energies (ΔH) of these clusters with respect to bulk Pd and Ga. This is given by:

$$\Delta H = ((E_{M_N} + E_{ZPE}) - NE_M^{bulk})/N, \quad (4.2)$$

where E_M^{bulk} is the total energy of a single Pd/Ga atom in bulk and $E_{ZPE} = \frac{1}{2} \sum_{i=1,3N} \hbar\omega_i$ (ω_i is the vibrational frequency of the i^{th} mode of the cluster in the gas phase). Since the ZPE corrections for solid is usually very small (typically less than a few meV), we have neglected them in our calculations.

Moreover, for a cluster of size N , it is important to know whether the mixed clusters are stable with respect to the pure Pd and Ga clusters. This stability of the mixed clusters with respect to the pure Pd and Ga ones is given by the mixing energy (E_{mix}):

$$E_{mix} = E_b^{cl} - \frac{x}{N}(E_{Pd_N}) - \frac{y}{N}(E_{Ga_N}). \quad (4.3)$$

Here, E_{Pd_N} and E_{Ga_N} are the cohesive energies of the pure Pd_N and Ga_N clusters as defined in Eqn. 4.1. $E_b^{cl} = E_{Pd_xGa_y} - xE_{Pd} - yE_{Ga}$, where $x + y = N$ and $E_{Pd/Ga}$ is the total energy of a single Pd/Ga atom in gas phase.

The strength of the interaction of tetramers (E_{2b}) when placed on MgO surface is calculated by the 4.4. Here, E_{M_N+MgO} is the total energy of the MgO supported tetramers. E_{MgO} is the energy of the clean MgO surface and E_{M_N} is the energy of a given tetramer in the gas phase.

$$E_{2b} = E_{M_N+MgO} - E_{MgO} - E_{M_N}, \quad (4.4)$$

In order to study the reactivity of these clusters we have looked into adsorption of hydrogen molecule and co-adsorption of hydrogen atoms (dissociated hydrogen). The adsorption/co-adsorption energy is given by:

$$E_{ads} = E_{Total}^{Pd_xGa_y+nX} - E_{Total}^{Pd_xGa_y} - E_{Total}^{H_2} \quad (4.5)$$

where $E_{Total}^{Pd_xGa_y+nX}$, $E_{Total}^{Pd_xGa_y}$ and $E_{Total}^{H_2}$ are the total energies of the cluster with n adsorbates, bare cluster (gas phase or MgO supported) and H_2 molecule (gas phase) respectively. X can be a H atom or a hydrogen molecule. If X is a hydrogen molecule then $n = 1$, else $n = 2$.

In order to determine the minimum energy pathway and barriers for hydrogen dissociation, we used have used climbing image (CI) Nudged Elastic Band (NEB) method [75]. The number of images used for each path depends on the length of the path. The shortest path had five images whereas the longest one had ten. The transition state was verified by calculating the phonon frequencies using DFPT; presence of a single unstable mode with imaginary frequency confirms that the geometry of the transition state indeed corresponds to a saddle point in the potential energy surface. [25]

4.3 Results and Discussion

4.3.1 Bare clusters in gas phase

4.3.1.1 Structure and stability

Dimers: Our calculations for the pure Pd dimer show that its ground state is a spin triplet one with a binding energy of -0.68 eV/Pd atom and a Pd-Pd bond length of 2.40 Å (Figure-4.1(a)). The binding energies reported from experimental measurements vary over a wide range, from 0.37 to 0.57 eV. [76, 77] We find that our computed values are slightly higher

than the experimental ones. However, this is consistent with other reports in literature where they have used GGA exchange correlation functional. [78] We note that with the revised-PBE (rPBE) functional, Ni *et al.* find the binding energy to be 0.36 eV/Pd and Pd-Pd bond length 2.61 Å. [79] This is in accordance with the typical trends exhibited by rPBE and PBE, i.e. compared to PBE, rPBE tends to underestimate binding energies and overestimate bond lengths. Like the Pd dimer, Ga₂ also prefers a spin triplet configuration in its ground state with Ga-Ga bond length of 2.44 Å (Figure-4.1(c)) and a binding energy of -0.74 eV/Ga atom. These are in excellent agreement with those obtained by Song *et al.* [80] using DFT and experimental values of dissociation energy reported in Ref. [81] and [82]. We find the formation of the dimers from their bulk phases are endothermic with ΔH of 3.03 and 1.88 eV/atom for Pd₂ and Ga₂ respectively.

For the bimetallic dimer there is only one possibility, namely PdGa (50 % Ga). The E_{mix} (-1.47 eV, Figure-4.2) of PdGa indicates that this cluster is thermodynamically more stable than the pure ones. The Pd-Ga bond length is 2.29 Å (Figure-4.1(b)). This is significantly smaller than the Pd-Pd and the Ga-Ga bond lengths in the pure clusters suggesting that the Pd-Ga bond is stronger than the Pd-Pd and Ga-Ga bonds. The reason for the relatively larger chemical stability of the Pd-Ga bond compared to those of the Pd-Pd and Ga-Ga bonds can be traced to the electronegativity differences between Pd and Ga. Since Pd is more electronegative compared to Ga, we find that upon Pd-Ga bond formation the Pd atom is negatively charged while the Ga atom is positively charged. Lowdin analysis of the charges on Pd and Ga atoms shows that Pd gains about 0.14 electrons upon forming the bimetallic cluster. Hence the covalent Pd-Ga bond has a partial ionic character that provides a relatively larger chemical stability compared to that of the Pd-Pd and Ga-Ga in Pd₂ and Ga₂. The Pd-Ga bond length in the bimetallic dimer is also shorter than the shortest Pd-Ga bond length (2.54 Å) observed in bulk PdGa. [83] The reason for this can be attributed to the reduced coordination number of the Pd and Ga atoms in the dimer (1) compared to that in the bulk (7). The bimetallic dimer has a magnetic moment of 1.0 μ_B .

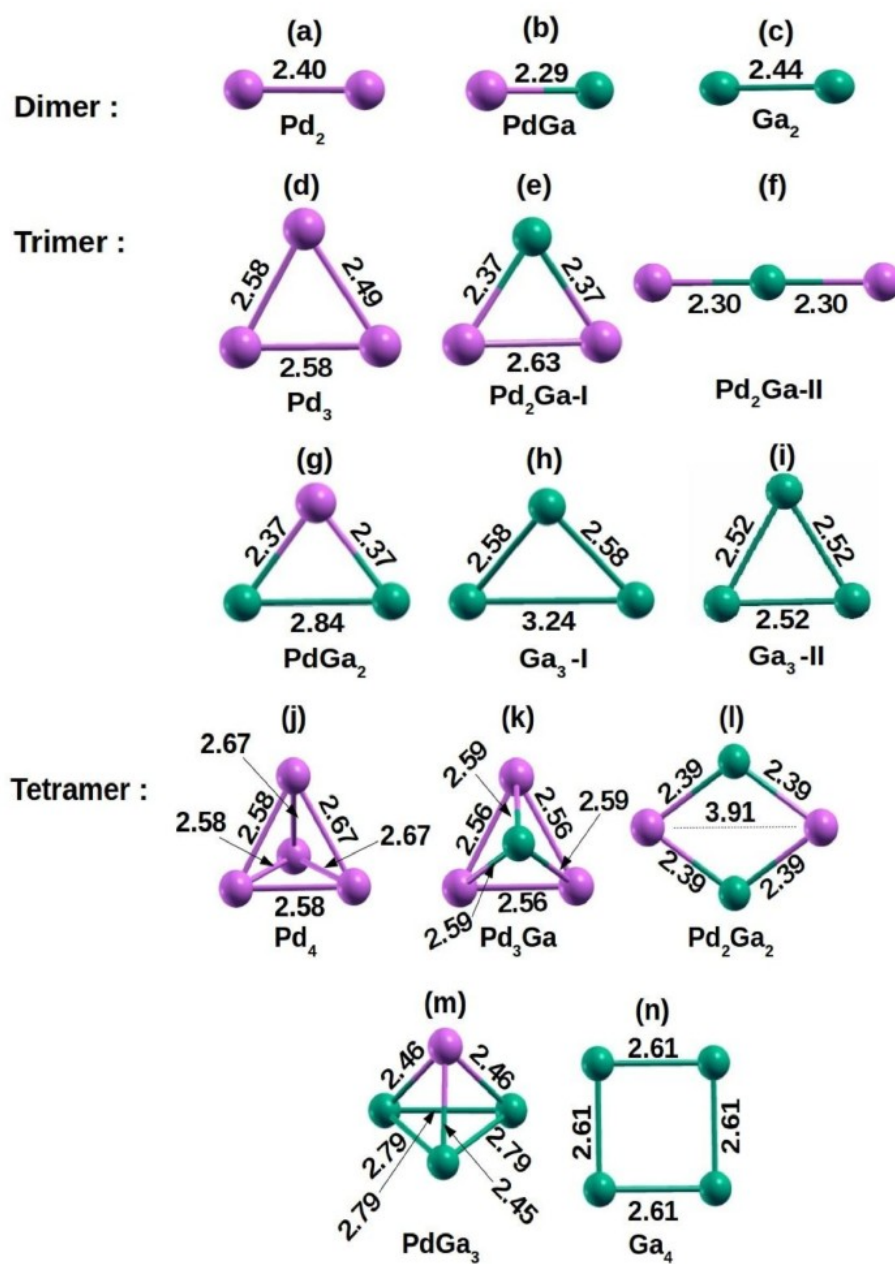


Figure 4.1: Lowest energy structures of gas phase Pd_xGa_y clusters. The green and magenta spheres denote Ga and Pd atoms respectively. The bond lengths are given in Å.

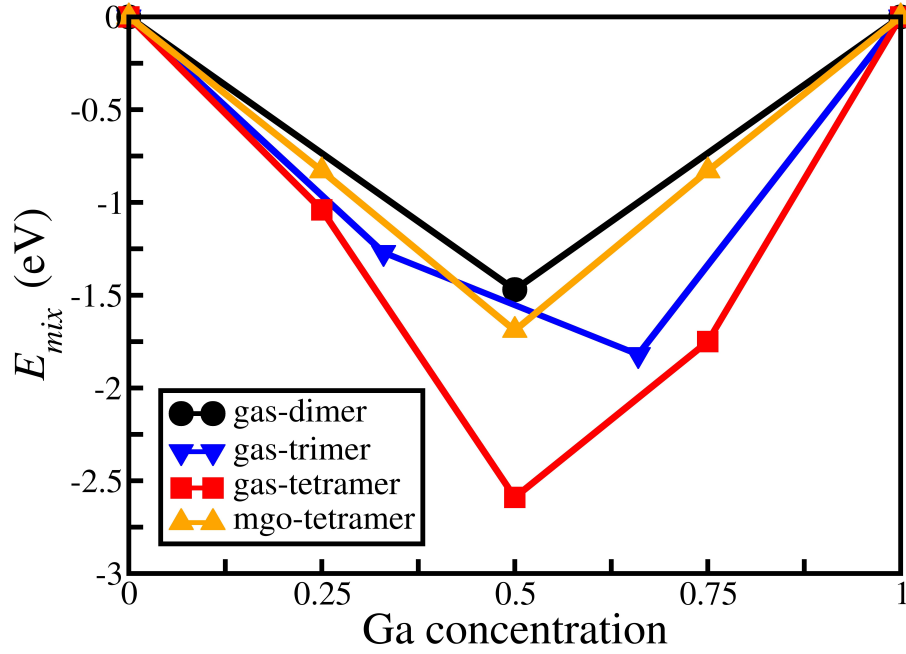


Figure 4.2: Stability of the mixed clusters with respect to the pure Pd and Ga cluster in gas phase and on MgO support. By definition (Eqn. 4.1) E_{mix} is zero for the pure Pd and Ga clusters.

Trimers: In order to determine the lowest energy structures of the trimers (both mixed and pure ones) we have considered linear and triangular geometries for each case. The lowest energy configurations are shown in Figure-4.1(d)-(i) and the other higher energy configurations are shown in Figure-B1 of the Appendix B. We find that usually the triangular configurations are more stable than the linear ones because in the former the coordination number of each atom is maximized, thereby enhancing their stability.

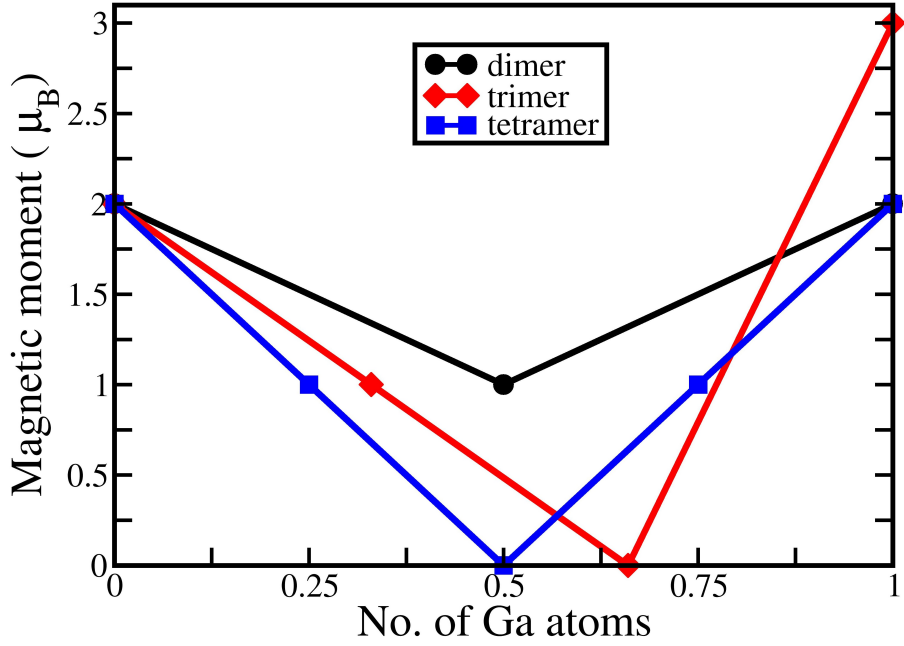


Figure 4.3: Magnetic moments of the clusters as a function of Ga concentration and cluster size in the gas phase.

There is a controversy in literature regarding the magnetic configuration of the Pd trimer in its ground state. According to the reports in literature, it is sensitive to the choice of exchange correlation functional. While calculations of Ni *et al.* [79] and Luo *et al.* [78] using rPBE and PW91-GGA respectively predicted the ground state to be singlet, Rogan *et al.* found the cluster to be in the triplet state from their DFT calculations using BLYP and PZ-LDA exchange-correlation functionals. [84] All these calculations show that the trimer forms an isosceles triangle because of Jahn-Teller distortion.

From our calculations we find that the most stable structure of Pd_3 is an isosceles triangle with two Pd-Pd bonds of lengths of 2.58 Å each and a third one 2.49 Å long (Figure-4.1(d)). It has a binding energy of -1.39 eV/Pd atom and total magnetization of $2.0 \mu_B$. In an effort to resolve the above mentioned controversy we relaxed the cluster in its equilateral geometry by constraining the cluster to be in the singlet and the triplet states. We find that when the cluster is constrained to be in its singlet state, after relaxation, it retains the equilateral geometry and has a binding energy of -1.26 eV/Pd atom and Pd-Pd bond length of 2.50 Å (Figure-B1(a) of Appendix B). However, when the cluster is constrained to be in its triplet state, we find that after geometry optimization, the cluster relaxes to the same geometry as that of the isosceles triangle mentioned earlier in the paragraph. These

results suggest that the Jahn-Teller distortion in the pure Pd trimer breaks the symmetry thereby driving the trimer to a spin triplet configuration. To the best of our knowledge there are no experimental reports available on Pd trimers.

Unlike Pd trimers, for the case of Ga, we find a degenerate ground state. There are two isomers with same lowest energy: one in which the trimer forms an equilateral triangle (spin doublet) and the other in which it forms an isosceles triangle (spin quartet). Both the configurations have a binding energy of -1.16 eV/Ga atom. In the equilateral triangle, the Ga-Ga bond lengths are 2.52 Å each (Figure-4.1(i)), while in case of isosceles triangle there are two short bonds, each having a bond length of 2.58 Å and a longer one with a bond length of 3.24 Å (Figure-4.1(h)). Similar to the dimers the formation of trimers are also endothermic with respect to the bulk phase with formation energies of 2.32 and 1.46 eV/atom for Pd and Ga respectively.

For the bimetallic trimers there are two possible compositions, namely Pd₂Ga (33 % Ga) and PdGa₂ (67 % Ga). Our calculations predict that both Pd₂Ga and PdGa₂ are stable compared to Pd₃ and Ga₃ with E_{mix} of -1.27 and -1.82 eV respectively (Figure-4.2). Both the clusters prefer to form an isosceles triangle (Figure-4.1(e) and (g)). For Pd₂Ga (PdGa₂) the Pd-Pd (Ga-Ga) bond length is 2.63 Å (2.84 Å) and the Pd-Ga bond lengths are 2.37 Å each. The Pd-Ga-Pd (Ga-Pd-Ga) bond angle is 67.40° (73.36°) for Pd₂Ga (PdGa₂). While Pd₂Ga is in a doublet spin state, PdGa₂ is non-magnetic. Further for Pd₂Ga we find another isomer which is only 0.03 eV higher in energy than the most stable one. The cluster is in a linear configuration with the Ga atom in the centre and two Pd atoms on either side. Each of the Pd-Ga bond lengths are 2.30 Å (Figure-4.1(f)). This also has a magnetic moment of 1.0 μ_B . To investigate the ease with which the cluster can transform from an isosceles triangle to a linear one, we scanned the potential energy surface of the cluster as a function of the Pd-Ga-Pd bond angle. We find the barrier associated with this process to be about 0.64 eV (Figure-B3 of Appendix B). In contrast, a similar configuration for the PdGa₂ in which the Pd atom is in the centre between two Ga atoms is 0.78 eV higher in energy than the lowest energy one. For this case each of the Pd-Ga bond lengths are of 2.39 Å and the cluster is non magnetic. Similar to the dimers, we find that the Pd-Ga bond lengths are much shortened compared to those of Pd-Pd and Ga-Ga bonds.

Tetramers: For Pd_4 we find the lowest energy structure to be a distorted tetrahedra (Figure-4.1(j)) with a magnetic moment of $2.0 \mu_B$ and binding energy of -1.77 eV/Pd atom . There are two types of Pd-Pd bonds, three long ones with a bond length of $2.67 \text{ \AA}$ and three shorter ones with a bond length of $2.58 \text{ \AA}$ (Figure-4.1(j)). The square planar structure with Pd-Pd bond lengths of $2.52 \text{ \AA}$ is the second lowest in energy (Figure-B1(g) in Appendix B). This is about 0.92 eV higher in energy than the distorted tetrahedron. In this case the Pd-Pd bond lengths are $2.52 \text{ \AA}$ and the cluster has a magnetic moment of $2.0 \mu_B$. This is in reasonably good agreement with that calculated by Luo *et al.* [78]. The formation energy of Pd tetramer with respect to bulk Pd is about 1.94 eV/atom .

Unlike the Pd cluster, Ga tetramer prefers a square planar geometry and has a binding energy of -1.45 eV/Ga atom . Each of the four Ga-Ga bond length are $2.61 \text{ \AA}$ long (Figure-4.1(n)). The cluster has a magnetic moment of $2.0 \mu_B$. This is in very good agreement with that obtained by Song *et al.* [80] The three dimensional tetrahedral geometry is about 0.55 eV higher in energy than the square one. For this the Ga-Ga bond lengths vary between $2.54\text{-}3.37 \text{ \AA}$ (Figure-B1(m) of Appendix B). The formation energy of Ga tetramer with respect to bulk Ga is about 1.18 eV/atom .

There are three possible compositions for the bimetallic clusters: Pd_3Ga (25 % Ga), Pd_2Ga_2 (50 % Ga) and PdGa_3 (75 % Ga). Additionally, for each cluster type, there are several possible geometries. We have considered both the three-dimensional (tetrahedral) and planar (square, rectangle and rhombic) geometries. Our calculations show that their relative stability, geometry and spin states of the ground state configurations depends on the Ga/Pd concentration in the clusters. From the mixing energies we find that the most stable one among the bimetallic tetramers is Pd_2Ga_2 with a $E_{mix} = -2.59 \text{ eV}$ (Figure-4.2). This cluster has equal number of Pd and Ga atoms. The cluster is non-magnetic with a two-dimensional rhombus geometry (each Pd-Ga bond length is $2.39 \text{ \AA}$ (Figure-4.1 (l)). The Pd-Ga-Pd and Ga-Pd-Ga bond angles are 109.99° and 69.99° respectively. Additionally, we find another structure in which the two planes formed by two Pd and a Ga atoms are at an angle of 103.41° (Figure-B1(i) of Appendix B). This configuration is about 0.72 eV higher in energy than the flat one. We have also found a tetrahedral configuration for this case in which is about 2.12 eV higher in energy than the most stable rhombus one (Figure-B1(k) of Appendix B).

The Pd rich (Pd_3Ga) and Ga rich (PdGa_3) clusters prefers to be in three dimensional tetrahedral configuration (Figure-4.1(k) and (m) respectively). The Pd-Ga bond lengths in Pd_3Ga (PdGa_3) are 2.59 Å (2.46 Å) and the Pd-Pd (Ga-Ga) bond lengths are 2.56 Å (2.79 Å). Both the clusters have a magnetic moment of $1.0 \mu_B$.

Trends in magnetic moment: We looked into the trends in magnetic moment as a function of cluster size and Ga concentration. The results are shown in Figure-4.3. At 0% and 100% Ga concentrations (i.e. for the pure clusters) we do not observe any specific trends for the magnetic moments as a function of the cluster size. For a given cluster size, we find that the magnetic moment of the mixed clusters are always lower than the pure ones.

4.3.1.2 Electronic structure and magnetic properties

To understand the nature of bonding in the bimetallic clusters and how they differ from the pure ones, we have calculated the density of states (DOS), the contribution to the DOS from the different atomic orbitals (PDOS) and the wave functions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The results for the dimers, trimers and tetramers are shown in Figure-4.4, Figure-4.5 and Figure-4.6 respectively.

For the pure Pd clusters, we find that the HOMO and the LUMO comes from the same spin channel and have contributions primarily from the Pd-*d* states (Figure-4.4(d) and (g), Figure-4.5(e) and (i) and Figure-4.6(f) and (k)). The position of the HOMO, the negative of which gives an estimate of the ionization potential (IP) of the cluster, moves up in energy with increase in cluster size. For Pd_2 , Pd_3 and Pd_4 the HOMOs are positioned at -4.8 eV, -4.47 eV and -3.94 eV (Figure-4.4(a), Figure-4.5(a) and Figure-4.6(a)) respectively implying that the IP reduces as one goes from dimer to tetramer.

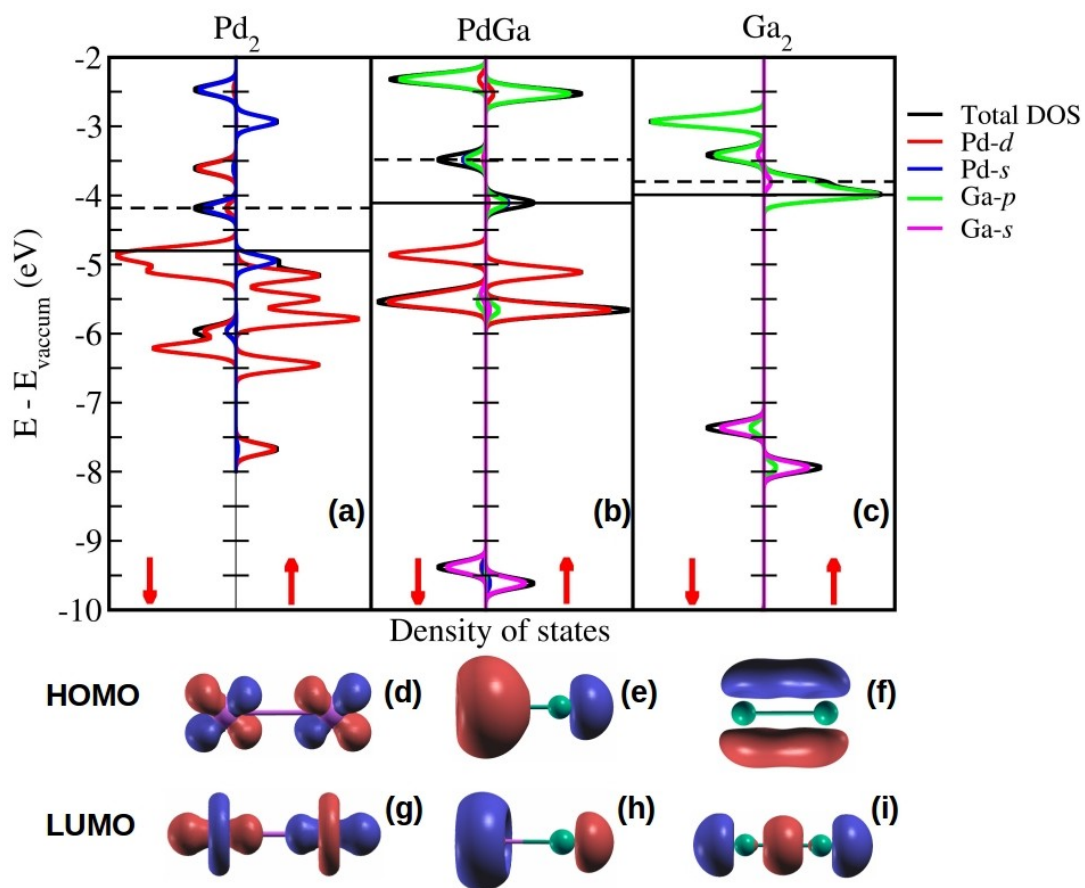


Figure 4.4: Total density of states (DOS) and the DOS projected on atomic orbitals of Pd_2 (a), PdGa (b) and Ga_2 (c) in gas phase. The highest occupied molecular orbitals (HOMO) ((d)-(f)) and the lowest unoccupied molecular orbitals (LUMO) ((g)-(i)) are also shown. The blue and red isosurfaces denote the negative and positive part of the wavefunctions.

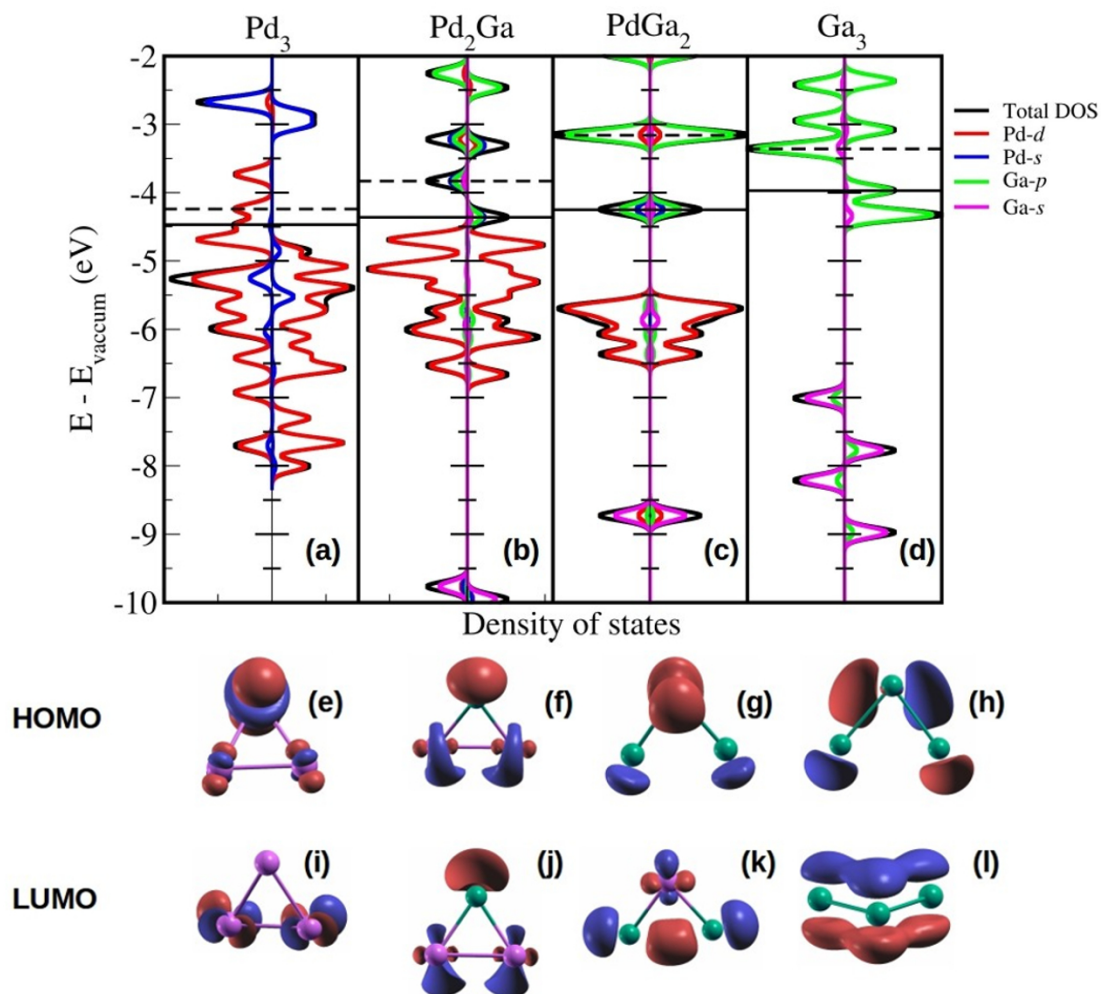


Figure 4.5: Total density of states (DOS) and the DOS projected on atomic orbitals of Pd₃ (a), Pd₂Ga (b), PdGa₂ (c) and Ga₃ (d) in gas phase. The highest occupied molecular orbitals (HOMO) ((e)-(h)) and the lowest unoccupied molecular orbitals (LUMO) ((i)-(l)) are also shown. The blue and red isosurfaces denote the negative and positive part of the wavefunctions.

Similar to the Pd clusters, the HOMO and the LUMO of the pure Ga dimer and tetramer are from the same spin channel (Figure-4.4(c) and Figure- 4.6(e) respectively). However, for Ga₃ the HOMO comes from spin up channel while the LUMO comes from the spin down one (Figure-4.5(d)). Unlike the Pd clusters, we do not observe any trend in the position of HOMO as a function of cluster size. For Ga dimer, trimer and tetramer the positions of HOMO are -3.99 eV (Figure-4.4(c)), -3.97 eV (Figure-4.5(d)) and -4.14 eV (Figure-4.6(e)) respectively. In Ga₂ the HOMO is purely from the Ga-*p* state forming a π -bonding orbital (Figure-4.4(f)), while the LUMO is formed from *sp*-hybridization of the Ga-*s* and *p* forming a σ -bonding orbital (Figure-4.4(i)). Both the HOMO and LUMO

of Ga_3 is from the hybridization of the s and p states (Figure-4.5(h) and (l)). Ga_4 , with a flat two-dimensional structure, have the HOMO formed from the p -states and forms a π -bonding orbital (Figure-4.6(j)). For this cluster the LUMO originates from mixing of s and p states (Figure-4.6(o)).

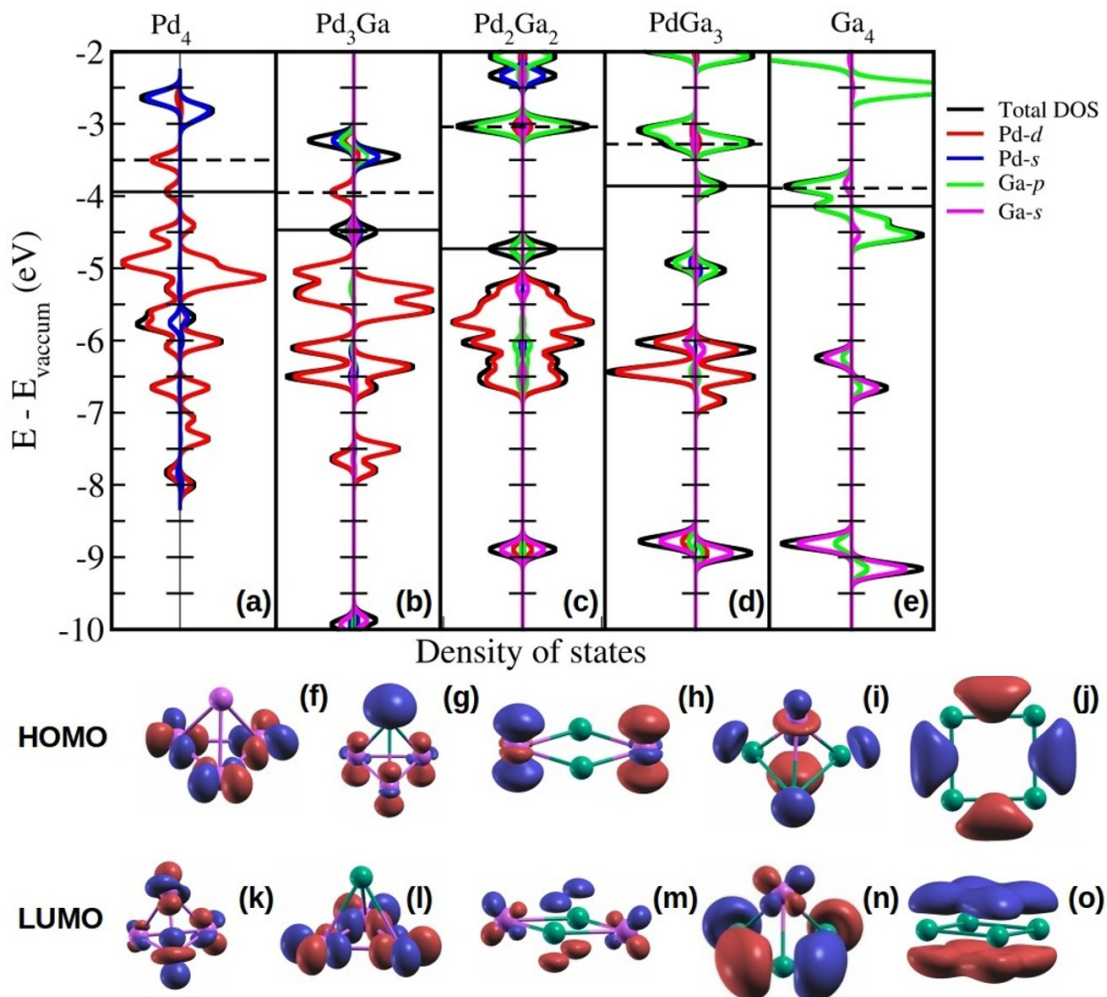


Figure 4.6: Total density of states (DOS) and the DOS projected on atomic orbitals of Pd_4 (a), Pd_3Ga (b), Pd_2Ga_2 (c), PdGa_3 (d) and Ga_4 (e) in gas phase. The highest occupied molecular orbitals (HOMO) ((f)-(j)) and the lowest unoccupied molecular orbitals (LUMO) ((k)-(o)) are also shown.

For bimetallic PdGa, both the HOMO and the LUMO are due to the hybridization between the Ga-*p* and the Pd-*s* resulting in a σ anti bonding orbital (Figure-4.4(e) and (h) respectively. This is in contrast with what has been observed for the pure dimers. The HOMO positioned in between that of the HOMOs of Pd₂ and Ga₂ at -4.11 eV is from spin up channel while the LUMO is from the spin down channel (Figure-4.4(b)). The HOMOs of bimetallic trimers Pd₂Ga and PdGa₂ the HOMOs are at -4.36 and -4.25 eV respectively as shown in Figure-4.5(b) and (c). Similar to the bimetallic dimer, for the bimetallic trimers the IP is in between that of the pure Pd and Ga trimers. In both the clusters, the HOMO and the LUMO is primarily due to the hybridization between Pd-*s* and Ga-*p* and *s* states (Figure-4.5(f) and (j) for Pd₂Ga and Figure-4.5(g) and (k) for PdGa₂). There is a slight contribution from Pd-*d* states also.

Unlike bimetallic PdGa and Pd₂Ga, for all the bimetallic tetramers, the HOMOs and the LUMOs come from the same spin channel. Except for PdGa₃ where the HOMO is above that of the pure clusters, for all others, it is positioned below that of the pure ones. This is in contrast with what we have observed for the dimers and trimers. The IP is largest for the most stable, non-magnetic Pd₂Ga₂ with the HOMO at -4.73 eV (Figure-4.6(c)). For Pd₃Ga and PdGa₃ the position of the HOMOs are at -4.47 eV (Figure-4.6(b)) and -3.86 eV (Figure-4.6(d)) respectively. While the HOMO of Pd₃Ga is due to the hybridization between Pd-*s* (minor contribution from Pd-*d*) and Ga-*p* and *s* states (Figure-4.6(g)), the LUMO is from the Pd-*d* states (Figure-4.6(l)). For Pd₂Ga₂ we find that in the HOMO there are contributions from Pd-*d* and *s* and from Ga-*p* (Figure-4.6(h)). In the LUMO, in addition to the above mentioned states, *s* states are also involved (Figure-4.6(m)). For PdGa₃, both the HOMO and LUMO have contributions primarily from Pd-*s* and Ga-*s* and *p* states (Figure- 4.6(i) and (n)). For the HOMO we find some contributions from Pd-*d* states also.

4.3.2 Tetramers on MgO surface

4.3.2.1 Structures and stability

Figure-4.7 shows the relaxed geometries of Pd_xGa_y clusters supported on MgO. These clusters bind to the surface primarily through Pd-O and Ga-O bonds. Pd₄ cluster has a three-dimensional tetrahedral structure having a binding energy of -2.07 eV and triplet spin state. The two Pd atoms lying on the Mg-O bridges have an elongated Pd-Pd bond

distance of 2.88 Å which is 0.21 Å longer than the longest Pd-Pd bond in the gas phase Pd₄. Rest of the Pd-Pd bond distances lie in between 2.60-2.63 Å and is similar to what is observed in the gas phase Pd₄. The third Pd atom interacting with the MgO surface sits directly on top of the surface O atom. The Pd-Mg bond length of 2.70 Å matches with the earlier reports of experimentally synthesized PdMg alloys (Mg_{0.9}Pd_{1.1}/MgPdC_xH_y) where Pd-Mg bond distance is 2.75 Å [85]. We note that our results are in excellent agreement with what has been reported earlier in literature. [86–88]

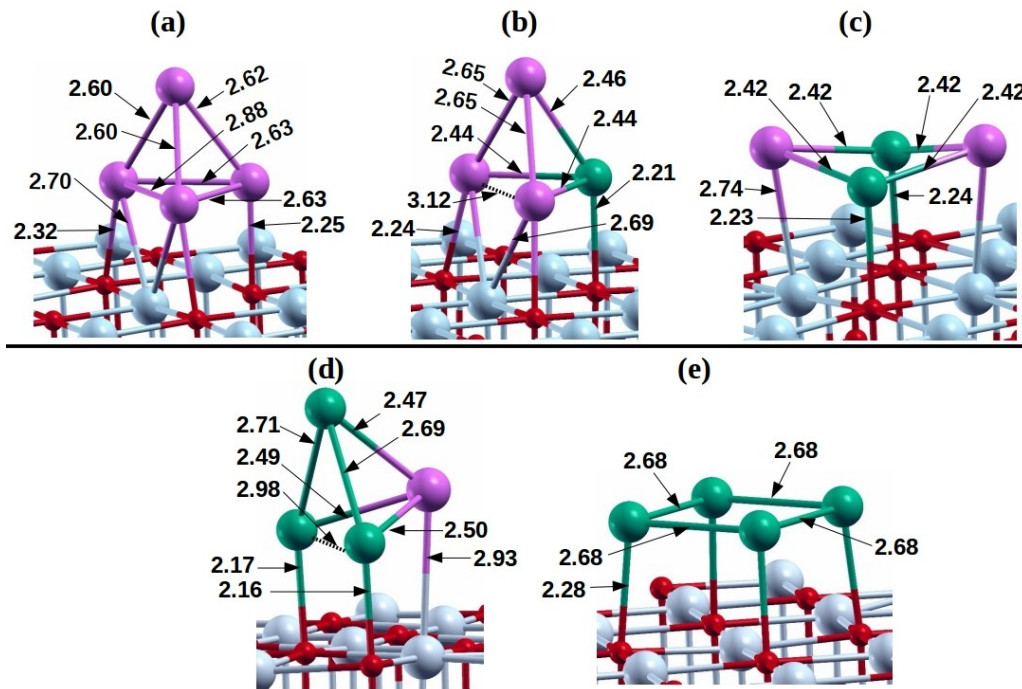


Figure 4.7: Lowest energy structures of MgO supported Pd_xGa_y clusters. The green and magenta spheres denote the Ga and Pd atoms respectively. The surface atoms Mg and O are represented by grey and red spheres respectively.

Pd₃Ga cluster has a distorted tetrahedral geometry having a binding energy of -1.87 eV. It is stabilized on the surface through two Pd-O and a Ga-O bond. The cluster has Pd-Mg and Pd-O bond lengths of 2.69 Å and 2.24 Å respectively. The Ga atom lying directly on O atom has a Ga-O bond length of 2.21 Å which is much longer than the Ga-O bond length ($d = 1.83\text{--}2.00$ Å) found in β -Ga₂O₃. Here, the Pd atoms attached to the surface have a much longer Pd-Pd bond length of 3.12 Å while the other two Pd atoms have a bond length of 2.65 Å. The cluster stays in doublet spin state similar to the gas phase Pd₃Ga.

The stoichiometric Pd_2Ga_2 cluster when put on MgO has a slight buckling of the planar geometry compared to that of a perfect rhombic geometry in the gas phase. The Pd-Ga (Ga-Ga) bond length is 2.42 Å (2.80 Å) which is 0.03 Å (0.06 Å) longer than that in the gas phase. It is bound on MgO surface by Pd-Mg ($d_{\text{Pd-Mg}} = 2.74$ Å) and Ga-O bonds ($d_{\text{Ga-O}} = 2.24$ Å). This bimetallic cluster has a binding energy of -1.18 eV and a singlet spin state.

Ga-rich mixed cluster PdGa_3 has a tilted tetrahedral geometry and binding energy of -1.18 eV. It forms strong Ga-O bonds with the surface O atoms having bond lengths of 2.16 Å and 2.17 Å. The Pd atom makes bond with Mg atom having a Pd-Mg bond distance of 2.93 Å. The Ga-Ga bond length between the two Ga atoms interacting with the surface is elongated to 2.98 Å. This is 6.81% longer compared to that observed in the gas phase. The PdGa_3 cluster remains in doublet spin state.

The Ga tetramer attains a perfect square planar geometry on surface having Ga-Ga bond distance of 2.68 Å (0.07 Å longer than the Ga-Ga bond in gas phase Ga_4 and Ga-O bonds lie between 2.28 Å and 2.29 Å. This cluster has a singlet spin state while in gas phase Ga_4 has a triplet spin state.

In summary, we find that there is an overall increase in Pd-Pd/Ga-Ga bond lengths between the Pd/Ga atoms of the clusters that are interacting with the surface. In order to understand this and to elucidate the interactions between the clusters and the substrate, we have plotted the charge transfer between them.

The charge transfer is calculated as $\Delta\rho(r) = \rho_{\text{cluster+MgO}} - \rho_{\text{cluster}} - \rho_{\text{MgO}}$ where ' ρ ' is the charge density and is shown in the Figure-4.8. We find that there is a redistribution of electron density upon interacting with the MgO surface which is a result of donation and back donation of charges between the clusters and MgO. The Pd/Ga atoms of the clusters primarily interact with the electrons rich O^{2-} ions of the surface.

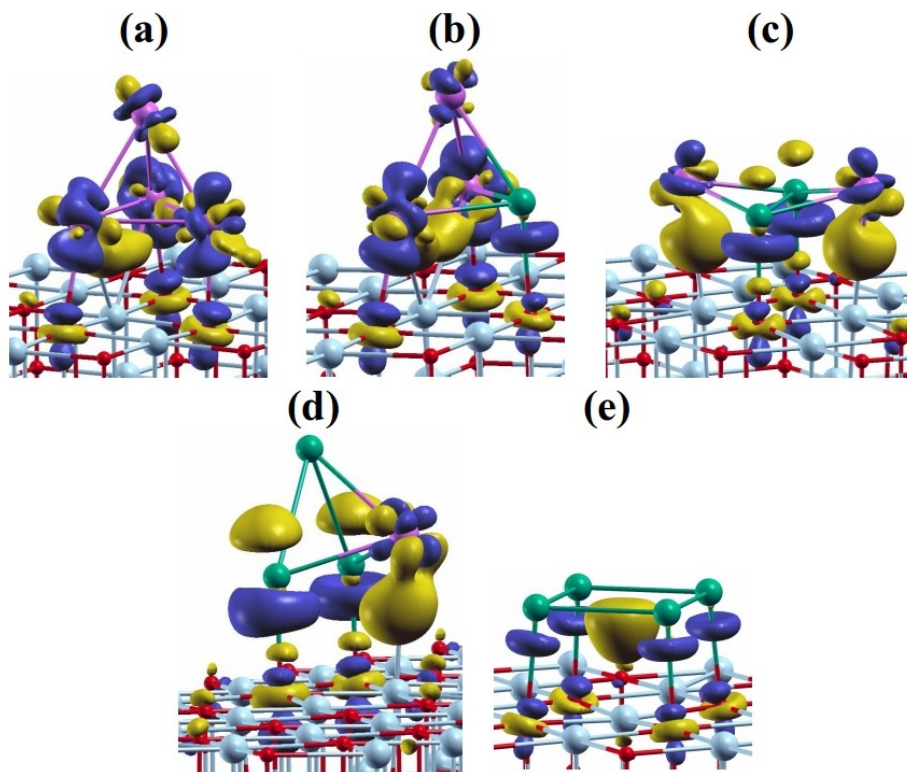


Figure 4.8: Charge transfer plots for the Pd_xGa_y tetramers supported on MgO surface. The blue and yellow isosurfaces represent the charge depletion and charge accumulation respectively.

From the Lowdin charge analysis, it is found that all the tetramers show a net loss of electrons and become positively charged. The Pd and Ga tetramers have net loss of 1.19 e and 2.10 e respectively. The most stable bimetallic cluster Pd_2Ga_2 has a charge loss of 1.59 e which is highest among all the bimetallic clusters. It can again be explained in terms of its planar geometry as well as the Ga-O (Pd-O) bonds present. The other two bimetallic clusters Pd_3Ga and PdGa_3 cluster have net loss of 1.34 e and 1.37 e respectively. The trends in the charge transfer can be explained in terms of the structure of the clusters on MgO (2D or 3D) and the number of low electronegative Ga atoms interacting with the surface. Among the clusters considered in this study, Pd_4 , Pd_3Ga and PdGa_3 have a 3D tetrahedral structure on MgO. Also the number of Ga atoms interacting with MgO increases from Pd_4 to PdGa_3 resulting in increase in the net positive charge on the cluster. Between Pd_2Ga_2 and PdGa_3 , where for both the clusters, there are two Ga atoms interacting with MgO, Pd_2Ga_2 loses more electrons because of the planar 2D structure that enables wetting of the surface by the cluster resulting in enhanced charge transfer to MgO.

To separate out the effects of change in geometry and that of the charge transfer between MgO and the cluster, we have performed the energy decomposition analysis (EDA) that provides a quantitative understanding of the above effects. The total binding energy of the cluster can be divided into the following three components:

$$E_{sur}^{def} = E'_{MgO} - E_{MgO}, \quad (4.6)$$

$$E_{cl}^{def} = E'_{PdGa} - E_{PdGa}, \quad (4.7)$$

$$E_{int} = E_{PdGa+MgO} - E'_{MgO} - E'_{PdGa}, \quad (4.8)$$

where, Eqn-4.6 denotes the energy cost of deformation of MgO substrate in order to adsorb PdGa cluster (E_{sur}^{def}), Eqn-4.7 denotes the energy cost of deformation of the PdGa cluster in order to bind to MgO surface (E_{cl}^{def}) and Eqn-4.8 is the energy gained due the interaction between cluster and MgO substrate (E_{int}). E represents the total energies of the relaxed systems while E' represents the respective total energies of PdGa cluster and MgO surface in the same geometry when PdGa cluster binds on the MgO surface. The respective energies for each of the tetramers are summarized in table-4.1.

Table 4.1: Energy decomposition analysis of Pd_xGa_y/MgO clusters.

Cluster	E_{sur}^{def} (eV)	E_{cl}^{def} (eV)	E_{int} (eV)	E_{2b} (eV)
Pd ₄	+0.20	+0.05	-2.32	-2.07
Pd ₃ Ga	+0.26	+0.23	-2.36	-1.87
Pd ₂ Ga ₂	+0.37	+0.15	-1.70	-1.18
PdGa ₃	+0.33	+0.05	-1.56	-1.18
Ga ₄	+0.29	+0.02 (+0.32)	-2.42 (-2.74)	-2.10

We find that the energy gained by the clusters due to charge transfer is significantly large than the energy cost for the deformation that the clusters undergo to accommodate the excess positive charge on them due to transfer of electrons to the MgO surface. For the Pd tetramer and PdGa₃, E_{cl}^{def} is about 0.05 eV, while for Pd₃Ga and Pd₂Ga₂ they are slightly larger, about 0.23 and 0.15 eV respectively. For Ga₄, the deformation energy cost is about 0.02 eV. Moreover, the cluster on the surface is non magnetic while in gas phase it is magnetic. This transition from non-magnetic to magnetic configuration amounts to an additional energy cost of 0.32 eV, resulting in a total energy cost of 0.34 eV.

4.3.3 H₂ adsorption on pure and bimetallic clusters

4.3.3.1 Gas phase clusters

Molecular hydrogen (H₂) : As a first step to study the reactivity of these bimetallic clusters and to compare the same with that of the pure ones, we have studied adsorption of molecular hydrogen on all the clusters described in Section 4.3.1. We have considered several possible adsorption geometries, details of which are given in the subsections below. This gives us enough confidence that the adsorption geometries obtained from our calculations corresponds to the global minimum. We find that the pure Ga clusters and the Ga rich bimetallic ones are not reactive towards hydrogen adsorption. For all the different hydrogen adsorption configurations that we have tried on the pure Ga clusters, molecular hydrogen desorbs. The lowest energy configurations, magnetic spin states, adsorption energies and geometrical parameters of molecular hydrogen adsorbed on the clusters are summarized in Figure-4.9 and Table-4.2.

Dimers: On pure Pd dimer, we have tried the following hydrogen adsorption geometries: (a) the hydrogen molecule atop the Pd atom with H-H bond parallel to the Pd-Pd bond (atop-hori), (b) hydrogen molecule binding to a single Pd with the molecule axis in line with the dimer axis (atop-endon), (c) H₂ bound to a single Pd atom with the molecule axis perpendicular to the cluster axis (atop-perp), (d) the molecule in a Pd-Pd bridge position with the molecular axis perpendicular to the cluster axis (bridge-perp) and (e) the molecule in a bridge position with the molecular axis parallel to the cluster axis (bridge-para). Amongst these above mentioned configurations, the molecule dissociates in both the bridge-perp and bridge-para configuration. In the former one the two hydrogen atoms bind to the Pd atoms in a bridge form on either sides of the dimer. In the bridge-para configuration also the hydrogen molecule dissociates with H-H distance being 1.09 Å. Further, for the atop-endon configuration, H₂ does not bind. We find the atop-perp configuration to be the most stable one with the hydrogen binding energy of -0.73 eV/H₂ molecule (Figure-4.9(a)). This is consistent with the findings of Ni *et al.* [79] The H-H bond is activated with a bond length of 0.83 Å. The Pd-Pd bond is elongated to 2.52 Å after hydrogen adsorption. The Pd-H bond lengths are 1.82 Å each. We find that the magnetic state of the dimer does not change upon hydrogen adsorption. In addition to the above mentioned configuration, we find another isomer (atop-hori) which is 0.03 eV higher in energy than the most stable one (Figure-4.9(b)). In this case the H-H bond length

is about 0.84 Å. The dimer elongates to 2.55 Å. The average Pd-H bond length is 1.76 Å. On PdGa, we tried similar configurations as mentioned for Pd₂. In all the cases, where

Table 4.2: Adsorption energy (E_{ads}), H-H bond length (d_{H-H}), Pd-H bond length (d_{Pd-H}), Pd-Ga bond length (d_{Pd-Ga}) and Pd-Pd bond lengths (d_{Pd-Pd}) for H₂ adsorbed on Pd_xGa_y clusters in the gas phase. The energies are given in the ‘eV’ units and bond lengths are given in Å.

Cluster size	Composition	E_{ads}	d_{H-H}	d_{Pd-H}	d_{Pd-Ga}	d_{Pd-Pd}
2	Pd ₂	-0.73	0.83	1.82	-	2.52
	PdGa	-0.25	0.82	1.79, 1.87	2.35	-
3	Pd ₃	-0.60	0.85	1.76	-	2.47, 2.60 2.61
	Pd ₂ Ga	-0.74	0.86	1.74, 1.75	2.37, 2.41	2.64
4	Pd ₄	-0.57	0.85	1.77	-	2.58, 2.59 2.60, 2.72 2.73
	Pd ₃ Ga	-0.61	0.84	1.77, 1.78	2.56, 2.60	2.54, 2.58 2.61
	Pd ₂ Ga ₂ -flat	-0.16	0.79	1.97	2.39, 2.43	-
	Pd ₂ Ga ₂ -bent	-0.16	0.85	1.74, 1.76	2.48, 2.52	2.55

the adsorption site and/or configuration involves a Ga atom, the hydrogen molecule either desorbs or move towards the Pd atom. In contrast to Pd₂, the most stable configuration is the atop-hori one (Figure-4.9(c)) with a binding energy of -0.25 eV/H₂ molecule. The hydrogen molecule is weakly activated with the H-H bond length of 0.82 Å. The Pd-H bond lengths are 1.79 and 1.87 Å. The Pd-Ga bond length is elongated to 2.35 Å compared to that of 2.29 Å for the bare cluster. The more symmetric atop-perp configuration that was lowest in energy for Pd₂ is about 0.09 eV higher in energy than the atop-hori configuration for PdGa. In the atop-perp configuration the Pd-H bond lengths are 1.92 Å and H-H bond length is 0.80 Å (Figure-4.9(d)).

Trimers: Amongst the different configurations considered in our study, we find that on Pd₃ there is only one possible configuration in which hydrogen binds in a molecular form to the trimer (Figure-4.9(e)). The binding energy is -0.60 eV/H₂ molecule. For all the other configurations that we have tried, hydrogen either dissociates or desorbs after geometry optimization. Like that of the Pd dimer, the hydrogen molecule is activated having H-H bond length of 0.85 Å. The Pd-H bond lengths are of 1.76 Å each. The cluster retains its isosceles triangle geometry. Compared to the bare cluster, the shorter Pd-Pd bond is

slightly compressed to 2.47 Å while the longer ones are slightly elongated to 2.61 Å. The cluster with H₂ has a magnetic moment of 2.0 μ_B that is same as that of the bare one. Our results are in good agreement with that of Ni *et al.* [79]

Unlike PdGa where the hydrogen binding is much weak compared to Pd₂, on Pd₂Ga, hydrogen molecule binds much more strongly compared to Pd₃ with a binding energy of -0.74 eV. Similar to Pd₃, this is the only configuration in which hydrogen binds in the molecular form (Figure-4.9(f)). The H-H bond length of the adsorbed molecule is 0.86 Å. The Pd-H distance is 1.74 Å. The cluster loses its symmetry upon hydrogen adsorption and takes a scalene triangular form. Of the two equal Pd-Ga bond lengths of the bare cluster, the bond length of the one that has H attached to it, increases to 2.41 Å while the other remains unchanged. The Pd-Pd bond length also marginally increases to 2.64 Å. The cluster has a magnetic moment of 1.0 μ_B . Hydrogen molecule does not bind on PdGa₂.

Tetramers: We find only one configuration in which hydrogen binds in the molecular form on Pd₄. The binding energy is -0.57 eV/H₂ molecule. Here also the molecule is activated with H-H bond length of 0.85 Å (Figure-4.9(g)). Each of the Pd-H bonds are 1.77 Å long and the magnetic moment of the cluster is 2.0 μ_B . The Pd-Pd bonds involving the Pd atom on which hydrogen binds elongate to about 2.72 Å.

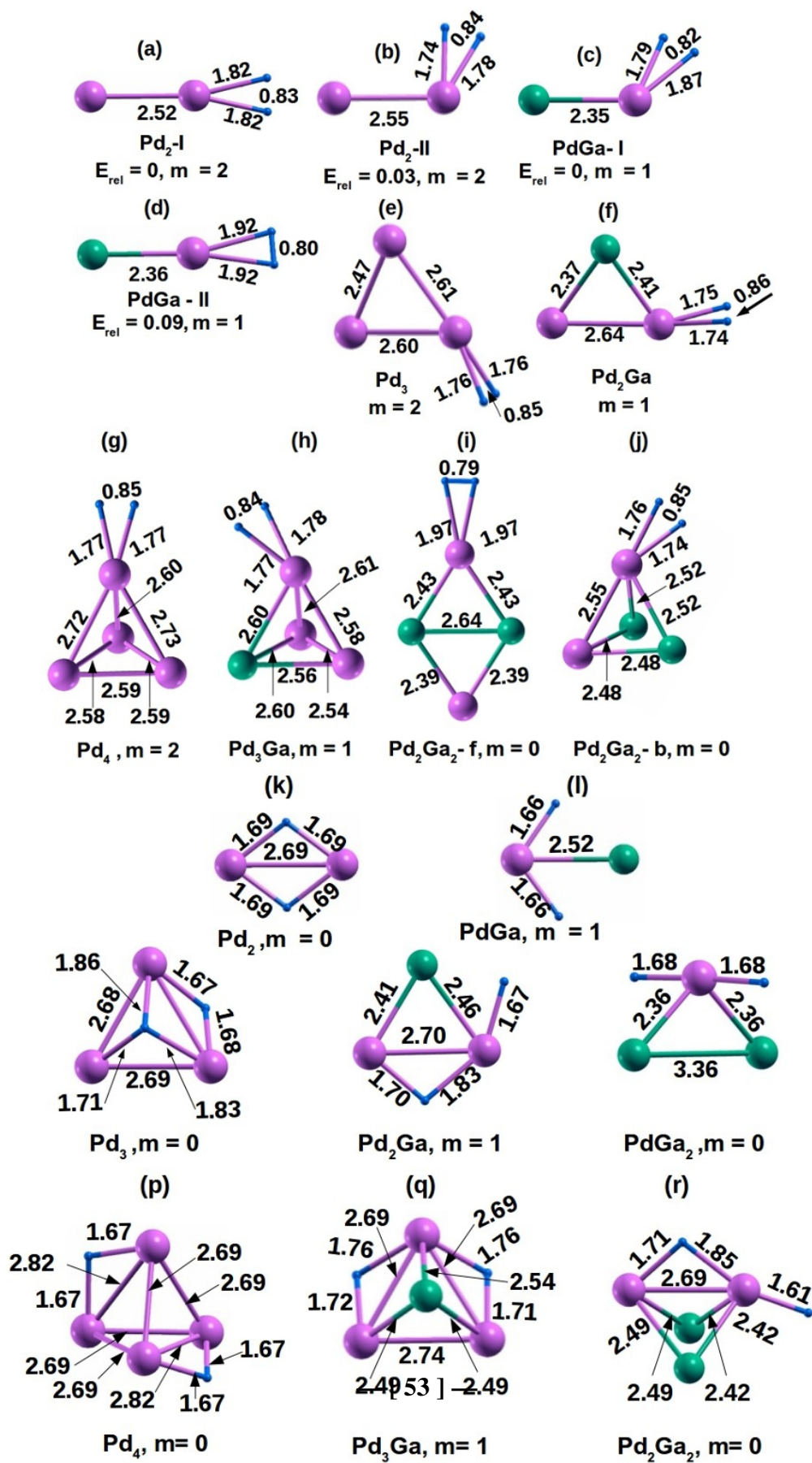


Figure 4.9: Lowest energy structures of the hydrogenated Pd_xGa_y clusters in the gas phase.

On Pd₃Ga, hydrogen binds in a configuration similar to that of Pd₄ with a binding energy of -0.61 eV/H₂ molecule. The H-H bond length is 0.84 Å (Figure-4.9(h)). The cluster have a magnetic moment of 1.0 μ_B that is same as in its bare form. The Pd-Pd bond lengths are of 1.77 Å. The Pd-Ga bond length between the Ga atom and the Pd atom to which hydrogen attaches is elongated to 2.60 Å.

For Pd₂Ga₂, we find two isomers each with a binding energy is -0.16 eV/H₂ molecule. In one of the isomers, the cluster remains flat and H-H bond length is 0.79 Å (Figure-4.9(i)). In the other one the cluster is bent and the H-H bond is activated with a H-H bond length of 0.85 Å (Figure-4.9(j)). In both the cases the clusters remain non magnetic. For the planar one, the Pd-Ga bond length involving the Pd atom to which H₂ binds is 2.43 Å while in the bent one it is 2.52 Å. For the planar and the bent configurations, each of the Pd-H bond lengths are 1.97 Å and 1.76 Å respectively.

Co-adsorption of dissociated hydrogen (H* + H*) : Hydrogen in dissociated form can bind to top, bridge or hollow sites in a given cluster depending upon the cluster size. On Pd dimer, H atoms bind strongly on Pd-Pd bridge with an adsorption energy of -2.10 eV. Meiyan and Zhi have reported this planar structure having a binding energy of 2.08 eV. [79]. According to their findings, this hydrogenated Pd₂ cluster has a Pd-H bond length of 1.68 Å and Pd-Pd bond length of 2.74 Å. From our calculations the bond distances d_{Pd-H} and d_{Pd-Pd} are obtained as 1.69 Å and 2.69 Å respectively. The net magnetic moment is reduced to zero while the bare Pd₂ cluster has magnetic moment of 2 μ_B . Adsorption of dissociative hydrogen on the bimetallic cluster PdGa is weaker compared to the Pd dimer. Here, both the H atoms bind solely to the Pd atom having an adsorption energy of -0.20 eV which is comparable with the adsorption energy of molecular hydrogen on PdGa. No quenching of magnetic moment occurs in case of PdGa cluster.

Trimers: We started with various possibilities of putting hydrogen in *top-top*, *bridge-bridge*, *top-bridge*, *top-facet*, *bridge-facet* and *facet-facet* for the trimers. For Pd₃, our results show that *bridge-facet* is more stable than that of *bridge-bridge* by an energy difference of 0.015 eV per H atom. The adsorption energy of H atoms on Pd trimer is -1.31 eV. The H atom binds at Pd-Pd bridge with an average Pd-H bond length of 1.68 Å. At the facet of Pd₃, the second H atom binds with an average Pd-H bond length of 1.80 Å. The cluster retains the isosceles structure but the Pd-Pd bond lengths are increased to 2.68 Å

and 2.75 Å respectively. This hydrogenated cluster is non-magnetic unlike the bare Pd₃ cluster.

On Pd₂Ga cluster, one H atom lies at Pd-Pd bridge (d_{Pd-H} = 1.70, 1.83 Å) while the second H atom binds on top site of one of the Pd atoms (d_{Pd-H} = 1.67 Å). The adsorption energy of H atoms on Pd₂Ga is -0.64 eV. The Pd-Pd bond is stretched to 2.70 Å from 2.63 Å (bare Pd₂Ga). The average Pd-Ga bond distance in this hydrogenated cluster is 2.44 Å which is 0.07 Å longer than the Pd-Ga bond length in gas phase Pd₂Ga. In case of Ga rich PdGa₂ cluster, both the H atoms bind at top of the Pd atoms having an adsorption energy of -0.60 eV and Pd-H bond distance of 1.68 Å.

Tetramers: The details of the geometry and energetics of various configurations for Pd₄, Pd₃Ga and Pd₂Ga₂ are given in Figures-B4, B5 and B6 respectively of the Appendix B. On Pd₄, in the lowest energy configuration, each of the H atoms binds in a bridge between two Pd atoms (Figure-4.9(p)) with a coadsorption energy of E_{ads} = -0.86 eV. The magnetic moment of the cluster is completely quenched. Each of the Pd-H bond lengths are about 1.67 Å. The distance between the Pd atoms that form the bridge site is about 2.82 Å. The other Pd-Pd bond lengths are about 2.69 Å. We find another configuration that is only 0.05 eV higher in energy compared to the most stable one. In this case, the H atoms occupy two of the hollow sites formed by the triangular faces of the tetrahedron (Figure-B4(a) of Appendix B). The magnetic moment of the cluster is completely quenched. For each of the hydrogen atoms there are three Pd-H bond: two long bonds, each of length 1.81 Å and a shorter one of length 1.73 Å. The cluster as a whole expands due to coadsorption of the H atoms with Pd-Pd bond lengths varying between 2.68 to 2.77 Å. Our results are in excellent agreement with those reported by Moc *et al.* [89]

On Pd₃Ga, the lowest energy configuration is the one in which the cluster is in the spin doublet state and each of the H atoms binds to the Pd-Pd bridge site on the Pd atoms forming the triangular base of the tetrahedron (Figure-4.9(q)). The coadsorption energy of H atoms in this configuration is -1.00 eV. This is about 0.14 eV stronger than what was observed on Pd₄. For each of the H atoms, the Pd-H bond lengths are 1.72 and 1.76 Å. In comparison to the bare cluster, two of the Pd-Ga bond lengths are shortened to 2.49 Å and the third one to 2.54 Å. The Pd-Pd bond lengths are increased to 2.74 and 2.69 Å. Further we find several metastable states for hydrogen coadsorption on this cluster. These

are shown in Figure B5 of Appendix B.

On Pd_2Ga_2 , in the most stable configuration, one of the H atoms binds on the Pd-Pd bridge site with Pd-H bond lengths of 1.71 and 1.85 Å (Figure- 4.9(r)). The second H atom forms a Pd-H bond (bond length of 1.61 Å) with the Pd atom that is 1.85 Å away from the first H atom. The coadsorption energy of the H atoms is -0.58 eV/ H_2 molecule. Like that of the hydrogen molecule, the binding of the atomic hydrogen is weakest on the Pd_2Ga_2 cluster.

4.3.3.2 Tetramers on MgO support

Molecular hydrogen (H_2) : As observed in the case of gas phase clusters, H_2 molecule does not bind to the Ga rich clusters (PdGa_3 and Ga_4) supported on MgO. The energetics and geometrical parameters of the hydrogenated tetramers are summarized in Table-4.3 while Figure-4.10 [(a)-(c)] shows the most stable structures of the same. On Pd_4 , H_2 binds on one of the Pd atoms binded directly to the surface O atom having an average Pd-H bond length of 1.74 Å and binding energy of -0.51 eV. In gas phase, the H-H bond length is 0.74 Å which lengthens to 0.88 Å when adsorbed on the cluster. The spin state of the Pd_4 cluster remains unaltered. The other configurations of H_2 binding to Pd_4 lie 0.20-0.25 eV higher in energy.

On Pd_3Ga , we have two possible configurations as we have two kind of Pd atoms present (a) Pd atoms interacting with MgO surface (Pd-I) and (b) Pd atom at the vertex of the tetrahedra (Pd-II). The two configurations differ by about 0.06 eV in energy with the latter one being thermodynamically slightly more favorable. The adsorption energy of the hydrogen bonded on top Pd atom is -0.44 eV. The hydrogen bonded on the vertex Pd has a H-H bond distance of 0.84 Å and Pd-H bond distance of 1.80 Å.

Table 4.3: Adsorption energy (E_{ads}), H-H bond length (d_{H-H}), Pd-H bond length (d_{Pd-H}), Pd-Ga bond length (d_{Pd-Ga}) and Pd-Pd bond length (d_{Pd-Pd}) for H_2 adsorbed on MgO/Pd_xGa_y clusters. The energies are given in the ‘eV’ units and bond lengths are given in Å.

Cluster	E_{ads}	d_{H-H}	d_{Pd-H}	d_{Pd-Ga}	d_{Pd-Pd}	d_{Pd-Mg}	d_{Pd-O}	d_{Ga-O}
Pd_4	-0.51	0.88	1.72, 1.76	-	2.59, 2.66	2.66, 2.67	2.30, 2.31	-
Pd_3Ga	-0.44	0.84	1.79, 1.81	2.41, 2.45	2.67, 2.68	2.69, 2.70	2.25, 2.33	2.21
Pd_2Ga_2	-0.24	0.81	1.90	2.42, 2.47	-	2.74, 2.81	-	2.22

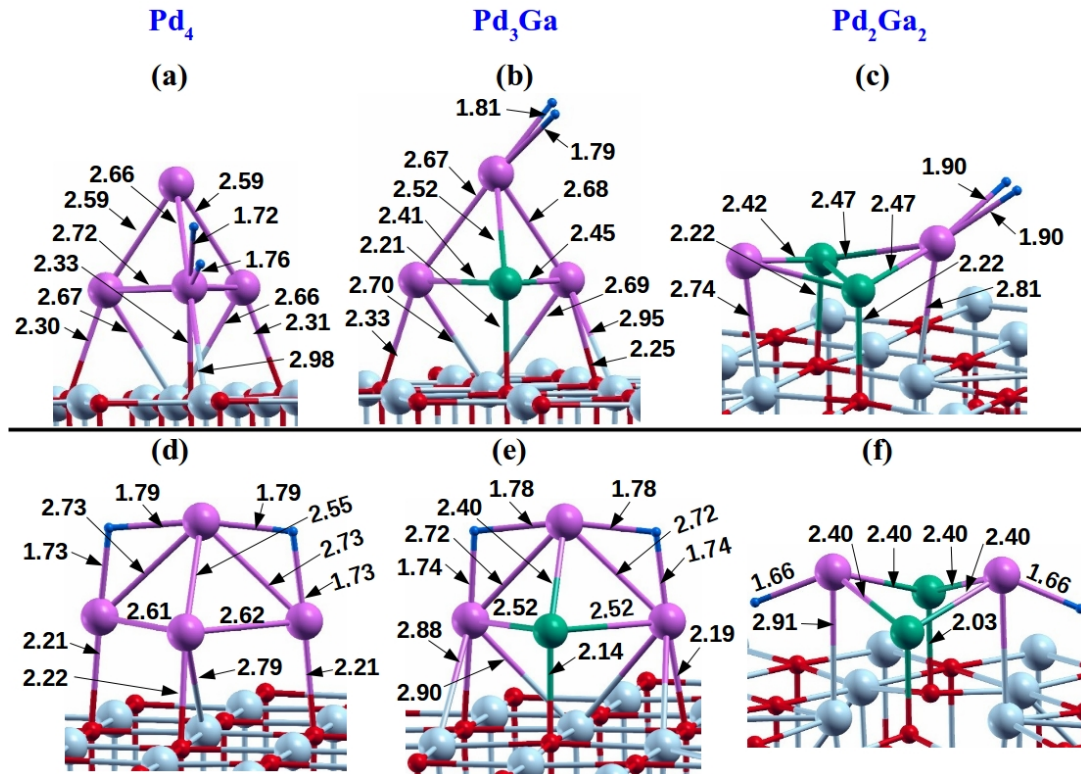


Figure 4.10: Lowest energy structures of MgO supported hydrogenated Pd_xGa_y tetramers. The blue, green and magenta spheres denote the H, Ga and Pd atoms respectively. The surface atoms Mg and O are represented by grey and red spheres respectively.

H_2 binding is weakest on Pd_2Ga_2 having an adsorption energy of -0.24 eV and Pd-H bond distance of 1.90 Å. We observe a decline in the binding strength of H_2 when moving from Pd_4 to Pd_2Ga_2 emphasizing on the effect of Ga concentration on the binding of hydrogen molecule on the clusters. This is discussed further in details of interaction mechanism between hydrogen molecule and the clusters.

Co-adsorption of dissociated hydrogen ($H^* + H^*$) : We started initially with many possible structures for the adsorption of dissociative hydrogen on the respective tetramers. The most stable geometries are shown in the Figure-4.10 [(d)-(f)]. H atoms bind most strongly at the Pd-Pd bridges on Pd_4 and Pd_3Ga clusters. However in contrast to that observed for molecular hydrogen, we find that co-adsorption of H atoms is stronger on Pd_3Ga than Pd_4 . The co-adsorption energy of hydrogen atoms on Pd_4 is -1.19 eV. The inequivalent Pd-H bond lengths at the Pd-Pd bridge are 1.73 Å and 1.79 Å. Unlike that of co-adsorption of H atoms on gas phase Pd_4 cluster where the magnetic moment is completely quenched, we find that on the support, the complex ($Pd_4 + H + H$) retains its magnetic moment (triplet state).

H atoms bind at Pd-Pd bridges of Pd_3Ga having a co-adsorption energy of -1.39 eV. The respective Pd-H bond lengths are 1.74 Å and 1.78 Å. We observe that the binding strength of H atoms on Pd_4 is weaker than Pd_3Ga by an energy of 0.20 eV while in gas phase this energy difference is 0.14 eV. On stoichiometric Pd_2Ga_2 , co-adsorption of H atoms is endothermic having co-adsorption energy of +0.03 eV.

Interaction mechanism between H_2 molecule and the clusters : In order to understand the mechanism through which hydrogen binds to the Pd atoms of the cluster and the influence of the Ga atom (for mixed clusters) for the same, we have computed the charge transfer between the molecule and the cluster upon binding. The charge transfer is given by $\Delta\rho(r) = \rho_{cluster+H_2} - \rho_{cluster} - \rho_{H_2}$, where ' ρ ' is the charge density. The first term in right hand side of the above equation is the charge density of the cluster with hydrogen bound to it, the second and the third terms are the charge densities of the cluster and hydrogen molecule (both in a geometry same as that of the interacting configuration) respectively. The isosurfaces are shown in Figure-4.11. For all the cases we see that hydrogen binds to the cluster through Kubas interaction [90], the charge transfer plots show that there is donation of electrons from the σ -bonding orbital of hydrogen to the cluster and back donation from Pd- d states to the σ -antibonding orbital of hydrogen. This results in elongation of the H-H bond length.

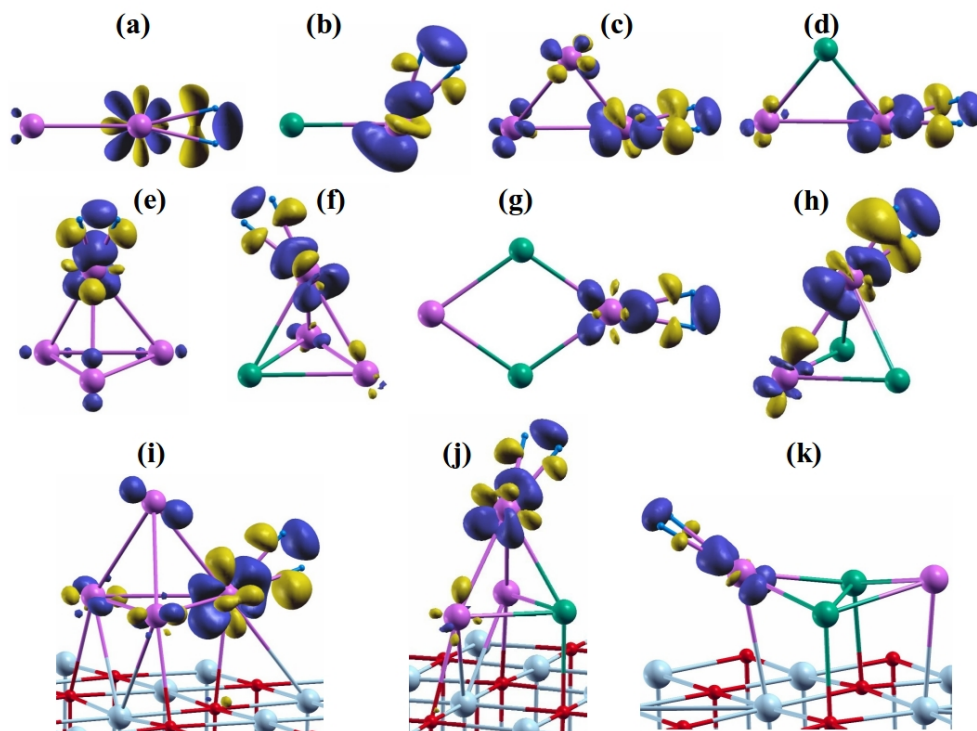


Figure 4.11: Charge transfer plots of the hydrogenated Pd_xGa_y clusters in gas phase [(a)-(h)] and on MgO support [(i)-(k)]. The blue and yellow isosurfaces represent the charge depletion and charge accumulation respectively.

The effect of the Ga atoms on the charge transfer is dependent on the Pd:Ga ratio. For example, in gas phase if Pd:Ga is 1:1, the Pd- d states that take part in the back donation is significantly lower in energy (between -4.5 to -5.0 eV for the bimetallic dimer and tetramer) compared to the hydrogen σ -antibonding orbital. This reduces the back donation from the Pd- d states, thereby resulting in a weaker binding of the molecule to the cluster (-0.25 and -0.16 eV for PdGa and Pd_2Ga_2 respectively). For the Pd rich bimetallic clusters, the Ga atom, due to its lower electronegativity compared to Pd, donates electron to the Pd atoms, making the latter electron rich centres. This enhances the back donation and hence results in a stronger interaction between the hydrogen molecule and the cluster (the adsorption energy of hydrogen molecule on the Pd rich bimetallic clusters are larger than the pure Pd ones). However, since the electron donated by the Ga atom is shared between more than one Pd atom, the effect is much weaker compared to other systems (for example coordination complexes studied by Kubas) showing similar mechanism.

4.3.4 Reaction mechanisms of Hydrogen dissociation on tetramers

4.3.4.1 Gas phase tetramers

Pd₄: Unlike that on the Pd surfaces, where H₂ can dissociate spontaneously, on the clusters there is a barrier associated with hydrogen dissociation. In the earlier sections we have seen that on Pd₄ the spin states of molecular hydrogen adsorbed on the cluster (initial state: IS) is different from that of the dissociated hydrogen (final state: FS). While the IS is in spin triplet state, the FS is in the singlet state. Hence during the reaction pathway there is a spin crossover. Since the total spin needs to be conserved during the reaction path, in our study we have considered hydrogen dissociation on Pd₄ through both the singlet and the triplet spin channels. The reaction profiles for both the spin channels, as shown in Figure-4.12(a), involve two barriers: (a) dissociation of the H₂ molecule, with a barrier of about 0.29 eV in each case and (b) diffusion of the H atoms to their final adsorption sites, with a barrier of 0.48 eV for the triplet channel (barrier less for the singlet channel) (both w.r.t. the IS). For the reaction to proceed, the system needs to switch from one spin channel to the other one. Transitions from one spin channel to the other is possible either through spin excitations or through LS coupling during the reaction pathway, depending on which ever involves a lower barrier. For this case if we consider that first there is a spin excitation in the IS from triplet to singlet, followed by the reaction proceeding through the singlet channel, the total barrier is about 0.98 eV (0.69 eV for spin excitation and 0.29 eV for hydrogen dissociation).

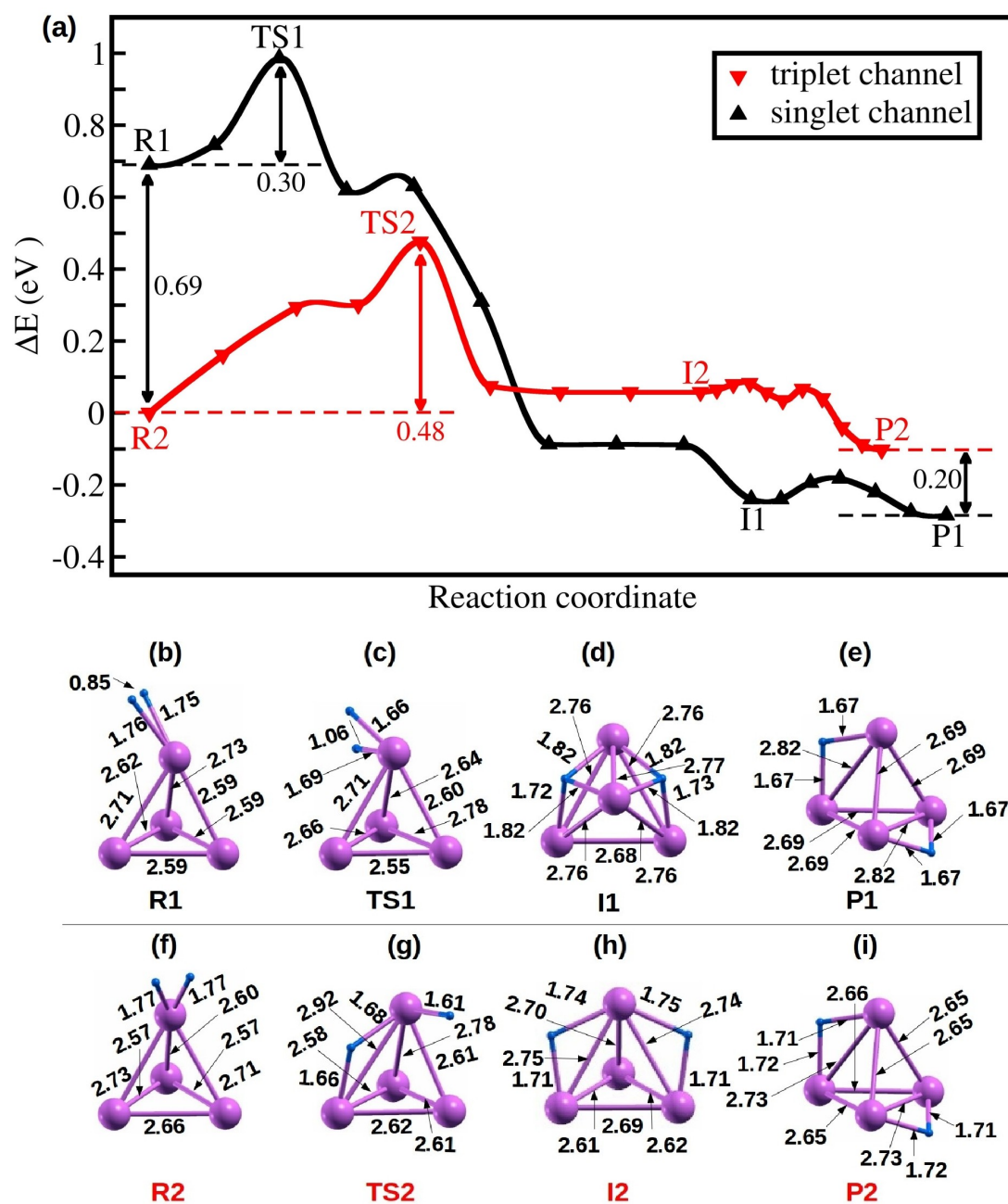


Figure 4.12: Energy profile for hydrogen dissociation on the Pd_4 cluster in gas phase.

However, for the reaction mechanism in which first hydrogen dissociates through the triplet channel followed by a transition from the triplet to the singlet channel through LS coupling involves a barrier of only 0.48 eV. This barrier is half that of the barrier required for hydrogen dissociation through spin excitation. Hence we feel that the H_2 dissociation mechanism will follow the second path mentioned above. The IS, FS and the transition states (TS) for both the spin channels are shown in the right panel of Figure-4.12. For the singlet channel the TS corresponds to the almost dissociated hydrogen molecule (H-H bond length of 1.06 Å; TS1 in Figure-4.12). However, both the H atoms are still bound to the Pd atoms to which it was initially bound to. In the triplet spin channel the TS corresponds to the configuration in which one H atom is on the Pd-Pd bridge while the other is rotated towards the second Pd-Pd bridge (TS2 in Figure-4.12).

Pd₃Ga: Similar to Pd₄, on Pd₃Ga, the path from IS to FS can be divided into two parts, namely, hydrogen dissociation and diffusion of the dissociated hydrogen atoms to the most stable configuration in the FS. However, unlike that in Pd₄, here both the IS and FS are in the spin doublet configuration. Hence we have considered only the spin doublet channel. From our calculations, we find that the reaction proceeds through a metastable intermediate (labelled I in Figure-4.13(a)) in which one of the H atoms move to the hollow site formed by the three Pd atoms (Pd-H bond lengths are 1.75, 1.87 and 2.05 Å) and the other H atom stays at the Pd atom to which it was initially bound (Figure-4.13(d)). For the second H the Pd-H bond length is 1.60 Å. The rate limiting step is the dissociation of H_2 and has a barrier of 0.30 eV. This is similar to that on Pd₄. The TS for this is shown in Figure-4.13(c). The H-H bond length is 0.93 Å. Compared to the IS, the Pd-Ga bonds are significantly compressed. In the second part of the path where there is diffusion of the H atoms, there are two barriers of 0.09 and 0.12 eV. For the first barrier (TS-II, Figure-4.13(e)) the TS involves transfer of the H atom in the hollow site to the Pd-Pd bridge and simultaneous rotation of the H atom attached to a single Pd atom. In the second TS for the H diffusion (TS-III, Figure-4.13(f)) there is further rotation of the H atom and transfer of the second H atom from one Pd-Pd bridge to another. In comparison with that of Pd₄, we find that the hydrogen dissociation barrier on both Pd₃Ga and Pd₄ are similar (about 0.29 eV). However, in the later, the diffusion of atomic H is much faster (0.12 eV compared to that of 0.48 eV on Pd₄).

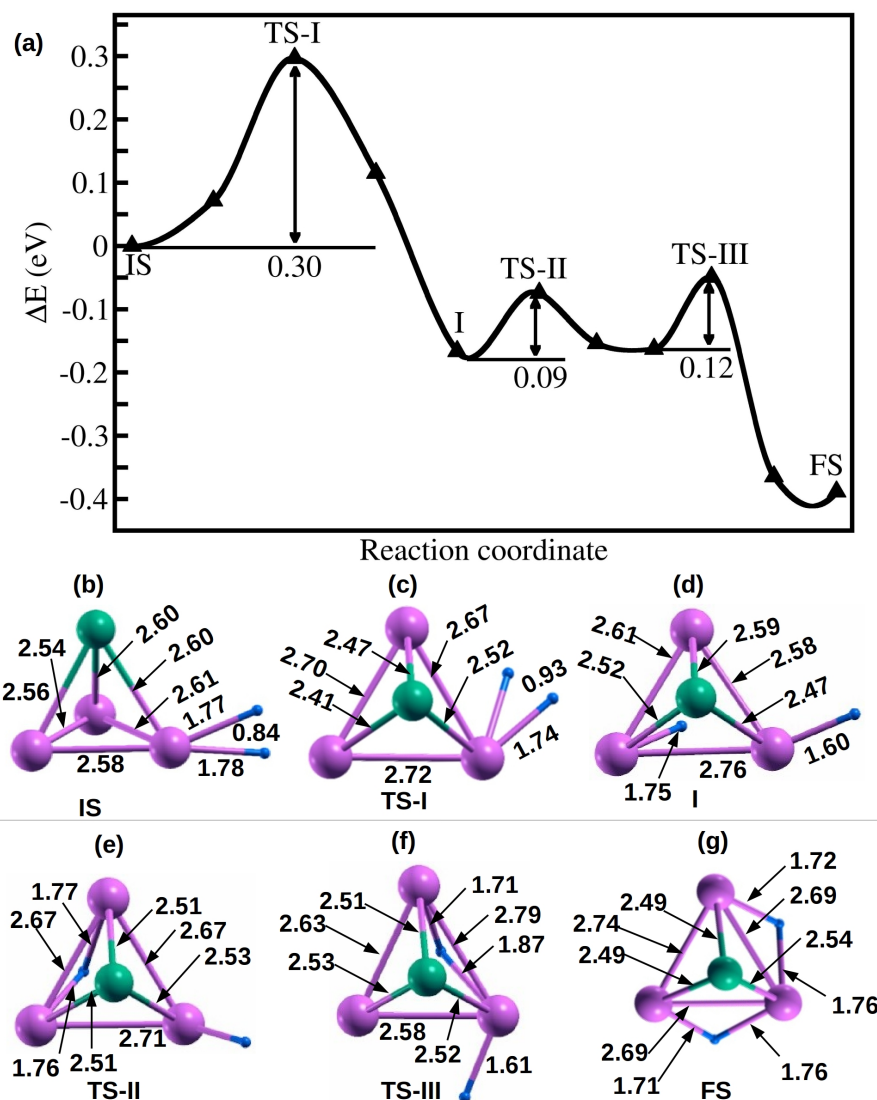


Figure 4.13: Energy profile for hydrogen dissociation on the Pd₃Ga cluster in gas phase.

Pd₂Ga₂: Hydrogen dissociation on Pd₂Ga₂ proceeds through the singlet channel because both the IS and FS are in the singlet state. However, compared to Pd₄ and Pd₃Ga, the dissociation barrier is significantly larger, of about 0.79 eV. In the TS the H₂ molecule is already dissociated with a H-H bond length of 1.57 Å. Both the H atoms are still bound to the Pd atoms as shown in the Figure-4.14.

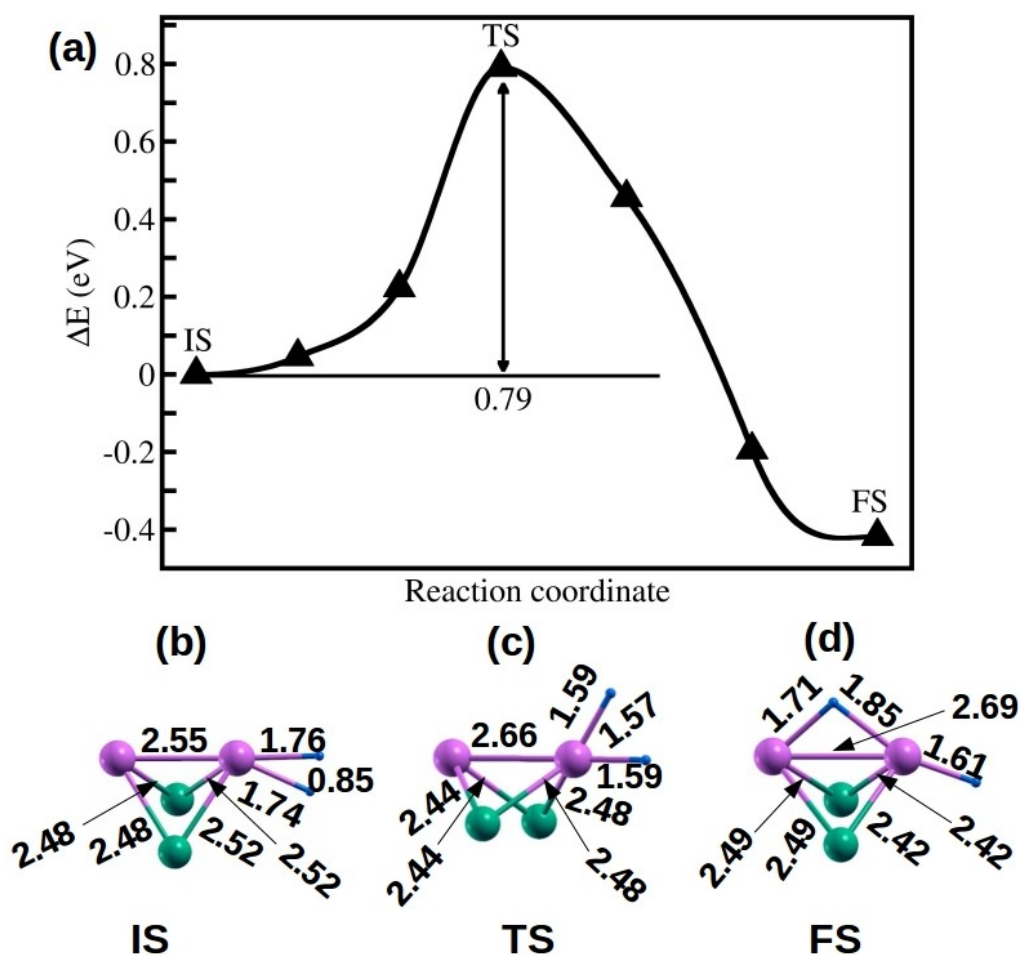


Figure 4.14: Energy profile for hydrogen dissociation on the Pd₂Ga₂ cluster in gas phase.

4.3.4.2 MgO supported tetramers

Unlike in the gas phase Pd₄ cluster, there is no spin crossover between the molecular hydrogen adsorption and dissociated hydrogen adsorption on MgO supported Pd₄. On the support, both the initial and final states are in the triplet spin configuration. The hydrogen dissociation passes through several intermediate states and different binding sites of H atoms as seen in the Figure-4.15. The first step of the reaction is the dissociation of the hydrogen molecule into H atoms followed by a metastable intermediate formation where one of the H atoms from the surface Pd atom moves to the Pd-Pd bridge. At the transition state, the H-H bond lengthens to 1.29 Å and it involves a barrier of 0.16 eV. The reaction proceeds through other intermediate states that mainly involves the diffusion of the H atoms through the different bridge sites of Pd₄ cluster. The overall hydrogen dissociation

have a barrier of 0.20 eV. On the other hand, the hydrogen dissociation on pristine Pd₄ occurs via crossing an activation energy of 0.48 eV. This suggests that hydrogen diffusion and dissociation is more facilitated on the supported Pd tetramer than in the gas phase.

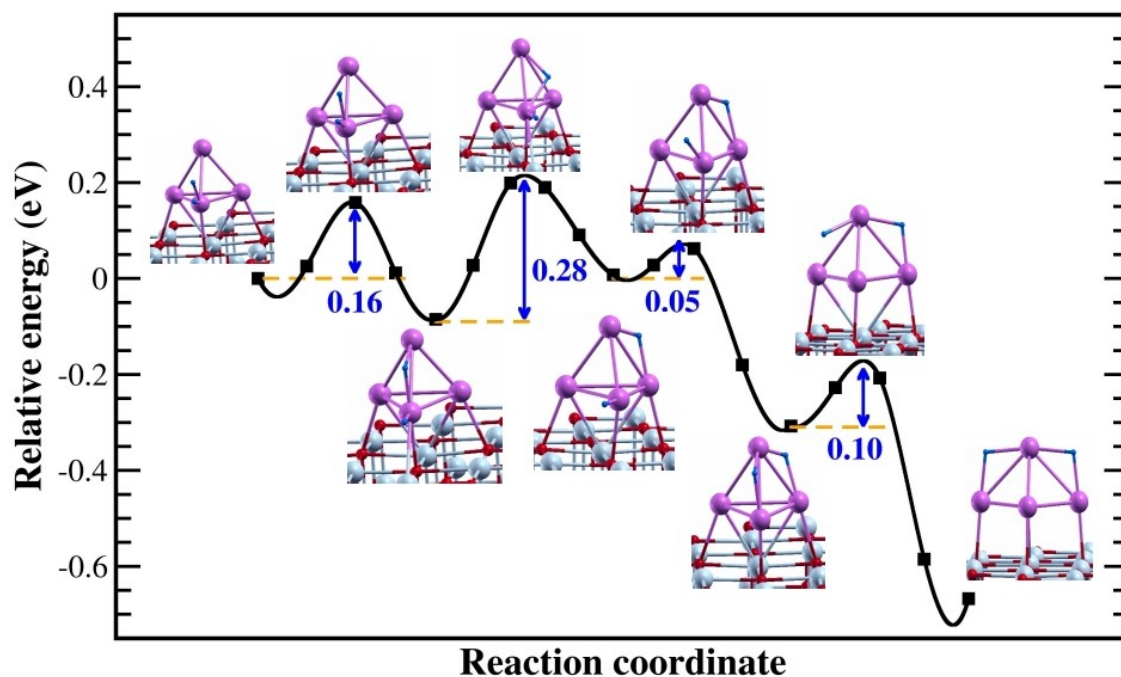


Figure 4.15: Energy profile for hydrogen dissociation on the Pd₄ supported on MgO surface.

On Pd₃Ga, the hydrogen dissociation has an activation energy of 0.44 eV (Figure-4.16). At the transition state, the molecular hydrogen is dissociated into two hydrogen atoms where one of the H atom moves to Pd-Pd bridge. The H-H separation increases to 1.85 Å. However on gas phase Pd₃Ga, this dissociation barrier is 0.14 eV lower in energy. Hence, we observe that in contrast to the Pd₄ cluster, the hydrogen dissociation on supported Pd₃Ga is not as facile as in case of gas phase Pd₃Ga.

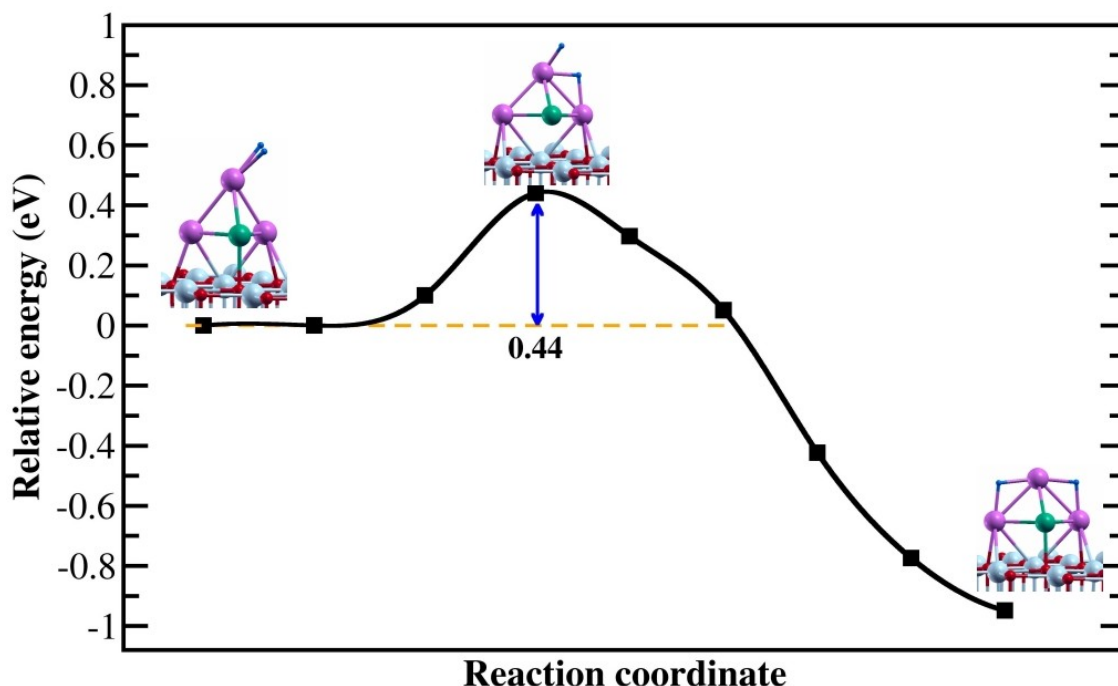


Figure 4.16: Energy profile for hydrogen dissociation on the Pd_3Ga supported on MgO surface.

Trends in dissociation barriers: Amongst the three clusters considered in the gas phase, we find that the barrier associated with hydrogen dissociation and diffusion is anti-correlated with both the adsorption and coadsorption energies. We find that stronger the binding of the adsorbates to the cluster in their IS and FS, lower is the reaction barrier. On Pd_3Ga , the over all barrier is much lower compared to that on Pd_4 and Pd_2Ga_2 . Compared to the bimetallic surfaces, the hydrogen dissociation barrier is much lower on Pd_3Ga . For example on $\text{PdGa}(\overline{111})$ and $\text{PdGa}(111)$ surfaces, the hydrogen dissociation barriers are 0.60 and 0.70 eV respectively. [62] The former surface is characterized by presence of Pd trimers that acts as active sites. In contrast on Pd_3Ga cluster, where again Pd trimer is the active site, the hydrogen dissociation barrier is only 0.30 eV. This suggests that these small intermetallic clusters can be good candidates as catalysts for hydrogen dissociation.

4.4 Outlook and summary

In summary we have studied the stability, structure and electronic properties of small bimetallic PdGa clusters in gas phase as well as on oxide support. We find that the properties of the clusters can be tuned by varying both their size and composition. We have tried diverse geometries linear/planar and three dimensional structures for finding the lowest

energy structures of trimers and tetramers. In most of the cases, tetramers acquire three dimensional structures while in trimers triangular ones are energetically more stable than the linear ones. The thermodynamic stabilities of the bimetallic clusters is investigated by calculating the mixing energies. We found that all the bimetallic Pd_xGa_y clusters are more stable than the pure Pd and Ga clusters in gas phase as well as on oxide support. The clusters are stabilized primarily due to hybridization between the Pd-*s* states and the Ga-*s* and *p* states. In the gas phase the contribution of the Pd-*d* states in the HOMO is either very small or zero. This is in contrast to bulk PdGa where the electronic states around the Fermi energy involves the Pd-*d* states also.

To test the reactivity of the clusters we have studied molecular hydrogen adsorption (on all these clusters in gas phase) and dissociation (in gas phase and MgO supported tetramers). We find that hydrogen molecule adsorbs only on the Pd rich clusters in an activated form. Hydrogen dissociation barrier on Pd_3Ga in gas phase is lowest among the tetramers. When the clusters are put on MgO(100) surface, we find strong interaction between the clusters and support resulting in significant charge transfer between them. This is reflected in the changes of the Pd-Pd, Pd-Ga or Ga-Ga bond lengths of the clusters. On the supported clusters (except Pd_2Ga_2), the strength of the interaction of H_2 with the clusters is reduced. The trend of the hydrogen dissociation on MgO supported Pd_4 and Pd_3Ga is reversed when compared to the respective clusters in gas phase. We note that these calculations are done at 0K and one would need to incorporate the finite temperature effects that might significantly change the energetics.

Chapter 5

Selective hydrogenation of acetylene on Pd_xGa_y tetramers

5.1 Introduction

Ethylene is used as a feedstock for polymerisation reactions. Few traces of acetylene present in ethylene poisons the polymerization catalyst [54,55] thereby making it is necessary to remove acetylene by selectively converting it to ethylene. Though Palladium (Pd) is commonly used as a catalyst for this reaction [58–60] and exhibits high activity, selectivity is very poor, i.e. ethylene is further hydrogenated to ethane. This is primarily because of the strong binding of ethylene to the catalysts that provides sufficient time to the H adsorbed in bulk Pd to diffuse to the surface and carry out the hydrogenation. Moreover, under the hydrogenation reaction conditions, the formation of subsurface species like hydrides and carbides further degrades the catalyst [91–97].

The isolation of active Pd sites by inclusion of inactive metals prevent the formation of Pd ensembles with the neighbouring Pd atoms. This not only reduces further hydrogenation but also prevent the side reactions to occur. Several attempts have been made to improve the catalytic properties of the Pd catalysts by adding promoters that form bimetallic cluster with Pd or by alloying Pd with second metal. Many metallic dopants have been proposed, e.g. tin (Sn) [98,99], lead (Pb) [98,100–102], gold (Au) [103–107], silver (Ag) [108–112], copper (Cu) [113–116] etc. These bimetallic catalysts show better selectivity and reactivity. However their stability and selectivity degrades with time because of the ease of Pd phase segregation at the reaction conditions. This limits their long term usage.

Recently Osswald *et. al* showed that Pd-Ga intermetallic compounds (IMCs) as the most promising candidates for selective hydrogenation reaction. [61, 117–119] Intermetallic

compounds (IMCs) are homogeneous mixtures of the constituent elements exhibiting well-defined crystal structures [61, 120] unlike the catalysts made of Pd based alloys. The strong covalent bonding between Pd and Ga atoms not only enhances the thermal stability but it inhibits the subsurface chemistry, segregation, and hydride formation quite effectively.

Most of the catalysts mentioned in the previous paragraphs are typically surfaces and/or large nanoparticles. However, over the last couple of years small metal clusters on oxide supports are being used as catalysts. For example there are experimental reports that for CO oxidation on Fe clusters, it is the 3-5 atoms clusters that are the reactive ones. For the selective hydrogenation reaction, to the best of our knowledge, there are primarily theoretical studies of the acetylene hydrogenation reactions using Pd and Pd-Ag nanocatalysts (Pd_4 and Pd_xAg_y ($x+y=4$) clusters). [121, 122]. None of these catalysts are predicted to exhibit selectivity. Motivated by the results of hydrogen dissociation on the small bimetallic clusters in the previous chapter, in this chapter we present the results of our studies where we have explored the feasibility of using Pd_xGa_y as nanocatalysts for the selective hydrogenation of acetylene.

5.2 Computational details

The DFT calculations have been performed using the Quantum Espresso software. [41] Electron-ion interactions are described using the ultrasoft pseudo potentials [42]. The electron-electron exchange and correlation are described using Perdew, Burke and Ernzerhof parameterization of generalized gradient approximation (GGA-PBE) [9]. To speed up convergence Marzari-Vanderbilt smearing [20] with a width of 0.002 Ry have been used. We have used kinetic energy cut offs of 35 Ry and 400 Ry for wavefunctions and charge density respectively. To minimize the interactions between the periodic images, the clusters have been placed in a large cubical box such that along each direction, the periodic images are separated by about 10 Å. Brillouin Zone integrations are done using the Γ -point only.

We note that for the clusters with adsorbates on them, determining the global minima is most challenging since, to the best of our knowledge, there does not exist any single method which can provide the global minima of a complex PES. To address this problem

we have computed several possible configurations for each case (the details of which are given in the Appendix C) and we are sufficiently confident that the structures reported for the clusters with adsorbates in our work are the global minima. Further for each of the lowest energy configurations, we have calculated the vibrational frequencies to ensure that there are no unstable modes, thus ensuring that the structures are at the minima of the PES.

The minimum energy pathway and transition states (TS) have been determined using the climbing image nudged elastic band (CI-NEB) [75]. We further calculated the vibrational modes and looked for a single imaginary frequency of the TS as a further confirmation that the TS is a first-order saddle point in the potential energy surface (PES). The rate constant (k) and the pre-exponential factors (A_0) are determined based on the harmonic-TS theory [123]:

$$k = \frac{k_B T}{h} \frac{q^{TS}}{q^{IS}} \exp\left(-\frac{E_{ZP}^a}{k_B T}\right) = A_0 \exp\left(-\frac{E_{ZP}^a}{k_B T}\right), \quad (5.1)$$

where k_B is the Boltzmann constant, T is the temperature, q^{TS} and q^{IS} are the vibrational partition functions of the TS and the initial state (IS) respectively, and E_{ZP}^a is the zero-point energy (ZPE) corrected activation energy (E^a). The activation energy is given by the difference in total energies of the TS and IS. The ZPE is given by $ZPE = \frac{1}{2} \sum_i h\nu_i$, ν_i are the computed vibrational frequencies using the density functional perturbation theory [25].

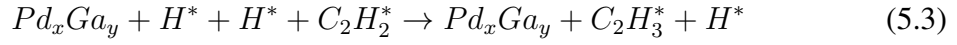
5.3 Results and Discussion

In order to study the reactivity and the selectivity of the clusters towards selective hydrogenation of acetylene (C_2H_2) to ethylene (C_2H_4), we will concentrate on the tetramers, namely, Pd_4 , Pd_3Ga_1 and Pd_2Ga_2 . Further Pd_1Ga_3 and Ga_4 are not considered due to the fact that for the former there are not enough adsorption sites to coadsorb hydrogen and acetylene while for the latter the reactants do not bind. The reaction can be divided into several steps. Here we will consider the path based on Horiuti-Polanyi mechanism given as follows [124]:

(a) Coadsorption of dissociated H_2 and acetylene



(b) Conversion of acetylene to vinyl

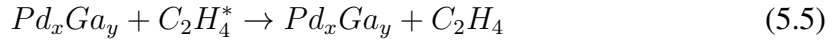


(c) Hydrogenation of vinyl to ethylene

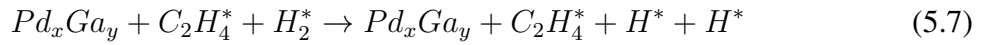
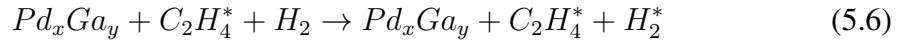


Once C_2H_4 is formed, there are two possibilities. The ethylene molecule can desorb (Possibility-I) and the reaction stops or the reaction might proceed forward and ethylene is further hydrogenated (Possibility-II) as shown below.

Possibility-I : Desorption of ethylene



Possibility-II Further hydrogenation of ethylene



The * in the above equations denotes that the adsorbate is bound to the cluster. The selectivity of these catalysts depends on the ethylene desorption barrier (Eqn. 5.5, E_{des}) and the effective barrier associated with further hydrogenation (E_{hyd2}). A high selectivity implies $E_{hyd2} \gg E_{des}$. As a first step towards understanding the reactivity and selectivity of these clusters towards ethylene formation, we present the results on the study of the thermodynamic stability of the coadsorption of the reactants on these clusters.

5.3.1 Thermodynamics of coadsorption of reactants and products on the clusters

Coadsorption of acetylene and dissociated hydrogen. For the coadsorption of acetylene and hydrogen atom on the tetramers, we considered three configurations in which acetylene can bind: (a) π -mode, where a single Pd atom binds with both of the carbon atoms, (b) a di- σ mode, where each of the C atoms of acetylene binds to two different Pd atoms in a horizontal bridge configuration, and (c) $\eta^1\text{-}\eta^2$ mode, where one carbon atom

binds to a single Pd atom while the second one binds to the Pd-Pd bridge. We note that for Pd_2Ga_2 the $\eta^1\text{-}\eta^2$ mode is not possible. On all the three clusters, we find that there are several possible configurations that are similar in energy thereby making it challenging to explore the potential energy surface and uniquely determine the minima. The different configurations obtained after the geometry optimizations are shown in Figures C1, C4 and C5 of Appendix C. Acetylene binds in an activated form on Pd_4 via di- σ binding with a coadsorption energy of -2.47 eV and having a singlet spin state (Figure-5.1(a)). The C-C bond length is increased to 1.30 Å compared to 1.20 Å in the gas phase. The C-H bonds are also slightly elongated to 1.09 Å compared to 1.07 Å for gas phase acetylene. The bond angles $\theta_{\text{C-C-H}}$ and $\theta_{\text{H-C-H}}$ change to 135.2° and 114.9° compared to 180° in the gas phase, hence, suggesting that the acetylene no longer remains *sp* hybridised after adsorption on the cluster. The C-C triple bond stretching frequency ($\nu_{\text{C-C}}$) of the molecule on the cluster softens to 1559.61 cm^{-1} compared to 1997 cm^{-1} in the gas phase. This is consistent with the 8.3 % increase in the C-C bond length of acetylene upon adsorption. Additionally depending on the position of the pre-adsorbed dissociated H atoms, we find another di- σ configuration which lies 0.02 eV higher in energy (Figure C1(a) of Appendix C) than the lowest energy structure. We note that our lowest energy geometry of acetylene is different from that reported by Yang *et al.* where they have found the $\eta^1\text{-}\eta^2$ mode to be more stable [121]. We found two possible $\eta^1\text{-}\eta^2$ configurations, however they lie 0.10 eV and 0.12 eV higher in energy than our lowest energy structure (Figure C1 (b) and (c) in Appendix C).

On the bimetallic clusters, acetylene binds through π bonding (Figure-5.1(b) and (c)). Hence, these clusters show weaker binding of acetylene compared to Pd_4 which is reflected in their co-adsorption energies also tabulated in the Table-5.1. The C-C bond length of activated acetylene is 1.26 Å (1.24 Å) on Pd_3Ga_1 (Pd_2Ga_2) and the coadsorption energy is -2.37 eV (-1.62 eV). The acetylene bound Pd_3Ga_1 and Pd_2Ga_2 have doublet and singlet spin states respectively. The $\theta_{\text{C-C-H}}$ and $\theta_{\text{H-C-H}}$ bond angles are 156.5° (162.4°) and 145.6° (154.3°) on Pd_3Ga_1 (Pd_2Ga_2). We find that as the concentration of Ga atoms in the cluster increase, there is a reduction in the coadsorption energies of acetylene and hydrogen atoms. This can be attributed to the unavailability of the active sites (Pd atoms) on the cluster. This is consistent with the change in C-C stretching frequencies on these clusters. The $\nu_{\text{C-C}}$ stretching frequency are 1751 cm^{-1} and 1829 cm^{-1} on Pd_3Ga_1 and Pd_2Ga_2 respectively and are relatively harder compared to that observed on Pd_4 .

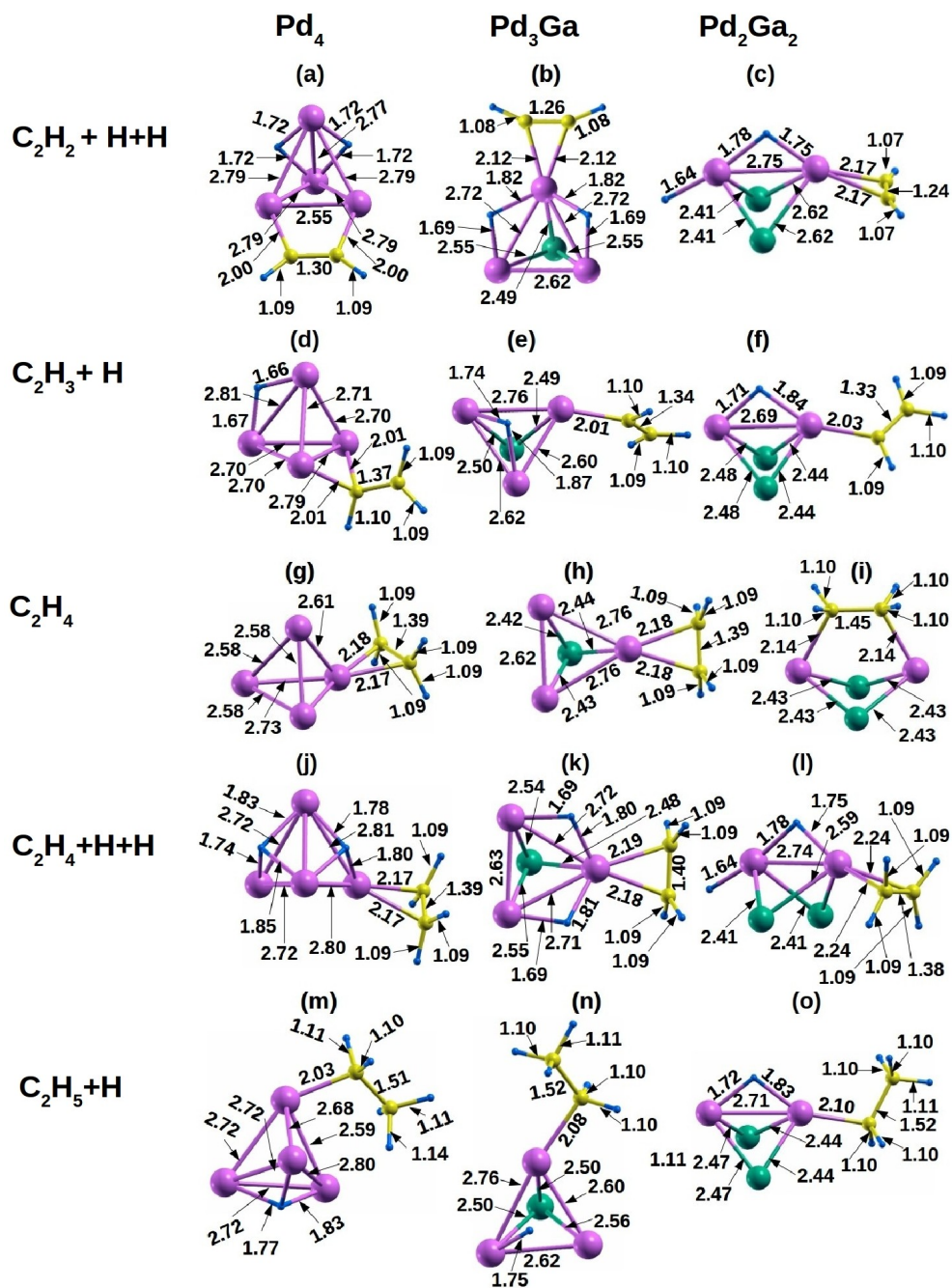


Figure 5.1: Lowest energy structures of different adsorbates on Pd_xGa_y clusters. The blue, yellow, green and magenta spheres in these figures and all other figures in this chapter denote the H, C, Ga and Pd atoms respectively. The bond lengths are given in Å.

Coadsorption of vinyl and H. Similar to co-adsorption of acetylene and H atoms, for the coadsorption of vinyl and H on these clusters, we examined several possible configurations. These configurations are primarily related to the orientation of the vinyl molecule (Figure-C2 (Pd₄), C4 (Pd₃Ga) and C5 (Pd₂Ga₂) of Appendix C). On Pd₄ vinyl adsorbs in a π -mode where the C-atom of the -CH moiety binds to the cluster. The coadsorption energy is -3.24 eV and cluster remains in the singlet spin state (Figure-5.1 (d)). The H atom remains bound to the Pd-Pd bridge site. We note that this adsorption geometry of vinyl is different from that reported by Wang *et al* where η^1 - η^2 binding mode is the most stable configuration for vinyl adsorption. [121] The difference between the two adsorption geometries of vinyl is due to the presence of hydrogen atoms in our clusters. We have also tried the η^1 - η^2 mode for vinyl. However, we found that after geometry relaxation it goes back to the π -bonded configuration. The different configurations were tested w.r.t the rotation of the vinyl group as well as the different spin states for the Pd₄ cluster.

On the bimetallic clusters, vinyl prefers a σ -mode where the C atom of -CH moiety makes bond with single Pd atom (Figure-5.1(e) and (f)). The coadsorption energies are -2.93 eV and -2.66 eV on Pd₃Ga and Pd₂Ga₂ respectively, suggesting that increase in Ga concentration weakens the binding of the vinyl molecule. For all the cases, the C-C bond length varies between 1.34-1.37 Å and the Pd-C bond lengths lie in between 2.00-2.04 Å. While for Pd₃Ga the H atom occupies the hollow site formed by three Pd atoms, on Pd₂Ga₂ it is bound to the Pd-Pd bridge. Both Pd₃Ga and Pd₂Ga₂ have spin states similar to the acetylene adsorption mentioned earlier. The calculated C-C bond stretching frequencies shows consistency with the lowering of adsorption energies of vinyl on Pd₄, Pd₃Ga and Pd₂Ga₂ clusters. The respective ν_{C-C} stretching frequencies are 1460 cm⁻¹ (Pd₄), 1555.6 cm⁻¹ (Pd₃Ga) and 1570 cm⁻¹ (Pd₂Ga₂).

Table 5.1: Adsorption energies (E_b , eV) of different adsorbates on the Pd_xGa_y clusters. Zero point energy corrected binding energies are marked in the brackets.

Adsorbate	Pd ₄	Pd ₃ Ga ₁	Pd ₂ Ga ₂
C ₂ H ₂	-2.47 (-2.33)	-2.37 (-2.25)	-1.62 (-1.53)
C ₂ H ₃ + H*	-3.24(-3.10)	-2.93 (-2.82)	-2.66 (-2.55)
C ₂ H ₄	-1.22(-1.17)	-1.25 (-1.20)	-0.78 (-0.77)
C ₂ H ₄ + H* + H*	-2.17 (-2.05)	-2.40 (-2.28)	-1.67 (-1.54)
C ₂ H ₅ + H*	-2.09 (-1.99)	-2.36 (-2.25)	-2.12 (-2.00)

Adsorption of ethylene. The lowest energy configurations of ethylene adsorption on the clusters are shown in Figure-5.1(g)-(i). Ethylene prefers to bind in the π -mode on Pd_4 and Pd_3Ga . Unlike acetylene and vinyl molecules, the Pd_4 cluster turns magnetic (triplet state) after ethylene binds to it. However no changes in the spin states are observed on Pd_3Ga and Pd_2Ga_2 clusters. The binding energies of ethylene on Pd_4 and Pd_3Ga are -1.22 eV and -1.25 eV respectively. In the gas phase, ethylene has C=C bond length of 1.33 Å. Upon adsorption on the clusters, the C-C double bond elongates to 1.39 Å on Pd_4 and Pd_3Ga and 1.45 Å on Pd_2Ga_2 . On Pd_2Ga_2 ethylene binds via di- σ mode but having a lower binding energy of -0.78 eV in comparison to the other Pd rich tetramers. We note that the ethylene adsorption causes enormous structural changes in the Pd_2Ga_2 cluster. Hence, the energy gained due to binding of the molecule is lost to accommodate the structural changes that the cluster undergoes resulting in a smaller value of binding energy. The π -mode adsorbed ethylene on Pd_2Ga_2 has an adsorption energy of -0.76 eV. Hence, both di- σ mode and π -mode are equally favorable for ethylene adsorption on Pd_2Ga_2 cluster under the experimental reaction conditions. In the gas phase, the C=C bond stretching in ethylene molecule occurs at 1636.5 cm^{-1} which shifts to 1503.7 cm^{-1} (Pd_4), 1511.3 cm^{-1} (Pd_3Ga) and 1500.5 cm^{-1} (Pd_2Ga_2) after chemisorption which are in accordance with the adsorption energies of the ethylene molecule on the respective clusters.

Coadsorption of ethylene and dissociated H. The lowest energy structures of coadsorption of ethylene and dissociated H atom on the clusters are shown in Figure-5.1(j)-(l). The adsorption geometries of ethylene on these tetramers in presence of H atoms are similar to that observed in absence of H. Unlike the acetylene adsorption on hydrogenated Pd_4 , where hydrogen atoms shifted away from the hollow sites to the bridge sites, there is no such effect observed for ethylene. The hydrogen atoms retain the hollow sites and ethylene binds to the cluster via π bonding. However, the cluster attains a singlet spin state unlike the pristine ethylene bonded Pd_4 (triplet). The coadsorption energy of hydrogen and ethylene on Pd_4 is -2.17 eV. On the bimetallic cluster Pd_3Ga , hydrogen and ethylene co-adsorbs with a stronger binding energy of -2.40 eV than Pd_4 . The Pd_2Ga_2 clusters shows slight effects of the orientation of the ethylene adsorption. The ground state has C=C bond lying parallel to the Pd-Pd bridge with a coadsorption energy (-1.67 eV) of ethylene.

Coadsorption of ethyl and H. Ethyl binds through single Pd-C σ -bond on all the tetratomic clusters. The lowest energy configuration on Pd_4 is a singlet spin state where

the hydrogen atom resides at the Pd₃ hollow site. The coadsorption energy is -2.09 eV (Figure-5.1 (m)). The Pd-C and C-C bond lengths are 2.04 Å and 1.49 Å respectively. This lower energy structure is isoenergetic with another structure (Figure-C3(m) in Appendix C) where H is attached to a Pd-Pd bridge. There is an increase in the binding strength of ethyl on Pd₃Ga where the hydrogen atom resides in a hollow site and ethyl lies parallel to the Pd₃ base of the cluster with a Pd-C bond length of 2.08 Å (Figure-5.1 (n)). The coadsorption energy of ethyl and H is -2.36 eV on Pd₃Ga. We tried several configurations of ethyl on Pd₂Ga₂ cluster by placing H atom at the Pd-Pd bridge and on top of one of the two Pd atoms. On Pd₂Ga₂, coadsorption energy is -2.12 eV where hydrogen atom is pre-adsorbed at the Pd-Pd bridge (Figure-5.1 (o)). The top site placed hydrogen showed a weaker tendency to bind to the ethyl molecule.

5.3.2 Reaction mechanisms

To study the reactivity and selectivity of the clusters towards hydrogenation of acetylene in ethylene we have determined the reaction pathways on these clusters. The results are summarized in Table 5.2.

Acetylene to vinyl conversion. In this reaction step, both the initial state (IS) and final state (FS) are in the same spin configuration for all tetramers. While on Pd₄ and Pd₂Ga₂ they are in the singlet state, on Pd₃Ga they are in the doublet state. On Pd₄, the reaction barrier is about 0.77 eV. This is similar to that obtained by Wang *et al.* [121] where the vinyl formation from acetylene on the gas phase Pd₄ has an activation barrier of 0.75 eV. The path involves breaking of Pd-H bond and diffusion of the H atom towards the acetylene molecule. In the transition state (T₁) the H atom moves closer to acetylene bound to Pd₄ having a C-H distance of 2.50 Å (Figure-5.2 (b)). This is followed by formation of vinyl through H transfer and further rotation of the vinyl molecule to reach the FS. The hydrogenation of acetylene to vinyl on Pd₃Ga involves a path similar to that of Pd₄ but barrier for this process is 0.90 eV. The corresponding transition state (T₁) is shown in Figure-5.3(b). On Pd₂Ga₂ cluster, vinyl formation proceeds through a metastable state (imd) involving the diffusion of both H atoms. The H atom attached to Pd-Pd bridge moves towards the Pd atom bonded to acetylene and the second H atom from top site moves to the Pd-Pd bridge. The Pd₂Ga₂ cluster flattens at the intermediate state where Pd-Pd distance increases to 3.31 Å compared to that of 2.74 Å in the IS. The transition from IS to imd involves a barrier of 1.60 eV. This is the rate limiting step of the conversion

of acetylene to vinyl. The second part of the reaction involves reaching the final vinyl configuration from the metastable state (imd) by crossing an activation barrier of 0.65 eV. Here, the first H atom moves to form vinyl while the second H atom moves to the Pd-Pd bridge.

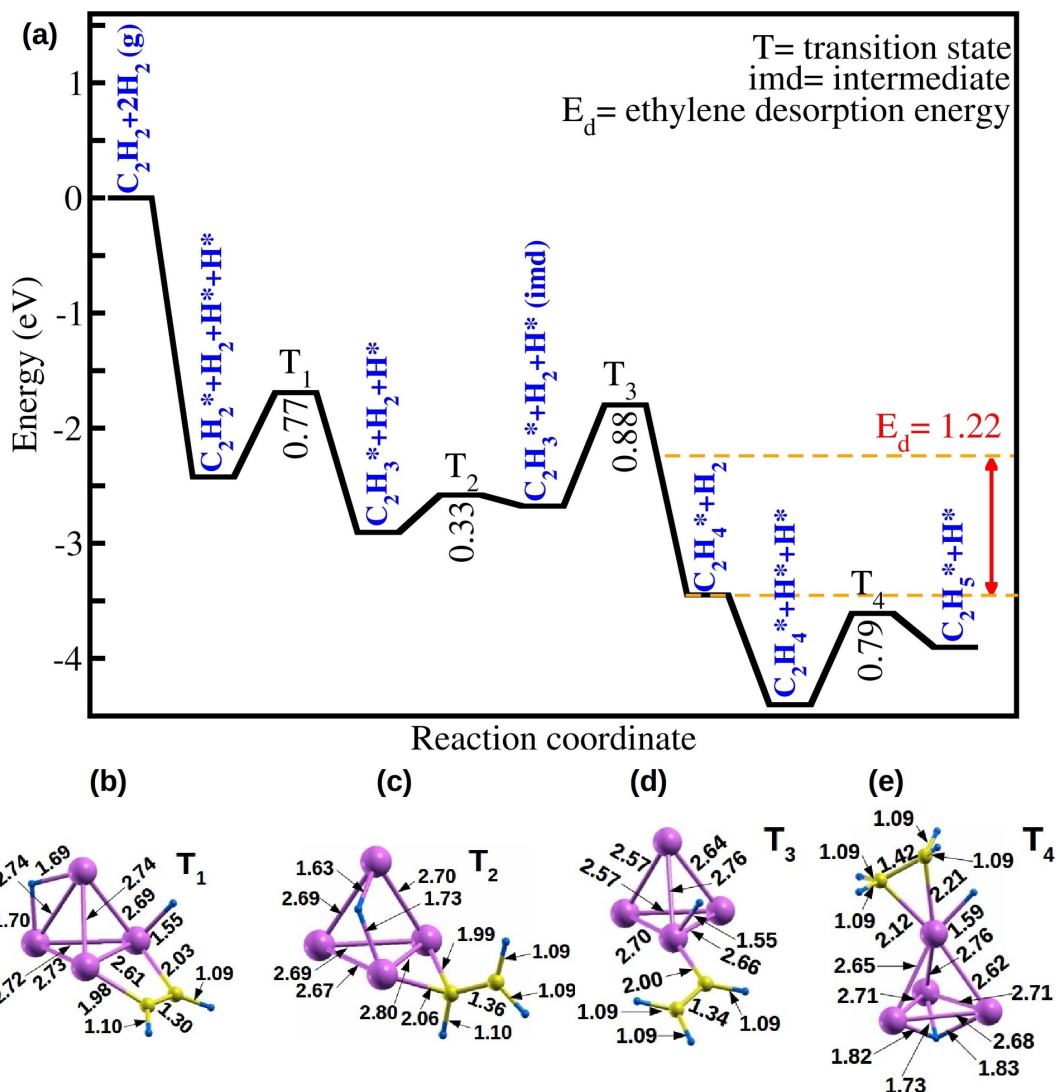


Figure 5.2: (a) Energy profile for the reaction mechanism of hydrogenation of acetylene to ethylene on Pd_4 cluster. (b)-(e) show the structures of the transition states for different reaction steps. The bond lengths are given in Å.

Vinyl to ethylene conversion. For vinyl to ethylene conversion on Pd_4 , the spin states of the IS and FS are different as discussed earlier. Hence for Pd_4 we have considered both the singlet and the triplet channel. Figure-5.5 shows the energetics of the reaction

profile through the two possible spin channels. While in the IS the singlet configuration is 0.09 eV lower in energy than the triplet one, in the final state the triplet configuration is about 0.68 eV lower in energy than that of the singlet one. In the triplet channel, ethylene adsorbs in a π -mode while in the singlet channel ethylene adsorbs in a di- σ mode. For the singlet channel the reaction barrier is about 1.17 eV. In the triplet channel, ethylene formation involves two barriers:(a) the first one involves breaking of a Pd-C bond and conversion of the vinyl from a π mode to a σ mode involving a barrier of 0.76 eV (wrt to the singlet IS) and (b) second one involves the migration of hydrogen to the vinyl group to form ethylene that involves a barrier of 0.88 eV. Comparing the energetics of the two paths, we can infer that cluster is likely to undergo a spin excitation at the IS from singlet to triplet and will follow the triplet channel as the overall barrier is much lower for this path compared to the singlet one.

On Pd₃Ga the conversion of vinyl to ethylene occurs via crossing a barrier of 0.73 eV. The H atom bound to the Pd-Pd bridge diffuses, through the hollow site formed by the Pd atoms, towards the vinyl to form ethylene. The TS (T₂) is shown in the Figure-5.3(d). The conversion of vinyl to ethylene on Pd₂Ga₂ requires a barrier of 1.22 eV. The reaction proceeds by breaking of the Pd-H bond, diffusion of the H atom to the Pd atom to which vinyl is bound and formation of ethylene. The transition state T₃ is shown in Figure-5.4 (d). The C-H bond is 1.83 Å.

5.3.3 Selectivity toward ethylene formation.

In order to investigate the selectivity of the clusters, we need to compare the desorption barrier of ethylene with the barriers involved in further hydrogenation. On the surfaces, the relevant reaction barrier is formation of ethyl from ethylene. The ethyl formation on Pd₄ cluster occurs via passing through a singlet spin channel. The activation barrier is about 0.79 eV. The energetics and the corresponding transition state (T₄) are shown in the Figure-5.2. In the transition state, the hydrogen atom moves from the initial hollow site towards the π -bonded ethylene molecule. The structure of the transition state is similar to that determined by Wang *et al.* [121], however their calculations yielded a much lower barrier (0.65 eV).

On Pd₃Ga, the adsorption of H₂ molecule and H atoms in presence of ethylene is exothermic while the formation of ethyl from ethylene is endothermic. The IS of the ethyl forma-

tion on Pd₃Ga corresponds to the H atoms bound to the Pd-Pd bridge and ethylene binded in a π — mode.

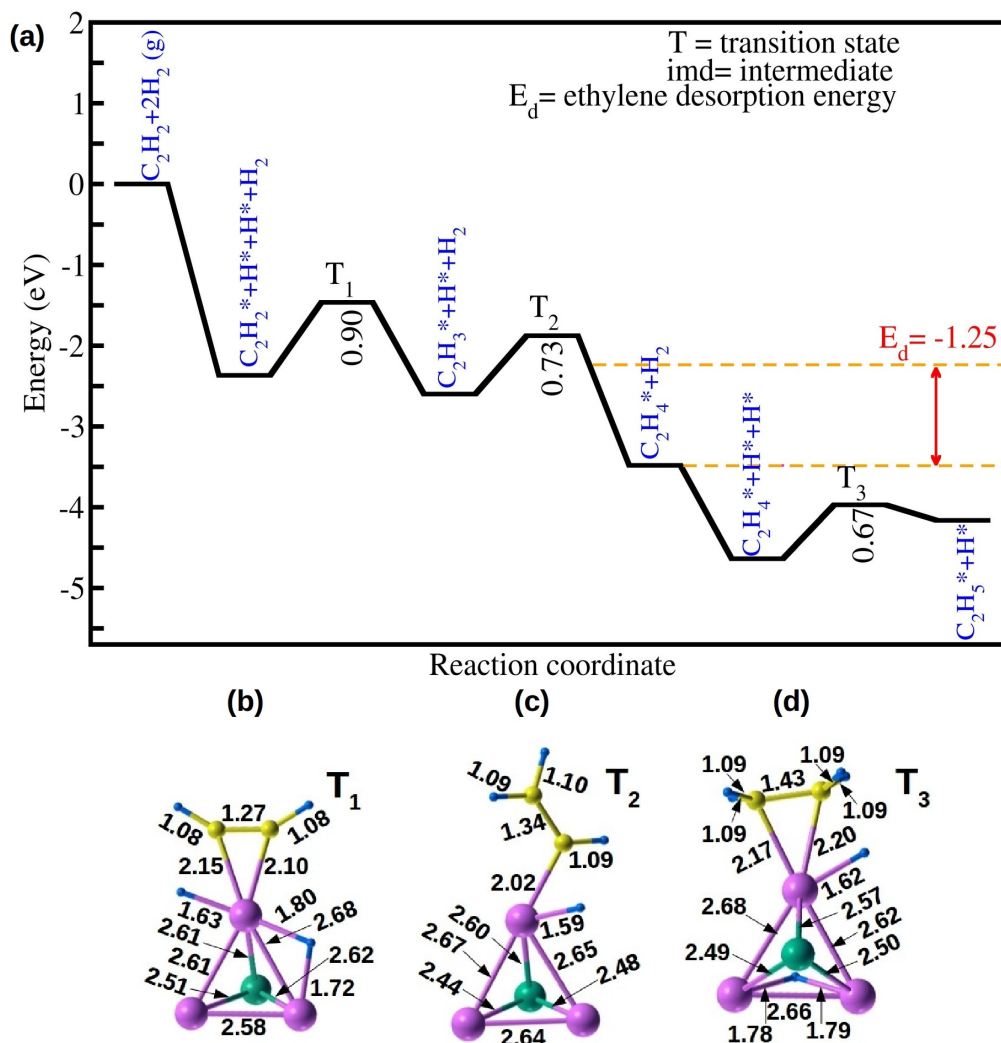


Figure 5.3: (a) Energy profile for the reaction mechanism of hydrogenation of acetylene to ethylene on Pd₃Ga cluster. (b)-(d) show the structure of the transition states for the different reaction steps. The bond lengths are given in Å.

In the reaction process one of the H atom moves to form ethyl while the other H atoms move to a Pd-Pd bridge site formed by the Pd atoms not attached to ethyl. Ethyl binds on the Pd₃Ga cluster forming a Pd-C σ bond. The reaction involves a barrier of 0.67 eV and the corresponding transition state (T_6) is shown in Figure-5.3 (g).

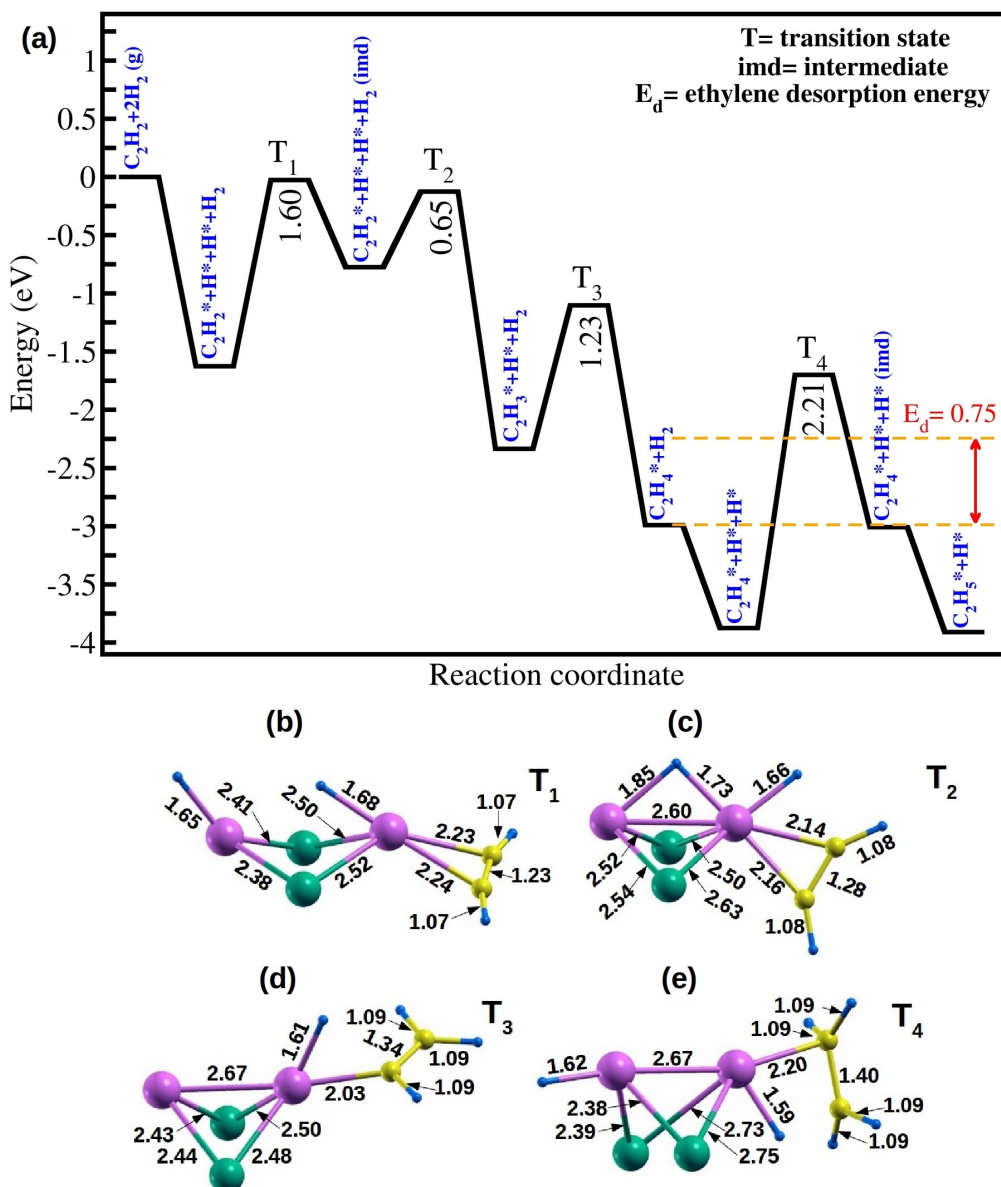


Figure 5.4: (a) Energy profile for the reaction mechanism of hydrogenation of acetylene to ethylene on Pd_2Ga_2 cluster. (b) shows the structure of the intermediate step through which the second hydrogenation occurs. (c)-(e) show the structures of the different transition states. The bond lengths are given in Å.

The reaction profile and the transition state (T_4) on Pd_2Ga_2 is shown in Figure-5.4 (a) and (e) respectively. Further hydrogenation involves a barrier of 2.21 eV. We note that on Pd_3Ga the desorption barrier is about 1.25 eV while on Pd_2Ga_2 it is 0.76 eV. Comparing these desorption barriers with the hydrogenation barriers, we find that both on Pd_4 and Pd_3Ga , further hydrogenation of ethylene to form ethyl is easily feasible. On the other

hand on Pd_2Ga_2 , the barrier for further hydrogenation is almost thrice than that of ethylene desorption. Hence we conclude that in the gas phase the Pd_2Ga_2 cluster will exhibit high selectivity towards the selective hydrogenation of acetylene to ethylene.

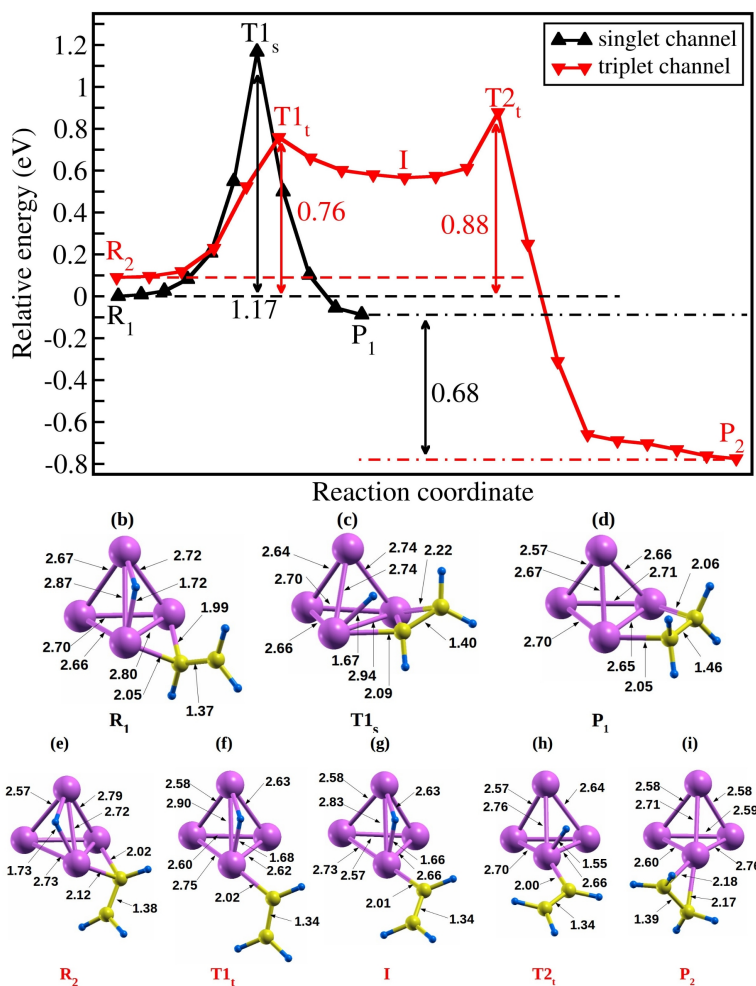


Figure 5.5: (a) Energy profile for vinyl to ethylene conversion on Pd_4 cluster through singlet and triplet spin channels. (b) and (e) show the structure of the IS in singlet and triplet configurations respectively. (c) shows the structure of the TS in the singlet channel while (f) and (h) show the TS in the triplet channel. (g) shows the structure of the intermediate step. (d) and (i) show the structure of the FS in singlet and triplet configurations respectively. The bond lengths are given in Å.

Table 5.2: Activation barriers (in eV) for different steps of hydrogenation of acetylene to ethylene on the Pd_xGa_y clusters. The ZPE corrected barriers are given in parenthesis.

Reaction Step	Pd_4	Pd_3Ga	Pd_2Ga_2
$\text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_3$	0.77 (0.72)	0.90 (0.89)	1.60 (1.51)
$\text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_4$	0.88 (0.88)	0.69 (0.66)	1.23 (1.22)
C_2H_4 desorption energy	1.22 (1.17)	1.25 (1.20)	0.76 (0.70)
$\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5$	0.79 (0.78)	0.67 (0.67)	2.21 (2.16)
$\Delta E_{\text{selectivity}}$	+0.43 (+0.39)	+0.58 (+0.50)	-1.45 (-1.46)

5.4 Outlook and summary

In the present work, we have studied the selective hydrogenation of acetylene on small Pd_xGa_y tetramers. As we move from Pd_4 to Pd_2Ga_2 , the binding of acetylene to the clusters is reduced as evident from the binding energies. Based on the energy pathways for acetylene hydrogenation, we have noticed that with the more Ga substitution for Pd atoms, there is a rise in the activation energy of acetylene to vinyl conversion. Nonetheless there is no such consistent trend noted for vinyl to ethylene conversion. Hydrogenation on Pd_4 proceeds via spin flip from singlet to triplet state in the IS followed by hydrogenation of vinyl to ethylene. While on the bimetallic clusters, the rate limiting step for the hydrogenation is the conversion of acetylene to vinyl, on Pd tetramer it is the conversion of vinyl to ethylene. Amongst the clusters considered in this study, only the stoichiometric bimetallic Pd_2Ga_2 shows highest selectivity. However it exhibits poor reactivity compared to Pd_4 and Pd_3Ga .

At this point it would also be interesting to compare the energetics of the hydrogenation reaction on these clusters with the Pd-Ga surfaces. On Pd-Ga surfaces, the diffusion of H atoms to come close to reactants is the rate limiting step during the course of hydrogenation of acetylene to ethylene. Similarly, for the clusters considered in this study, we find that the rate limiting steps are primarily the diffusion of the H atoms from their most stable adsorption sites to the reactants so that the hydrogenation reaction can proceed.

We also note that the clusters are in the gas phase while in practise these are usually on some oxide support. Hence further investigations will be needed, which will tell us how the above results change when the clusters are put on support.

Chapter 6

Adsorption of cyclododecadiene (CDD) on different Pd(100) surface models

6.1 Introduction

Amongst the wide variety of selective hydrogenation reactions of polyunsaturated alkynes to alkenes, conversion of 1,5,9-c,t-cyclo-dodecatriene (CDT) to cyclo-dodecene (CDE) is important for the synthesis of laurilactam, which is used in the production of Nylon-12. This used to be typically carried out by the conversion of CDT to cyclododecane (CDA) followed by oxidation to cyclododecanone (CDO). However, the selectivity of this oxidation is about 80%. Wilke *et al.* showed an alternative route in which CDT is selectively hydrogenated to CDE, followed by epoxidation of CDE by H_2O_2 and transformation to cyclododecanone (CDO). [125] While the epoxidation and transformation reactions can be carried out with 100% selectivity, the most challenging part is to selectively hydrogenate CDT to CDE.

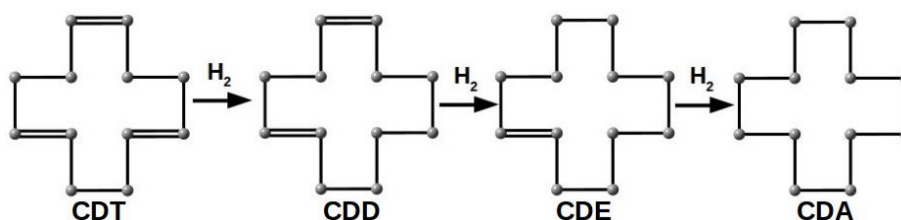


Figure 6.1: Schematic representation of catalytic hydrogenation of cyclo-dodecatriene (CDT) to cyclo-dodecadane (CDA)

Usually Pd is commercially used as a catalyst for this reaction. Though Pd shows high reactivity, it exhibits very poor selectivity. Hence there have been efforts over the last several years to modify the catalysts and the reaction conditions to improve the selectivity.

ity. Patent application by McAllister as early as in 1968 claimed a CDE yield of 90% by using a powdered catalyst comprising of 5% Pd on charcoal and by stepwise reduction of the hydrogen partial pressure. [126] Nevertheless, the claims made by McAllister could not be reproduced using the same catalyst and similar reaction conditions. Using Pd supported on alumina, Wießmeir *et al.* achieved a CDE yield of 88%. [127] Unfortunately in their case the average reaction rate was extremely low for an industrial application.

Based on kinetic modelling using a Pd/Al₂O₃ catalyst in a slurry reactor and experiments in a range of hydrogen partial pressure, Benaissa *et al.* have observed that the yield of CDE increases with decrease in hydrogen partial pressure. [128] They found that it was crucial to include the reversible isomerization reactions in their model suggesting that probably reversible isomerization reactions play an important role. They also reported that the fraction of 1,5-c,t-CDD is always higher than 1,5-t,t-CDD. We note that this is in contradiction with more recent experiments performed by Gaube *et al.* [129] They have used a Pd/Al₂O₃ catalyst of egg-shell type and has performed liquid phase hydrogenation. They obtained a CDE yield of about 93%.

From the above discussions, we find that though the yield percentage and selectivity varies depending on the choice of catalysts, reaction conditions etc., there are some consensus regarding the overall nature of the reaction. Firstly, the reaction proceeds via CDT→CDD→CDE→CDA as shown schematically in Figure-6.1. Secondly, with a decrease in hydrogen partial pressure, there is an increase of CDE selectivity and this has been traced back to the increased rate of the isomerization of t,t and c,t-CDD to the more strongly adsorbed c,c-CDD. However, the hypothesis of increased rate of isomerization is primarily based on Hartree-Fock based gas phase study of the energetics as a function of the angle between the double bonds of 1,5-c,t-CDD. This energetics on a real catalyst may be different. Hence there is a need to have a microscopic understanding of what is actually happening during the reaction. However, to the best of our knowledge there is no such study available till date. As a first step to understand this, in this work we have studied the adsorption of 1,5-CDD (different isomers) on Pd(100) catalyst. Moreover, real life catalysts are large nanoparticles supported on oxide materials. These not only have different facets but also have active sites with varying coordination number due to presence of step edges and kinks. To model these and to understand how the binding of CDD is sensitive to the coordination number of the Pd atoms we have looked into CDD

adsorption on flat, stepped and Pd adatom on the flat surface. Further, the hydrogenation reaction happens in presence of hydrogen coadsorbed with the molecule and one of the factors that affect the selectivity is how strongly CDD is bind to the catalyst in presence of hydrogen (desorption barrier). To understand the effect of hydrogen partial pressures on the adsorption of CDD, we have looked into the CDD adsorption on these surfaces at different hydrogen coverages.

In Section 6.2 we provide the computational details. In Section 6.3.1 we describe the structures of the different model catalysts both in presence and absence of hydrogen. In Sections 6.3.2 and 6.3.3 we describe the energetics and adsorption geometries of the different isomers of 1,5-CDD on the clean and hydrogen covered surfaces respectively. Finally we discuss our results in context of the experimental observations and conclude in Section 6.4.

6.2 Computational details

The calculations are done using Quantum Espresso software. [41] Ultrasoft pseudopotentials are used to describe the electron-ion interactions. [42] The electron-electron exchange and correlation are described using the Perdew, Burke, and Ernzerhof parameterization of the generalized gradient approximation (GGA-PBE). [9] To speed up the convergence we have used a Marzari-Vanderbilt smearing, with a smearing width of 0.03 Ry. [20] We have used a kinetic energy cutoff of 30 Ry and 300 Ry for wavefunction and charge density respectively. The Brillouin Zone integration are done using the Γ point.

In order to understand the effect of reduced coordination number of Pd atoms on the adsorption of cyclododecadiene (CDD), we have considered three model surfaces, namely (a) Pd (100) flat surface, the surface Pd atoms have a nominal coordination number of 8, (b) Pd-(S)[7(100)x(111)] surface ('S' denotes stepped surface, '7(100)' denotes seven atoms wide 100 terrace and (111) denotes the 111 step) with the Pd atoms at the step having a nominal coordination number of 7 and (c) Pd adatom on the Pd(100) surface, the adatom have a coordination number of 4. Further, during the hydrogenation reaction, the surfaces are typically covered with atomic H. This also affects the binding of CDD on the surface. To understand how weakly/strongly CDD binds to the hydrogen covered Pd(100) surfaces, we have also calculated the adsorption energy of CDD on hydrogenated

Pd surfaces. For the flat surfaces, we have considered hydrogen coverages of 0.25, 0.5 and 1.00 ML (1 ML denotes that for every Pd atom there is one H atom). On the stepped surface and on the Pd adatom we have studied how the binding of CDD changes when the step and the adatom is covered with H respectively. Each of these surfaces are represented by an asymmetric slab of four layers of which the bottom two are kept fixed at bulk inter planar distance. The adatom and terrace are added on these four layered slab.

In order to test the pseudopotentials used in the calculations we computed the energetics of CDD in the gas phase and the lattice parameter of bulk Pd. CDD, a cyclic alkene, consists of two C=C bonds. Depending on the orientation of the C-H bonds, it can have three isomers: (i) *cis-cis*, where for both the double bonds, the C-H bonds are on the same side, (ii) *cis-trans*, where for one of the C=C bonds, the C-H bonds are on the same side while for the second one they are on the opposite side and (iii) *trans-trans*, where for both the C=C bonds, the C-H bonds are on the opposite sides. In order to calculate the energetics of the different isomers we placed them in a box having dimensions of $20 \times 20 \times 21$ (in Å). This ensures a minimum distance of 12.6 Å between the periodic images that we find sufficient to minimize the spurious interaction between them. The relaxed geometries and their relative energies are shown in Figure-6.2. We find that the *trans-trans* and *cis-trans* isomers (Figure-6.2(a) and (b) respectively) are isoenergetic with C=C bond length of about 1.34 Å. The *cis-cis* isomer is higher in energy than the other two isomers by about 0.28 eV. For bulk Pd we obtain a bulk lattice parameter to be 3.97 Å which is 2% larger than the experimental value of 3.89 Å [130] and is in excellent agreement with the calculated value (3.95 Å) from other GGA based DFT calculations. [131]

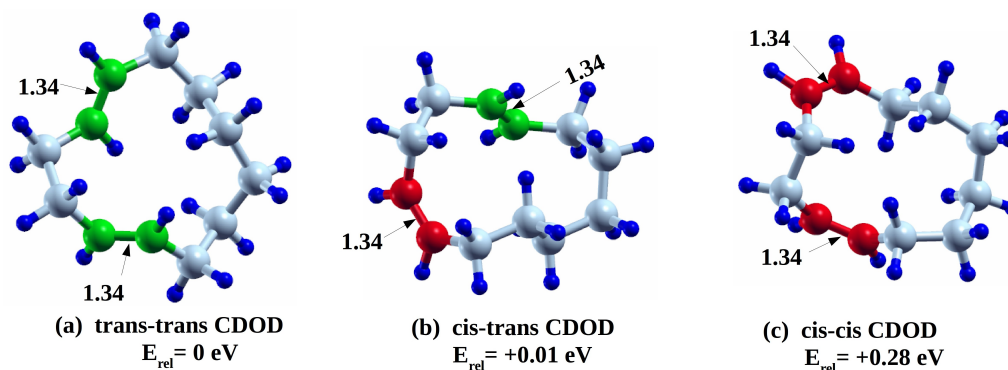


Figure 6.2: Different conformers of cyclo-dodecadiene in the gas phase.

In order to study how the stability of the different surfaces are affected by hydrogen partial

pressure and temperature, we have computed the change in free energies of the different surfaces ($\Delta G(p, T)$) with respect to the clean flat one at different temperatures (T) and hydrogen chemical pressure (p). $\Delta G(p, T)$ is given by:

$$\Delta G(p, T) = \frac{E_{sur} - E_{flat-clean} - n_{Pd}E_{bulk}^{Pd} - \frac{1}{2}n_H(E_H + RT - TS(T, p^0) + RT * \ln(p/p^0))}{ns}, \quad (6.1)$$

where, E_{sur} , $E_{flat-clean}$ and E_{bulk}^{Pd} are the total energies of the surface under study, the clean flat Pd surface and bulk Pd respectively. n_{Pd} is the difference between the number of Pd atoms in the slab and the clean flat surface and n_H is the number of hydrogen molecule. ns denotes the number of (1×1) unit cells present in the slab to model the surface. R denotes the universal gas constant. We note that we have neglected the effects of pressure, temperature and entropy on the slabs.

6.3 Results and discussion

6.3.1 Clean and hydrogen covered surfaces

6.3.1.1 Clean Pd surfaces

The relaxed structures of different surface models of Pd(100) surface are shown in Figure-6.3(a). Due to the reduction in coordination number of the surface atoms on creation of the (100) surface, the top two layers relax inwards with 1.7 and 1.5 % contraction of the interplanar distances compared to that of bulk. For the stepped surface there are three interplanar distances: (a) between the layer forming the terrace and the one below (d_{st1}), (b) between the layer below the terrace and the second layer of the slab (d_{12}) and (c) between the second and the third layer of the slab (d_{23}). The d_{t1} contracts inwards by about 3.9 % compared to that of the bulk. d_{12} and d_{23} shows a contraction of 6% each with respect to the bulk interplanar distance. We note that the contraction of the interplanar distances are larger than that of the flat (100) surface. Moreover, the in plane Pd-Pd bond lengths of the terrace varies between 2.75 and 2.81 Å. The Pd atoms forming the (111) step has a bond length of 2.78 Å. The adatom on the Pd(100) surface occupies a hollow site with Pd-Pd bond lengths of 2.66 Å. The contraction in the interplanar distances are similar to that observed in case of Pd(100) surface.

6.3.1.2 Hydrogenated surfaces

Since it is well known that atomic H binds dissociatively to the hollow sites, on the Pd(100) surface, we have considered H adsorbed at the hollow sites at coverages of 0.25, 0.50 and 1.00 ML. The adsorption energy of the H₂ is defined as:

$$E_b = \frac{E_{nHPd} - E_{Pd} - \frac{n}{2}E_{H_2}}{n/2}. \quad (6.2)$$

Here, E_{nHPd} is the energy of the Pd surface with ‘ n ’ hydrogen atoms adsorbed, E_{Pd} is the energy of the clean Pd surface and E_{H_2} is the energy of the hydrogen molecule in gas phase.

The H binding energies on the flat surface at the above mentioned coverages are -1.02, -1.08 and -0.99 eV/H₂ molecule respectively. The Pd-H distances are about 1.99 Å. Our results suggests that strength of the interaction between H and the flat surface is independent of the H coverage. We note that our results are consistent with that reported by Gladys *et al.* [132]. They also observed that as the hydrogen coverage increases the vertical adsorption height of hydrogen decreases. From our calculations, we have obtained the vertical adsorption heights of hydrogen to be 0.30 Å, 0.22 Å and 0.20 Å for 0.25, 0.50 and 1.00 ML respectively. We find that our results are also in excellent agreement with the experimentally measured value of -1.06 eV for 1ML H coverage on Pd(100) surface. [133] Similar adsorption energy and structural changes as a function of hydrogen coverage on Pd surfaces have been reported in other studies [134, 135].

At the step edge on the stepped surface, hydrogen atoms can adsorb on top, bridge and hollow sites. Amongst the hollow sites there are two possibilities, namely the fcc (have a Pd atom from the layer below the terrace, pink atom, triangle down in Figure-6.3(f)) and the hcp (Pd atom from the second layer of the slab, grey atom, triangle up in Figure-D2(a) of Appendix D) sites. Our calculations predict that when the step is fully covered with hydrogen, H has an equal probability to bind to either of these sites. The binding energy being about -0.94 (fcc) and -0.93 eV per hydrogen molecule (hcp). The Pd-H bond distances are about 1.81 Å.

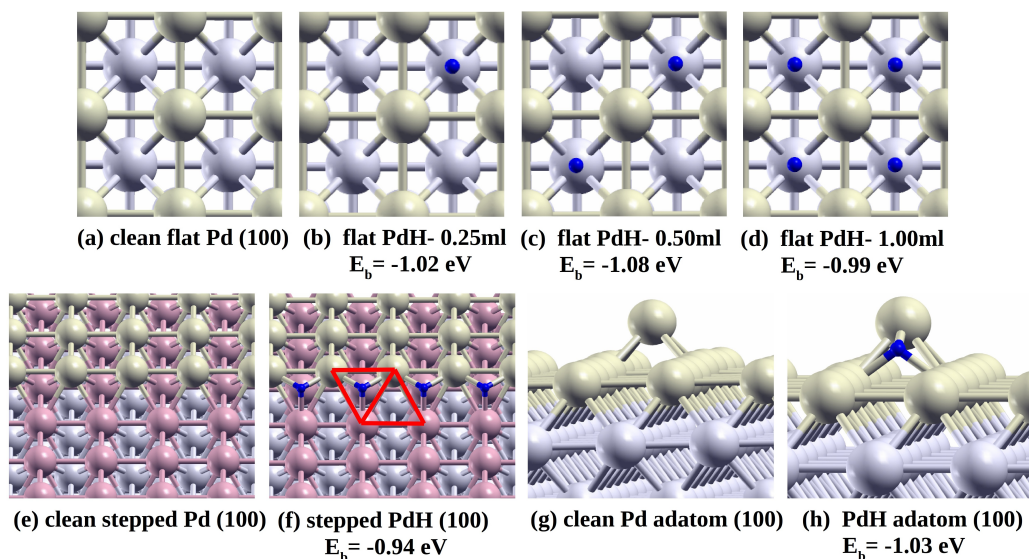


Figure 6.3: Optimized geometries of the different model catalysts used in this study.

The Pd atoms at the fcc triangle have an isosceles geometry having a shortest bond length of 2.81 Å (top terrace Pd atoms) and a longer one of 2.84 Å at the Pd atoms present on Pd(111) step. Similarly, in the *hcp* site, the Pd atoms form an isosceles triangle of Pd-Pd bond lengths 2.81 Å and 2.87 Å respectively. Similar to the flat surface, there is slight expansion of the top terrace Pd atoms when hydrogen binds in hollow sites and the net interlayer spacing d_{st1} decreases by 3.0% compared to 3.9% in the clean stepped surface. H adsorption on the top site is highly unstable. Upon geometry minimization, we find that H moves to the bridge site Figure-D2(b) of Appendix D. The H binding energy for this configuration is about -0.87 eV and Pd-H bond length is about 1.72 Å.

Similar to the stepped surface, H can bind in three different configurations (top, bridge site and hollow site) on the Pd adatom. Hydrogen binds most strongly at the hollow site (binding energy is -1.03 eV/H₂ molecule). In the hollow site, hydrogen atom makes two bonds with the surface Pd atoms (Pd-H = 1.83 Å) and one bond with Pd adatom having a bond length of 1.75 Å. The binding energy of the bridge configuration is -0.73 eV (Figure-D2(c) in Appendix D). Here, the Pd-H bond lengths are 1.69 Å and 1.70 Å respectively. On the top site binding of hydrogen is thermodynamically unfavorable (Figure-D2(d) in Appendix D).

Figure-6.4 shows how the free energy change of the different surfaces vary as a function of temperature under fixed hydrogen partial pressure. From this we plotted the temperature-

pressure phase diagram of hydrogen adsorption on these surfaces. The plot is shown in Figure-6.5. We find that there are cross-overs of stability of the surfaces depending on the temperature and partial pressure. For example, below 300 K we find that the flat surfaces remains completely covered with H. However, as the temperature is increased H is gradually desorbed and at low H partial pressures the clean surface becomes more stable. Hence depending on T and H partial pressure, the stability of the surfaces change. At this point it would be interesting to compare with the experimental range of temperatures and H partial pressure at which these reactions are carried out. From Ref- [136] we find that these reactions take place between 350-400 K and the H partial pressure is between 10^{-2} to 1.5 bar. Based on our thermodynamic analysis we find that the flat (100) surface with 1ML coverage is the most stable one (denoted by the box in Figure-6.5).

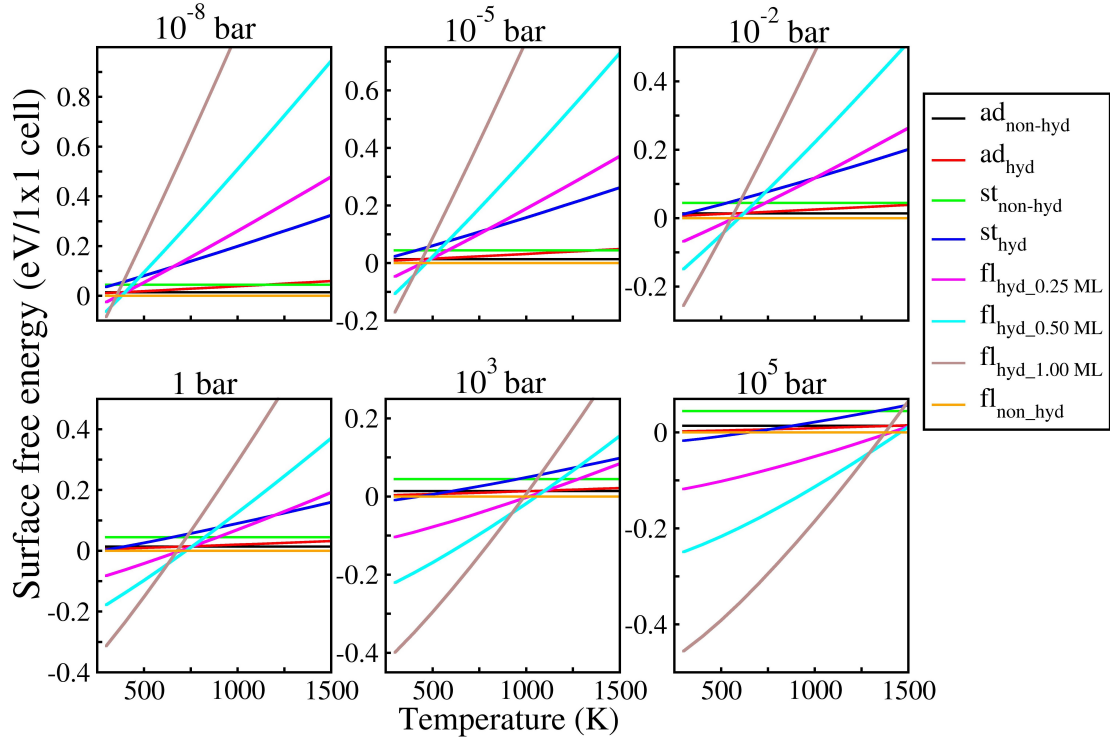


Figure 6.4: Surface energy as a function of temperature (K) under different hydrogen partial pressures for the Pd(100) surface models.

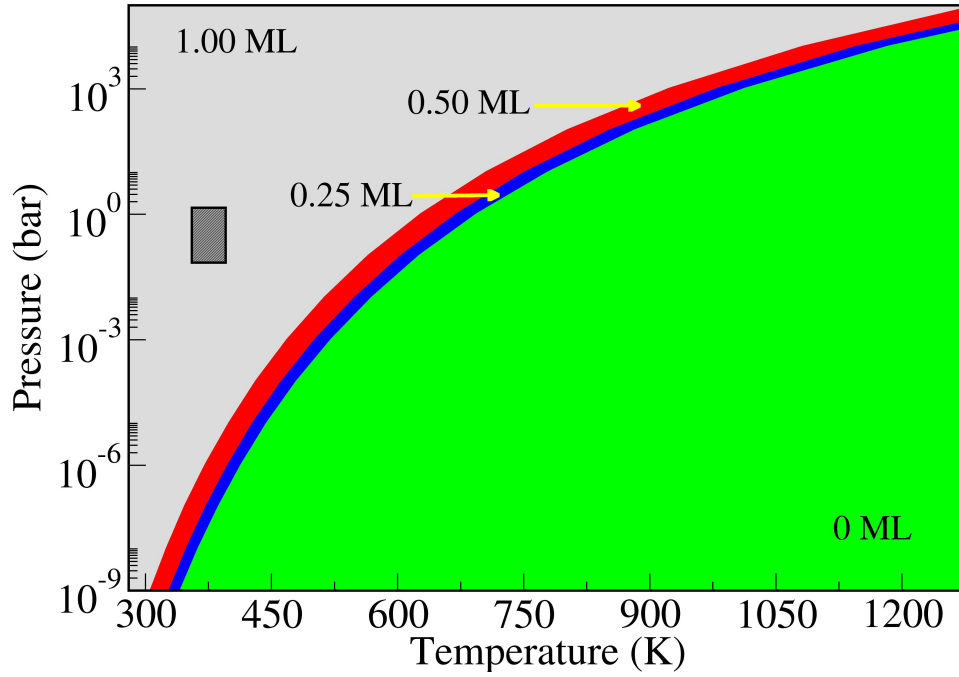


Figure 6.5: Phase diagram of hydrogenated flat Pd(100) surfaces as a function of pressure and temperature.

6.3.2 Adsorption of cyclo-dodecadiene (CDD) on Pd(100) surfaces

Earlier studies of adsorption of hydrocarbons (alkanes/alkenes/alkynes) on the transition metal surfaces show that they typically bind in two configurations: (a) di- σ bonding, where two C atoms bind to two Pd atoms forming two Pd-C σ bonds and (b) π -bonding where a single Pd atom binds to two C atoms [121, 137–140]. In order to determine the lowest energy configurations of the different isomers of CDD on the surfaces considered in this study, we have restricted ourselves to initial starting configurations where the molecule is bound in either of the two binding modes mentioned above. This is followed by geometry optimization. During the geometry optimization process we find that the molecule moves, rotates and undergoes large structural distortions. This gives us confidence that the molecule have explored a significant part of the potential energy surface before reaching the minima. The binding energy of CDD on the Pd catalyst is given by:

$$E_b^{CDD} = [E_{Pd+CDD} - E_{Pd} - E_{CDD(g)}]. \quad (6.3)$$

Here, E_b^{CDD} denotes the binding energy of given CDD on a Pd surface, E_{Pd+CDD} denotes the total energy of the CDD adsorbed Pd surface, E_{Pd} denotes the total energy of the clean

Pd surface, $E_{CDD(g)}$ denotes the total energy of most stable CDD in gas phase. We have used the energy of the *trans-trans* CDD as our reference for gas phase total energy of CDD.

Table 6.1: Binding energies (in eV) and different bond lengths (in Å) for the lowest energy structures of CDD adsorbed on different Pd surfaces. $d_{C=C}$ denotes the C=C bond length. The superscript ‘*int*’ denotes the C=C bond that is interacting with the catalyst. d_{Pd-C} denotes the Pd-C bond length.

Surface + molecule	most stable conformer	E_b^{CDD}	$d_{C=C}^{int}$	$d_{C=C}^{non-int}$	d_{Pd-C}
flat Pd	<i>cis-cis</i>	-0.55	1.36, 1.40	-	2.22, 2.28, 2.41
stepped Pd	<i>cis-trans</i>	-1.00	1.43	1.34	2.16, 2.19
Pd adatom	<i>cis-trans</i>	-1.06	1.40	1.34	2.19, 2.23
flat PdH (1.00ML)	<i>cis-trans</i>	+0.01	-	1.33, 1.34	-
flat PdH(0.50ML)	<i>trans-trans</i>	-0.19	-	1.33, 1.33	-
flat PdH(0.25ML)	<i>trans-trans</i>	-0.23	-	1.33, 1.33	-
stepped PdH	<i>trans-trans</i>	-0.63	1.39	1.34	2.26, 2.32
PdH adatom	<i>cis-trans</i>	-1.07	1.39	1.34	2.21, 2.23

6.3.2.1 Flat Pd(100) surface

Among the different possible adsorption configurations of the CDD isomers considered in this study, we find the *cis-cis* to be the most stable isomer on the clean flat Pd(100) surface (Figure-6.6(a)) with a binding energy of -0.55 eV. The molecule forms a horizontally lying S-like structure where the two *cis* C=C bonds acts as anchors to the surface. Further we also note that the double bonds are not parallel to the surface. The C=C bond that is closer to the surface (Pd-C distances of 2.22 and 2.28 Å) makes an angle of about 29.2° with the surface, while the second one (Pd-C distances of 2.41 and 3.24 Å) makes an angle of about 33.0°. The bond lengths of both the C-C double bond increases compared to that in the gas phase bond length of 1.34 Å. While for the C=C bond closer to the surface the bond length increases to 1.40 Å, for the one further away from the surface, the bond length increases to 1.36 Å. This suggests a strong interaction between the surface and the CDD. This is further corroborated by the charge transfer (CT) analysis(Figure-6.7(a)) and density of states (DOS) plot(Figure-6.7(b)).

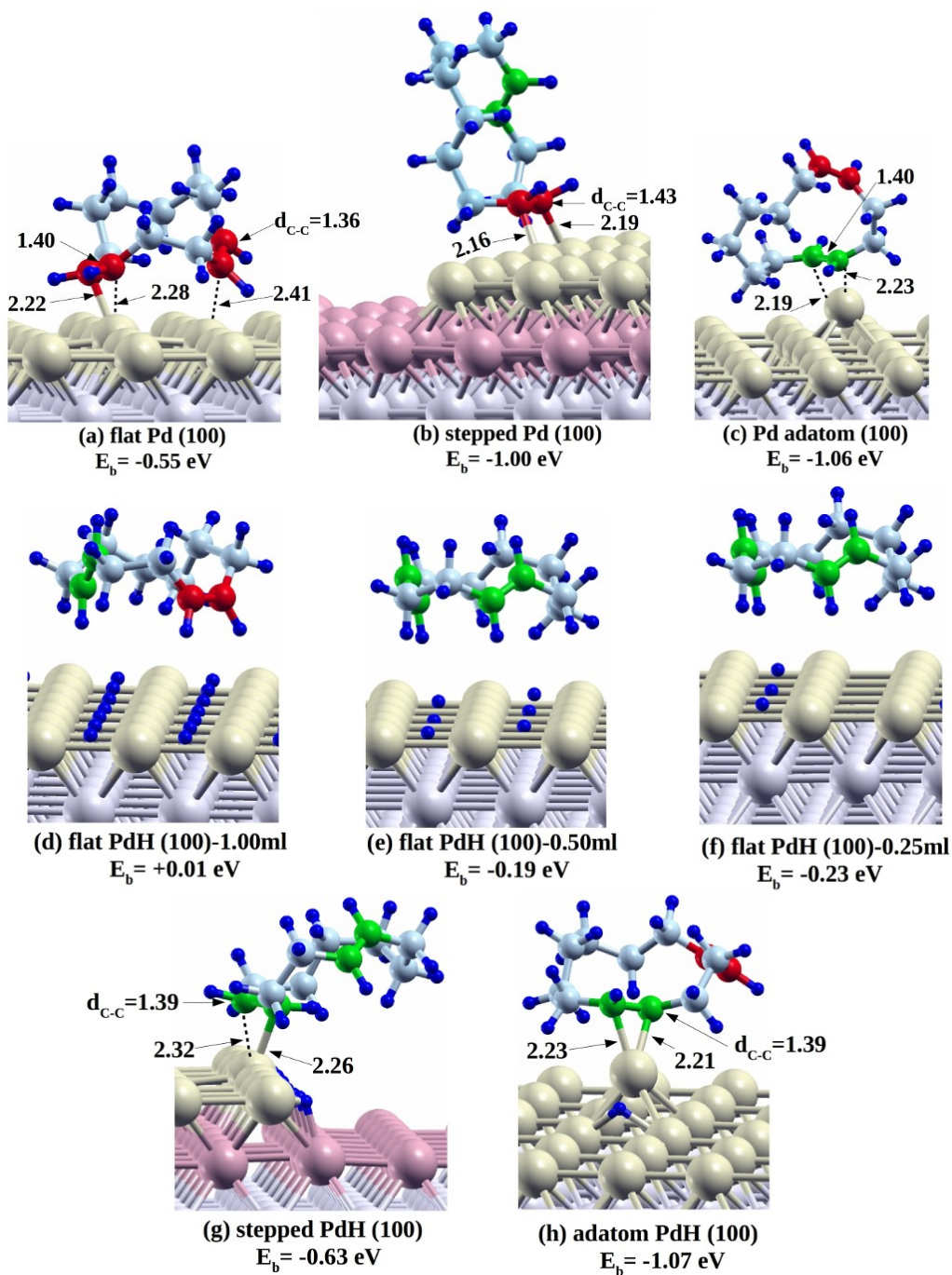


Figure 6.6: Lowest energy structures of adsorption of CDD on the non-hydrogenated and hydrogenated Pd(100) surface models. The red and green spheres denote the *cis-cis* and *trans-trans* C=C bond respectively while each Pd layer is shown with a different colored spheres. Same color notation is used in the rest of the structures.

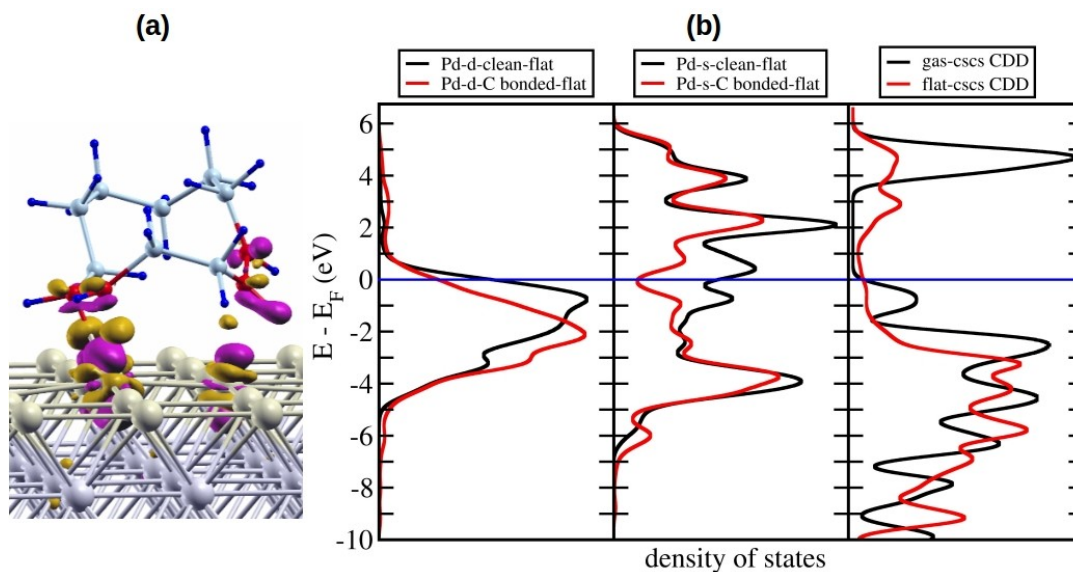


Figure 6.7: (a) Isosurface showing charge transfer (CT) plot between CDD and flat Pd. Yellow (pink) lobes denote the charge accumulation(depletion). (b) Density of states (DOS) of the CDD adsorbed on flat Pd surface.

We find that there is transfer of charge to and from the molecule. In gas phase CDD, the highest occupied molecular orbitals (HOMO) is primarily localized on the two C=C bonds and the C-C bond connecting these two double bonds (Figure-D1(a) of Appendix D). While on the double bonds it is π -bonding type, on the single bond it is σ -bonding type. The wavefunction corresponding to the lowest unoccupied orbital (LUMO) is π -antibonding type and is localized on the two C=C bonds (Figure-D1(d) of Appendix D). Upon adsorption on the surfaces, we find that there is donation of electrons from the surface to the LUMO of the molecule and back donation from the HOMO of the molecule to the Pd- d states. This d - π donation and back-donation results in a net transfer of 0.43 electrons from the molecule to the surface (Figure-6.7(a)). This is corroborated by the downward shift of the Pd- d states as observed in the DOS plot in Figure-6.7(b). Further, the interaction between the molecule and the surface gives rise to new states at about -3.22 eV below the Fermi energy and 2.89 eV above the Fermi energy (Figure-6.7(b)). The other two conformers, i.e. the *cis-trans* and the *trans-trans* are about 0.20 and 0.18 eV higher in energy than *cis-cis* conformer. Their structure and geometry are shown in Figure-D3(a) and D3(b) of Appendix D.

6.3.2.2 Stepped Pd surface

On the stepped surfaces, since the Pd atoms at the step edges are least coordinated (nominal coordination number 7), it is expected that CDD will bind preferentially at the step edges. Among the different isomers and their configurations, we find that the *cis-trans* isomer in which the *cis* C=C bond binds to the Pd atoms at the step edge is the most stable one with a binding energy of -1.00 eV. Similar to the flat surface, on the step edge the molecule binds in a di- σ mode. However, in contrast to that of the flat surface where the molecule lies horizontally on the surface, here the molecule prefers to stay vertical. The shorter Pd-C bond lengths of 2.16 and 2.19 Å compared to that on the flat surface suggests a stronger interaction with the Pd atoms. This is consistent with the significantly larger binding energy of the molecule at the step edge compared to the flat terrace. Further the *cis* C=C bond length increases enormously to 1.43 Å (suggesting that much of its double bond character is lost) compared to that of 1.34 Å in the gas phase and 1.40/1.36 Å on the flat surface. The *trans* C=C bond length remains unchanged. Similar to that of the flat surface, here also we find both donation (from HOMO of molecule) and back donation (to LUMO of molecule) of electrons resulting in a net loss of about 0.44 electrons from the molecule (Figure-6.8(a)). The DOS plot in Figure-6.8(b) displays notable rehybridization of the Pd-*d* states as well as the Pd-*s* states. The relative energies of the other isomers with respect to the most stable one is given in Figure-D4 of Appendix D. In contrast to the *cis-trans*, the *cis-cis* isomer binds to the steps in a π -configuration and is about 0.15 eV higher in energy. The *trans-trans* isomer is about 0.19 eV higher in energy than the most stable configuration reported in the previous paragraph.

6.3.2.3 Pd adatom on the (100) surface

Since the Pd adatom is the lowest coordinated one (nominal coordination of 4), it is expected that CDD will bind preferentially to the adatom than to the other surface Pd atoms. Hence, as our starting configurations, we have considered two possibilities for each of the isomers where one of the double bonds is placed near to the Pd adatom. This results in six configurations in which CDD can bind to the Pd adatom. Amongst these we find the *cis-trans* isomer to be most stable with a binding energy of about -1.06 eV. Unlike the stepped surface where the *cis* double bond showed a preference towards binding to the step edge over the *trans* double bonds, for the adatom the selectivity is lost. We find that both the C=C bonds (*cis* and *trans*) bind to the Pd adatom with a binding energy of -1.06 eV.

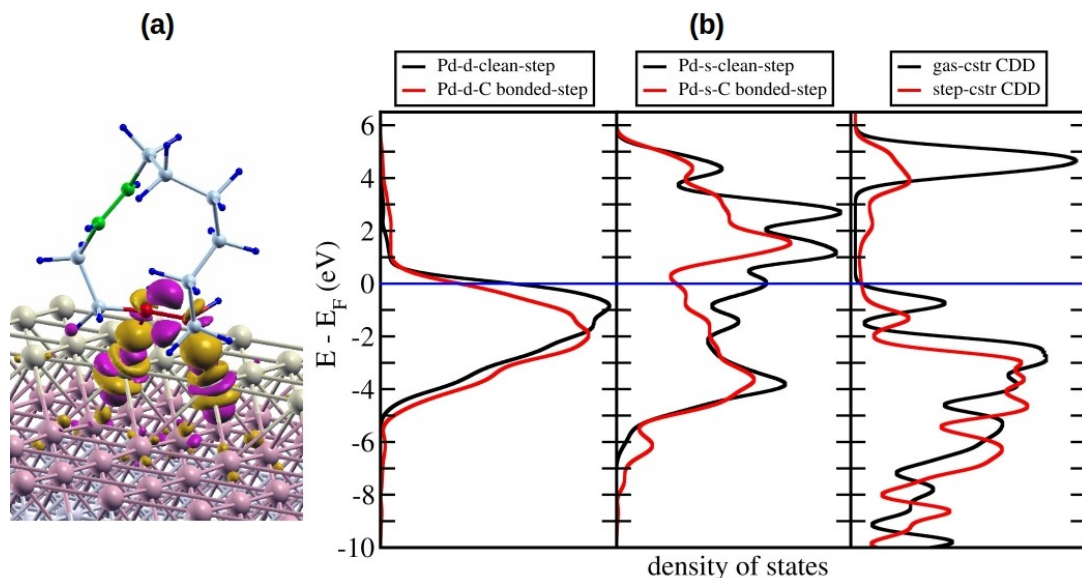


Figure 6.8: (a) Isosurface showing charge transfer (CT) plot between CDD and stepped Pd surface. Yellow (pink) lobes denote the charge accumulation(depletion). (b) Density of states (DOS) of the CDD adsorbed on stepped Pd surface.

CDD binds in a π -configuration with Pd-C bond lengths of about 2.19 and 2.23 Å for the *trans* C=C bond and 2.23 and 2.22 Å for the *cis* C=C bond. In both the cases, the C=C bond length is increased to 1.40 Å. Analogous to the flat surface the molecule lies horizontally on the surface. However, in this case the second C=C bond does not interact with the surface. The interaction of the molecule with the Pd adatom also results in elongation of the Pd-Pd bond lengths between the Pd adatom and those on the surface layer. Like the other two surfaces, here also we see d - π donation and back-donation of charges resulting in a net positive charge on the molecule with a loss of 0.46 electrons (Figure-6.9(a)).

In addition to the two above mentioned conformers of the *cis-trans* we find a configuration of the *trans-trans* isomer (Figure-D5(b) in Appendix D) to be only 0.02 eV higher in energy compared to the *cis-trans*. Moreover the *cis-cis* isomer (Figure-D5(d) in Appendix D) is only 0.25 eV higher in energy than the *cis-trans*. This suggests that unlike the other surfaces, it is possible to stabilize more than one isomer on the Pd surfaces in presence of an adatom.

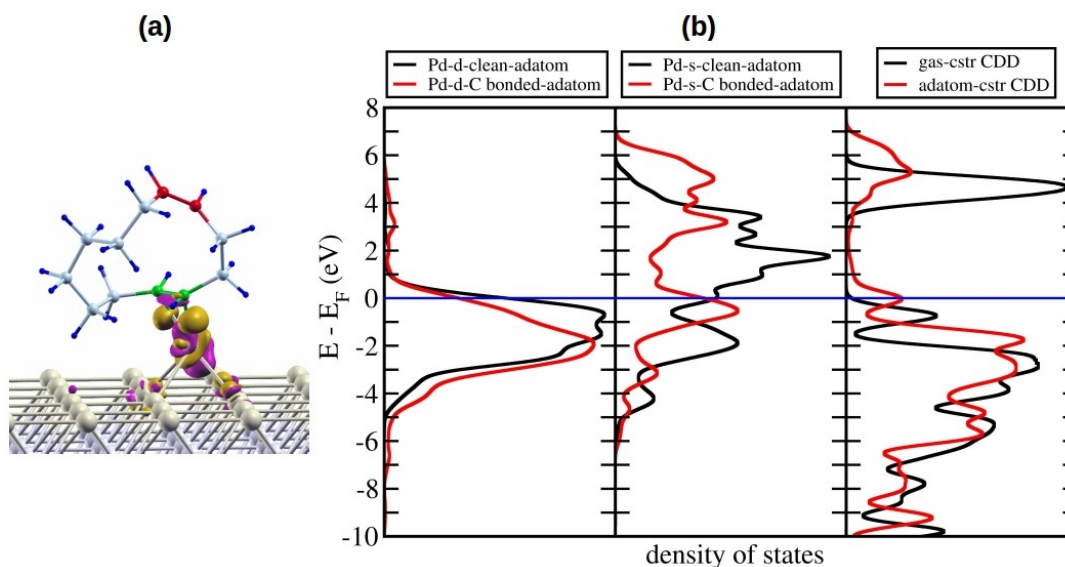


Figure 6.9: (a) Isosurface showing charge transfer (CT) plot between CDD and Pd adatom. Yellow (pink) lobes denote the charge accumulation(depletion). (b) Density of states (DOS) of the CDD adsorbed on Pd adatom.

6.3.3 Adsorption of cyclo-dodecadiene (CDD) on hydrogenated Pd surfaces

Since the selective hydrogenation reaction proceeds in presence of hydrogen adsorbed on the surface, in this section we present our results on the changes in the CDD-surface interactions when the surfaces are covered with H. For each conformer, we have prepared different initial structures by putting each of the two double bonds close to hydrogen for each kind of surfaces.

6.3.3.1 Flat Pd (100) surface

On the flat surface, in presence of 1.00 ML of hydrogen we find that adsorption of the CDD isomers are not thermodynamically favourable (Figure-6.6(d)-(f)). This is because of the steric repulsion experienced by the molecule due to the H atoms present on the surface as the molecule comes closer to the surface. Among the different isomers we find that the *cis-trans* is the lowest in energy with a binding energy of +0.01 eV. As the surface hydrogen coverage is reduced, we find that different CDD isomers starts to interact *weakly* with the surface. For example at 0.50 ML and 0.25 ML H coverages, the *trans-trans* isomers are stable with binding energies of -0.19 and -0.23 eV respectively. We

note that this is almost half the value observed on the clean (0 ML hydrogen) Pd(100) surface. Further, we do not find any significant changes in the C=C bond lengths of CDD compared to that in the gas phase.

6.3.3.2 Stepped Pd(100) surface

Covering the step edge with H not only results in weakening of the CDD binding to the step edge but also alters the stability of the isomers. While on the clean stepped surface we find that the *cis-trans* isomer is most stable, on the hydrogen covered stepped surface, *trans-trans* isomer is most stable with a binding energy of -0.63 eV (Figure-6.6(g)). The molecule adsorbs in a di- σ mode with Pd-C bond lengths of 2.32 and 2.26 Å. These are about 7.4 and 4.6% longer than the shortest Pd-C bond observed on the clean stepped surface. On the hydrogen covered surfaces the C=C bond is 1.39 Å. Here also there is both donation and back-donation of charges from the molecule to the surface resulting in a net positive charge. We find that adsorption of the other isomers are thermodynamically unfavourable when the step is covered with H. These observations are similar to the experimental reports of adsorption of 1,3-butadiene on Pt(111) surface pre-adsorbed with H where Haibo *et al* have shown that the presence of H atoms blocks the chemisorption of the 1,3-butadiene. [141]

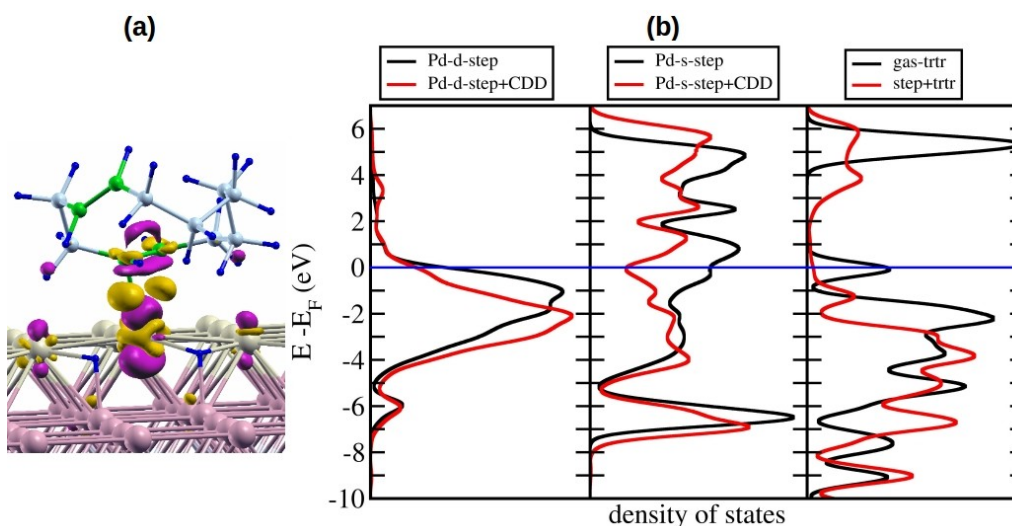


Figure 6.10: (a) Isosurface showing charge transfer (CT) plot between CDD and hydrogenated stepped Pd surface. Yellow (pink) lobes denote the charge accumulation(depletion). (b) Density of states (DOS) of the CDD adsorbed on hydrogenated stepped Pd surface.

Pd adatom on the (100) surface : When we adsorb a hydrogen atom on one of the hollow sites formed by the Pd adatom and the two surface Pd atoms, the *cis-trans* isomer is most stable with a binding energy of about -1.07 eV (Figure-6.6(h)). The *cis* C=C bond binds to the Pd adatom in a π -configuration. The C=C bond length is about 1.39 Å and the Pd-C distances are 2.27 and 2.29 Å. In this case also there is donation and back donation of charges between the molecule and the surface. The CDD molecule becomes positively charged by loss of 0.44 electrons to the Pd surface. In addition to the *cis-trans* isomer, we find the *trans-trans* isomer is only 0.07 eV higher in energy than the former (Figure-D8(b) in Appendix D). In this case also the molecule binds in a π -mode with Pd-C distances of 2.21 and 2.24 Å respectively and the C=C bond is elongated to 1.39 Å.

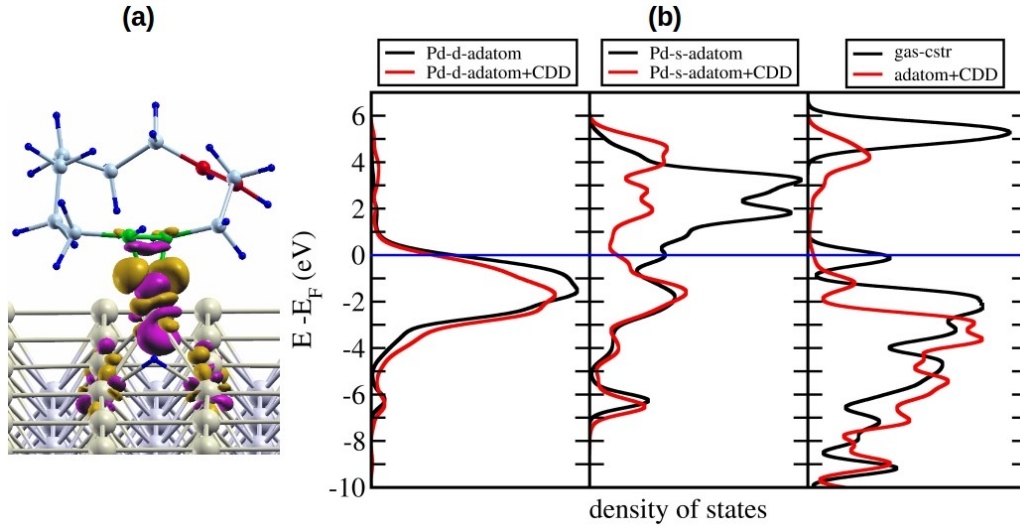


Figure 6.11: (a) Isosurface showing charge transfer (CT) plot between CDD and hydrogenated Pd adatom. Yellow (pink) lobes denote the charge accumulation(depletion). (b) Density of states (DOS) of the CDD adsorbed on hydrogenated Pd adatom.

In order to understand the driving force for the adsorption of the different isomers on the clean and hydrogen covered Pd surfaces and put them in perspective with the experimental observations and hypotheses mentioned in the introduction, we performed an energy decomposition analysis of the adsorption of CDD on the surfaces. The adsorption energy can be decomposed in three parts, namely, the energy gain due to the interaction between the substrate and the molecule (ΔE_{int}), energy cost in the deformation of the molecule in order to bind to the substrate (ΔE_{CDD}) and energy cost in the deformation of the surface

Table 6.2: Energy decomposition analysis (EDA) for the lowest energy structures of CDD adsorbed on each Pd surface models (non-hydrogenated+hydrogenated).

Clean surfaces					
Surface + molecule	ΔE_{int}	ΔE_{CDD}	ΔE_{CDD}^m	ΔE_{surf}	E_b^{CDD}
Pd(100)-Flat + c,c-CDD	-1.77	0.73	1.01	0.22	-0.54
Stepped surface + c,t-CDD	-1.81	0.75	0.76	0.04	-1.01
Adatom + c,t-CDD (t)	-1.47	0.38	0.39	0.02	-1.06
Adatom + c,t-CDD (c)	-1.55	0.45	0.46	0.03	-1.06
Hydrogenated surfaces					
Flat+0.25 ML H + t,t-CDD	-0.25	0.01	0.01	0.01	-0.23
Flat+0.50 ML H + t,t-CDD	-0.21	0.01	0.01	0.01	-0.19
Flat + 1.00 ML H + c,t-CDD	-0.12	0.11	0.12	0.01	0.01
Stepped + H + t,t-CDD	-1.09	0.33	0.33	0.13	-0.63
Adatom + H + c,t-CDD	-1.33	0.20	0.21	0.05	-1.07

in order to bind to the molecule (ΔE_{surf}). The contributions are calculated as follows:

$$\Delta E_{int} = E_{surf+CDD} - E'_{surf} - E'_{CDD}, \quad (6.4)$$

$$\Delta E_{CDD} = E'_{CDD} - E_{CDD}, \quad (6.5)$$

$$\Delta E_{surf} = E'_{surf} - E_{surf}. \quad (6.6)$$

In the equations above E denotes the total energies and E' denote the total energies of the surface and CDD when they are in the same geometry as that in their adsorption geometry. The energy cost associated with the deformation of the molecule needs to undergo, to adsorb on the surface is given by equation-6.5 where E_{CDD} can be the energy of the most stable isomer in the gas phase or the energy corresponding to the relaxed geometry of the isomer in the gas phase that adsorbs on the given surface. For the former, it is denoted by ΔE_{CDD}^m while for the latter, it is denoted by ΔE_{CDD} . Table 6.2 shows the energy decomposition analysis for the different conformers on the surface. In the absence of hydrogen, we find that ΔE_{int} between the molecules and the surfaces are quite large (varying between -1.77 and -1.47 eV). The unexpectedly large interaction energy on the flat Pd(100) surface arises from the fact that the *cis-cis* CDD molecule binds to the surface through both the C=C bonds thereby maximising the interaction energy. In order to do so, the molecule undergoes large distortion such that both the C=C bonds orient almost parallel to the surface. This involves a large energy cost of 0.73 eV (-1.01 eV with respect to the most stable *trans-trans* isomer in gas phase). However, the net energy gain

is significantly larger than the energy cost for structural distortion, thereby stabilising the molecule on the flat surface. Upon hydrogenating the surfaces, we find that on the flat hydrogen covered surface ΔE_{int} reduces significantly. This is due to the steric repulsion the molecule faces as it approaches the surface. However, on the hydrogen covered steps and adatoms we find that ΔE_{int} is still significantly large, though they are slightly reduced compared to the clean stepped surface and adatom. Based on these observations and the fact that the H binding energy is similar on the flat, stepped and adatom surfaces, we hypothesize that in presence of hydrogen the CDD molecules will most probably bind to the step edges or the adatom and these molecules will take part in the hydrogenation reaction.

6.4 Outlook and summary

In summary we have studied the adsorption of cyclododecadiene on flat Pd (100) surface and also on step edges and adatoms present in these surfaces as a first step towards understanding the microscopic mechanism of selective hydrogenation of cyclododecatriene to cyclododecene. While on the flat Pd surface we find the *cis-cis* isomers to be more stable, on the step edges and on adatoms, it is the *cis-trans* isomers that binds preferentially to the surface. The investigations also suggest that as we move from flat Pd $\rightarrow$ stepped Pd $\rightarrow$ Pd adatom, the binding of CDD on the Pd surface is strengthened due to the reduction in the coordination number of the surface Pd atoms. The repulsive interactions between surface hydrogens and the hydrogens attached to the unsaturated double bonds and the saturated bonds bring drastic changes in the chemical reactivity of the CDD on the given Pd surface model. In presence of hydrogen, the interaction of the molecule with the flat surface becomes weak. However, the molecule still interacts strongly with the hydrogen covered steps and adatoms suggesting that in presence of hydrogen, it is the molecules bound to the steps and adatoms will take part in the hydrogenation reaction. Further from the thermodynamic analysis we find that at experimentally relevant H partial pressures and temperature the completely H covered surface is the most stable. However, on this surface the molecule does not bind. Hence, our calculations suggest that the reactions are primarily taking place at the step edges and/or the adatoms that are covered with H.

Appendix A: Effect of semihydrogenation of graphene supported on fcc Co(111)

Similar to that observed on hcp-Co(0001) surface, we find that on the fcc Co(111) surfaces both the top-fcc (Figure A1(a)) and top-hcp (Figure A1(b)) configurations are thermodynamically favourable. The magnetization density plot of pristine graphene adsorbed on Co surface (Figure A3(a)) shows that there is an induced magnetic moment on the supported graphene sheet (on top-C atom is $-0.079 \mu_B$ while on fcc-C is $0.058 \mu_B$). Hence graphene turns ferrimagnetic with an average magnetic moment of $-0.021 \mu_B$. Due to strong interactions between Co-3d and C-2p states there is a splitting of spin-up and spin-down spin states of the C-2p orbitals. The bandgap of 0.41 eV and 0.06 eV are generated for spin-up and spin-down states respectively (Figure A4).

Hydrogenation of graphene results in quenching of magnetic moment of fcc-C from $0.058 \mu_B$ to $0.012 \mu_B$ and significantly enhancing the magnetic moment of top-C from $-0.079 \mu_B$ to $-0.14 \mu_B$ (Figure A3(b)). The hydrogenated graphene sheet remains ferrimagnetic with the net magnetic moment of $-0.13 \mu_B$ and aligned antiparallel to that of Co atoms. We observe a six-fold increase in the net magnetic moment of the graphene sheet upon hydrogenation. Moreover there is a significant opening of the bandgap at the K-point of BZ. From the KPDOS plot, the spin-up channel has bandgap of 2.82 eV and the spin down channel has the bandgap of 2.73 eV (Figure A5).

¹

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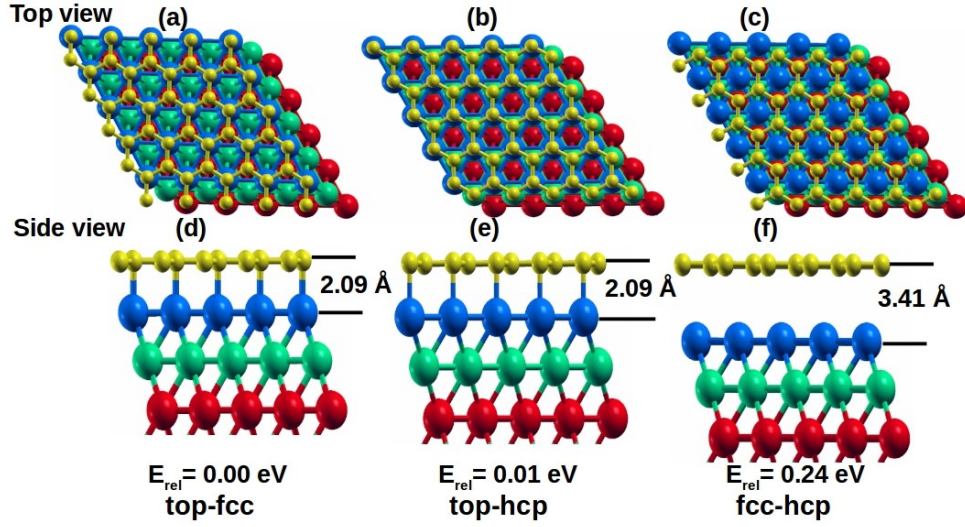


Figure A1: Top and side view of graphene on Co(111) in *top-fcc* (a and d), *top-hcp* (b and e) and *fcc-hcp* (c and f) configurations. The *top-fcc* configuration is energetically favorable with a binding energy of -0.31 eV/C atom. Reprinted (adapted) with permission from *AIP Conf. Proc.*, **2013**, 1512, 694-695. Copyright©2013 AIP Conference Proceedings

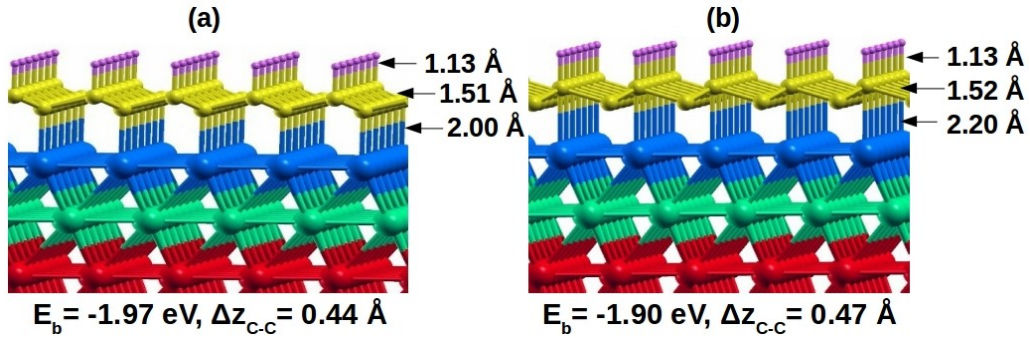


Figure A2: Configurations of hydrogenation of graphene (top-fcc configuration) on Co(111) surface. H atoms bind more strongly on fcc-C atoms and there is a buckling of graphene sheet upon hydrogenation. Reprinted (adapted) with permission from *AIP Conf. Proc.*, **2013**, 1512, 694-695. Copyright©2013 AIP Conference Proceedings.

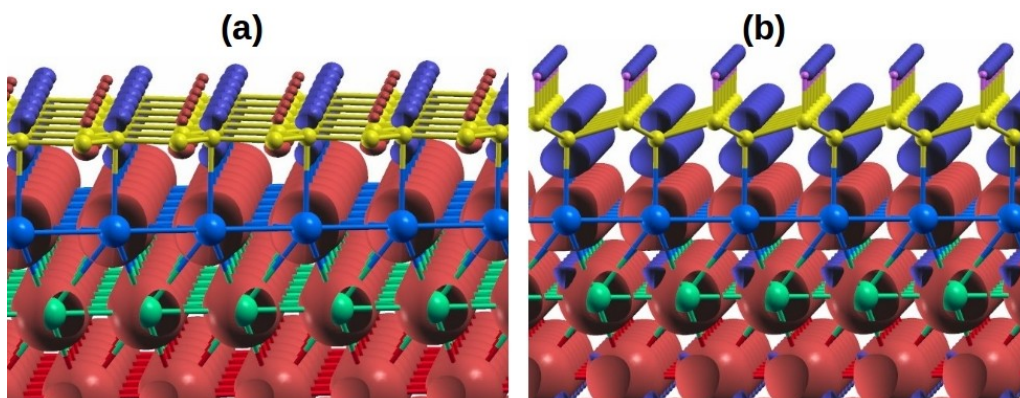


Figure A3: Magnetization density isosurfaces of the pristine (a) and hydrogenated graphene (b) on Co(111). Red(blue) isosurfaces denote spin-up(down) magnetization density. Reprinted (adapted) with permission from *AIP Conf. Proc.*, **2013**, 1512, 694-695. Copyright©2013 AIP Conference Proceedings.

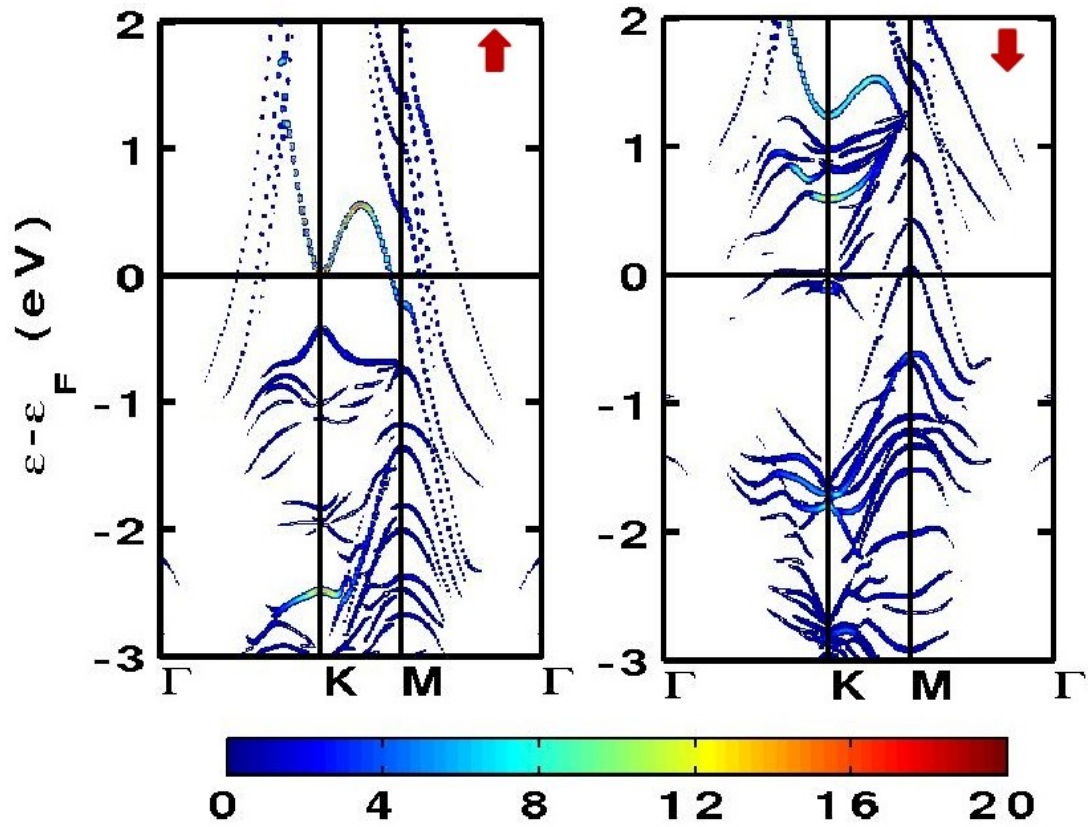


Figure A4: Contour plots of the contribution of the top and fcc C- p_z orbitals to the total density of states for spin-up and spin-down respectively, along the high-symmetry directions of the BZ of graphene supported on Co(111). Reprinted (adapted) with permission from *AIP Conf. Proc.*, **2013**, 1512, 694-695. Copyright©2013 AIP Conference Proceedings.

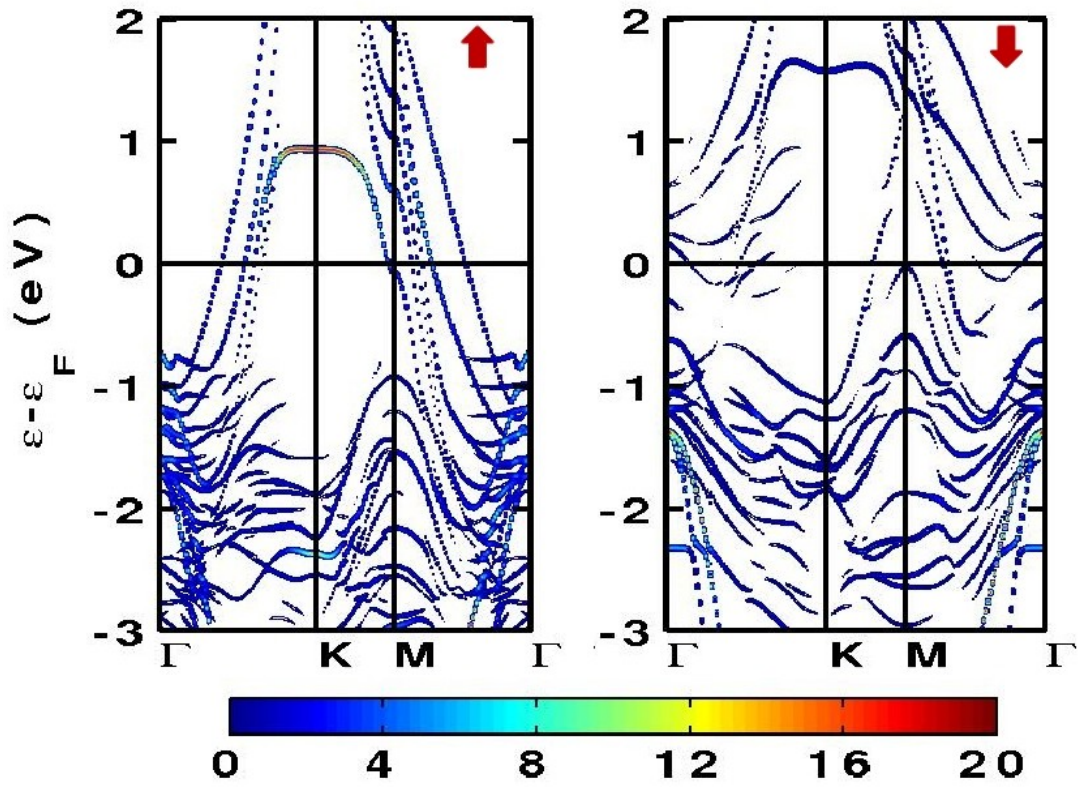


Figure A5: Contour plots of the contribution of the top and fcc C- p_z orbitals to the total density of states for spin-up and spin-down respectively, along the high-symmetry directions of the BZ for the hydrogenated graphene on Co(111). Reprinted (adapted) with permission from *AIP Conf. Proc.*, **2013**, 1512, 694-695. Copyright©2013 AIP Conference Proceedings.

Appendix B: Hydrogen dissociation on bimetallic PdGa clusters

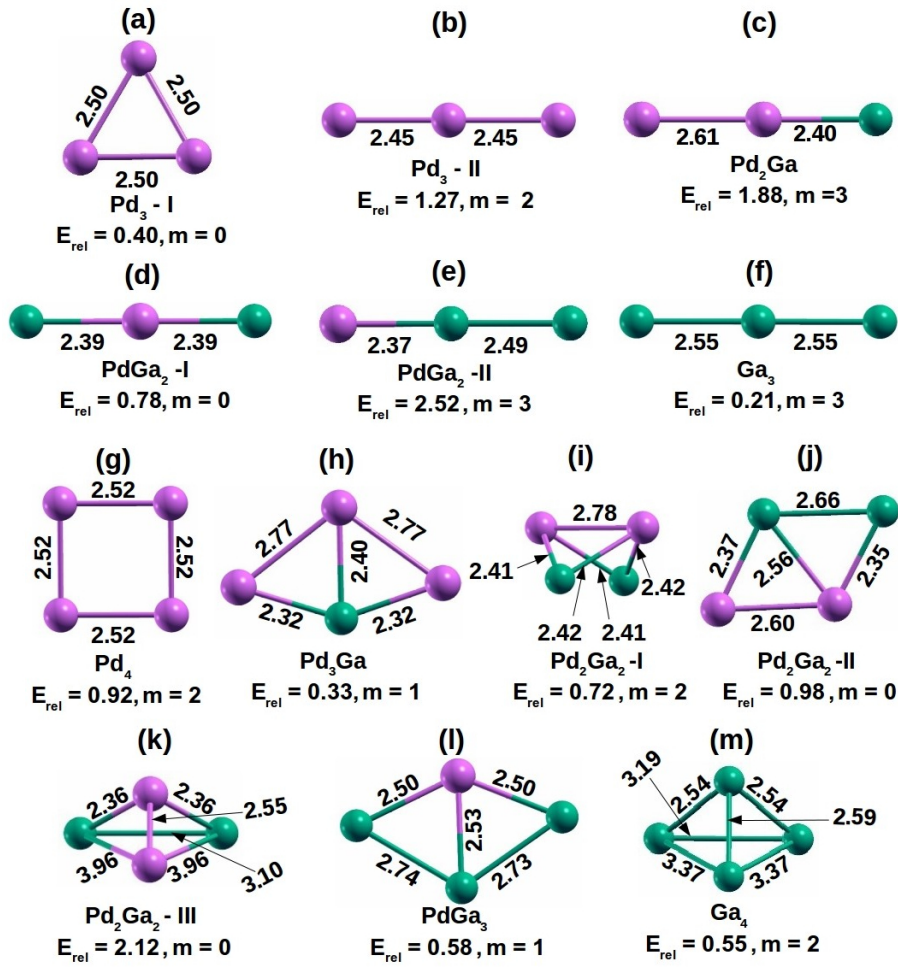


Figure B1: Different configurations for the pure and bimetallic dimers, trimers and tetramers. The bond lengths are in Å. E_{rel} is the relative energy (in eV units) of the cluster with that of the lowest energy one. ‘m’ denotes the magnetic moment (μ_B units) on the clusters. The green and magenta spheres denote the Ga and Pd atoms respectively.

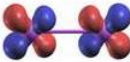
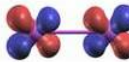
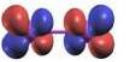
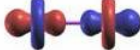
Cluster	Electronic state	PBE	LSDA	Rev PBE
Pd₂	HOMO			
	LUMO			
PdGa	HOMO			
	LUMO			
Ga₂	HOMO			
	LUMO			

Figure B2: HOMO and LUMO of the dimers using different exchange correlation functionals.

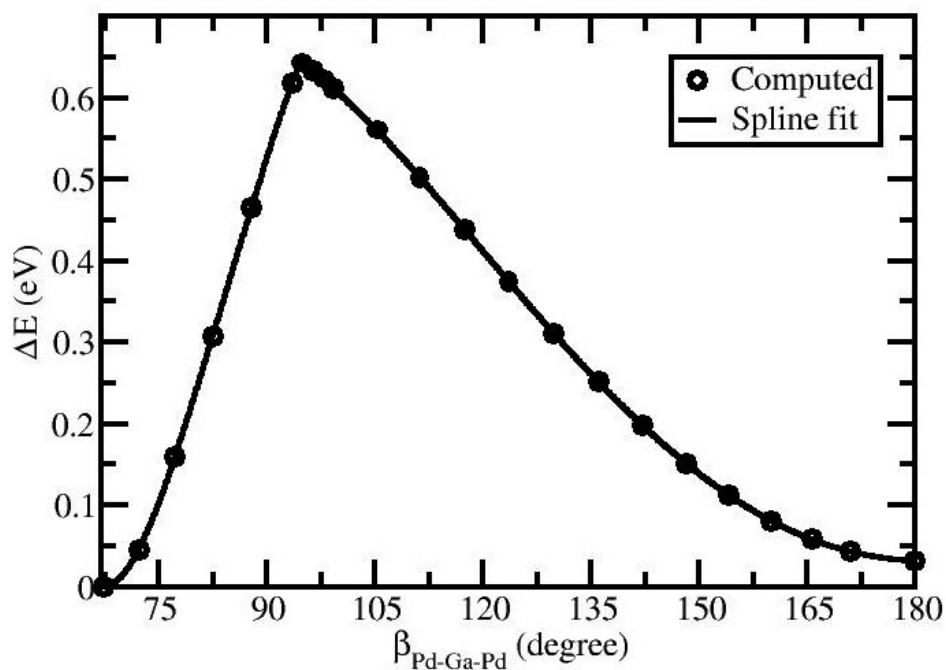


Figure B3: Energy barrier for bent to linear geometry transition of Pd₂Ga as a function of Pd-Ga-Pd bond angle.

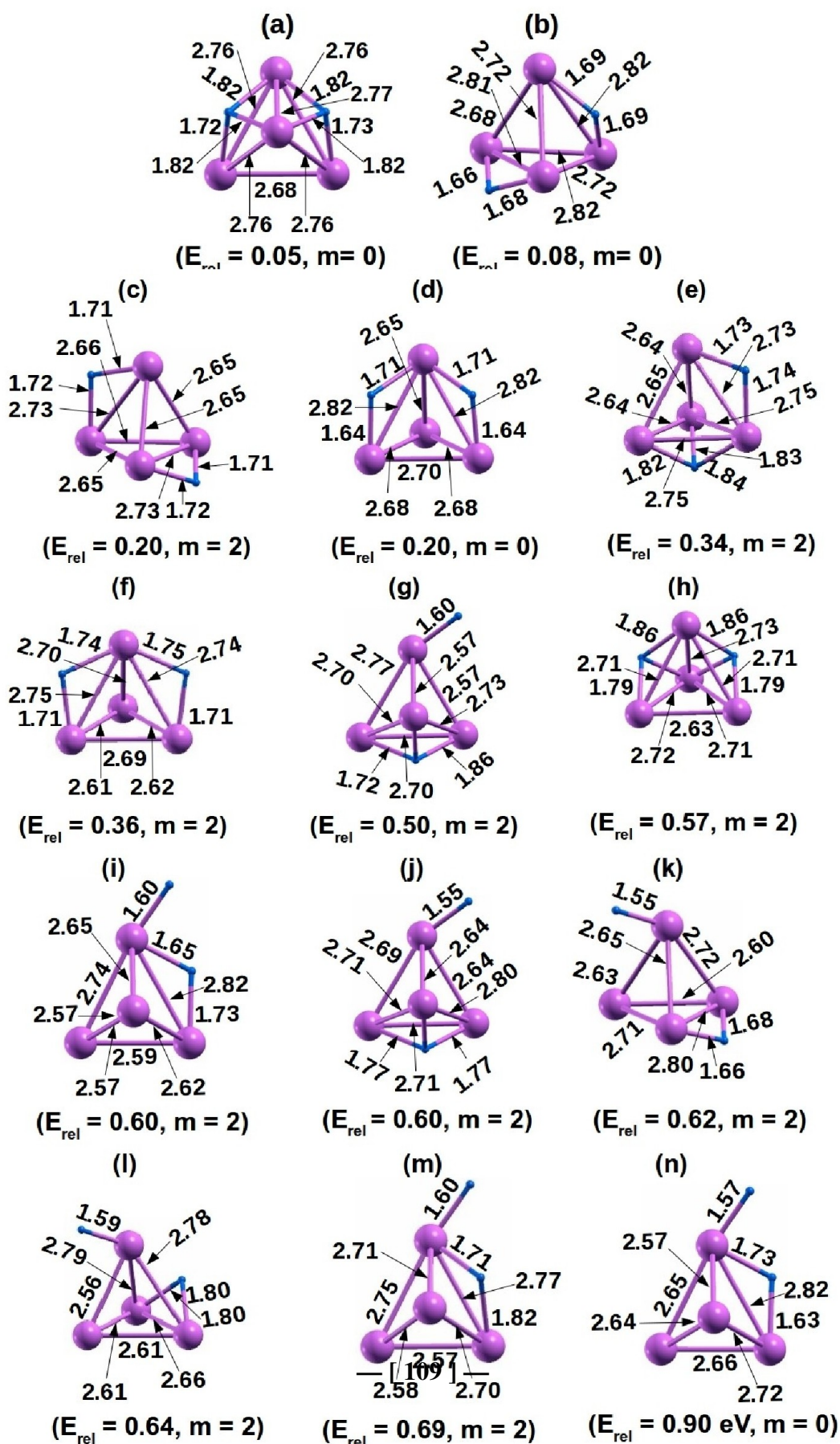


Figure B4: Different adsorption geometries of dissociated hydrogen molecule on Pd_4 . The blue and magenta spheres denote the H and Pd atoms respectively.

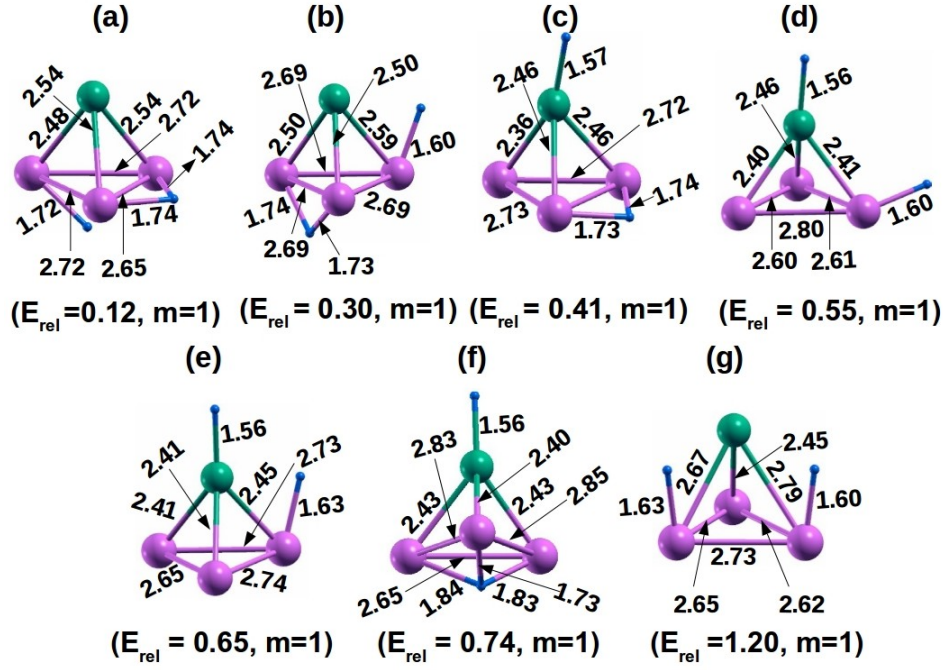


Figure B5: Different adsorption geometries of dissociated hydrogen molecule on Pd_3Ga . The blue, green and magenta spheres denote the H, Ga and Pd atoms respectively.

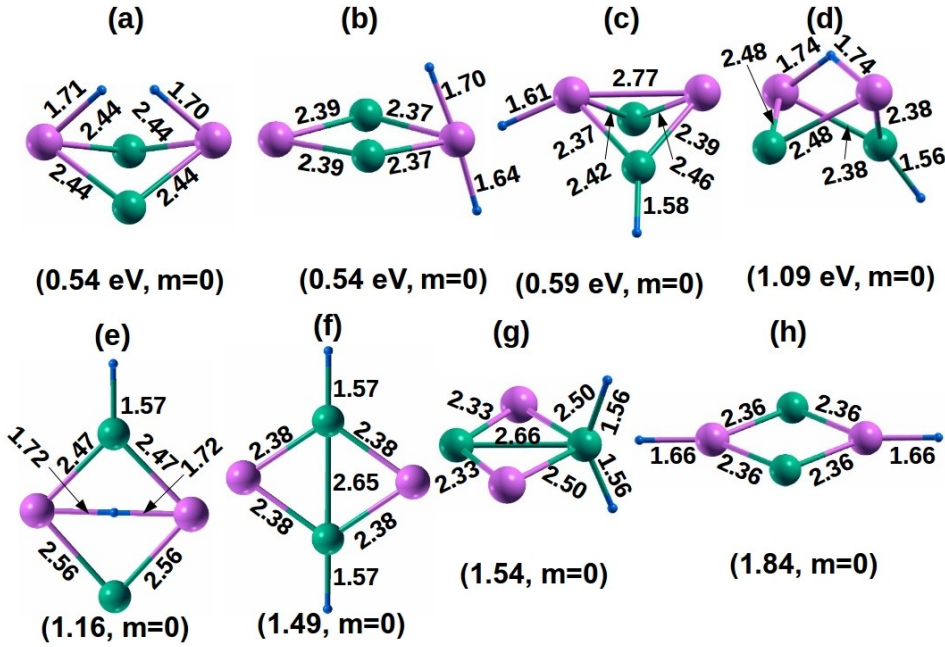


Figure B6: Different adsorption geometries of dissociated hydrogen molecule on Pd_2Ga_2 . The blue, green and magenta spheres denote the H, Ga and Pd atoms respectively.

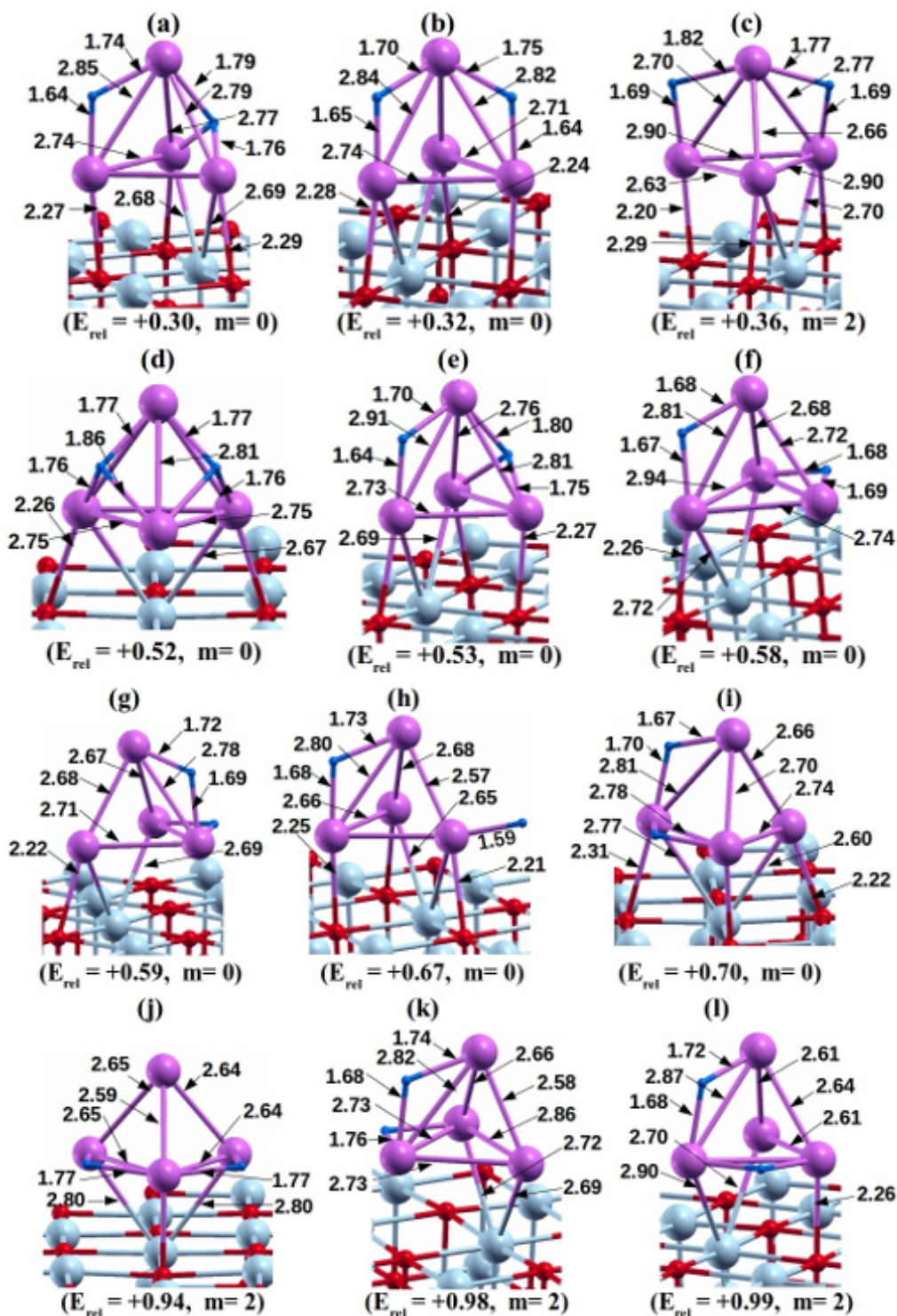


Figure B7: Different adsorption geometries of dissociated hydrogen molecule on Pd_4 supported on MgO surface. The blue and magenta spheres denote the H and Pd atoms respectively. The surface atoms Mg and O are represented by grey and red spheres respectively.

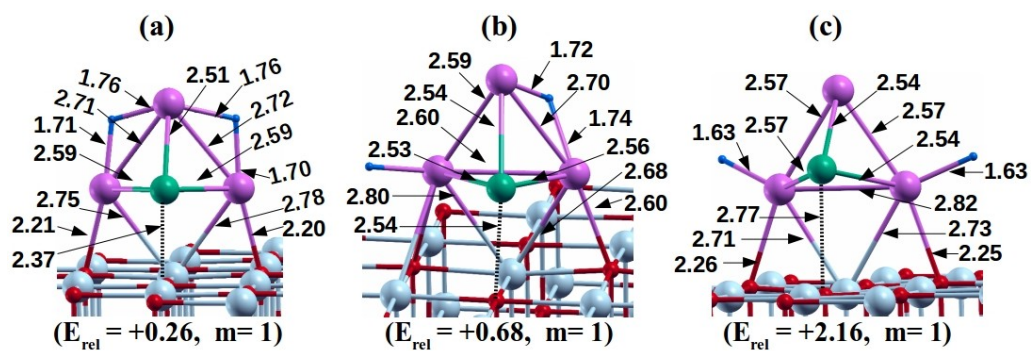


Figure B8: Different adsorption geometries of dissociated hydrogen molecule on Pd_3Ga supported on MgO surface. The blue, green and magenta spheres denote the H, Ga and Pd atoms respectively. The surface atoms Mg and O are represented by grey and red spheres respectively.

Appendix C: Selective hydrogenation of acetylene on bimetallic PdGa tetramers

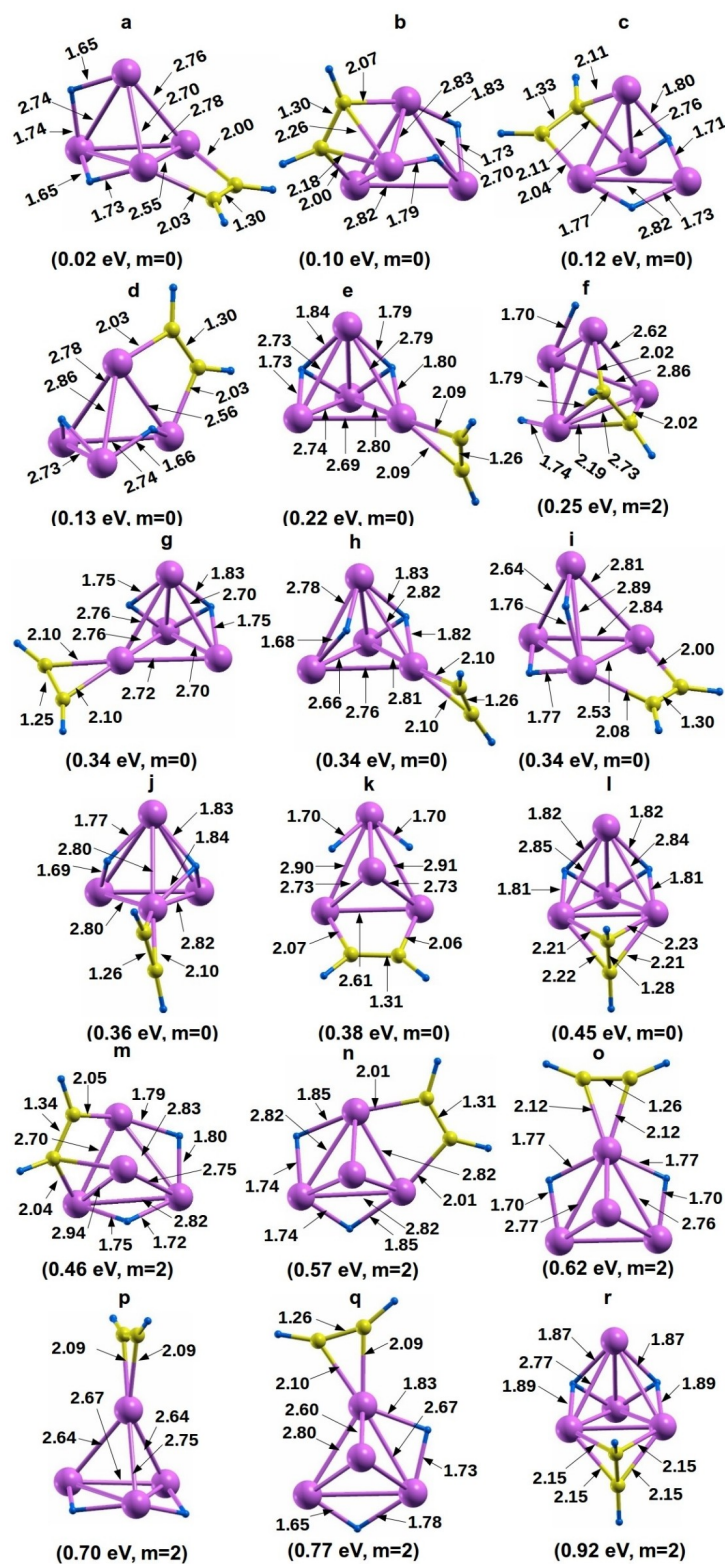


Figure C1: Various configurations of coadsorption of acetylene (C_2H_2) and dissociated hydrogen on the Pd_4 cluster. The magnetic moment is denoted by 'm' and the relative energies are represented by the numbers given in eV. The bond lengths are in Å.

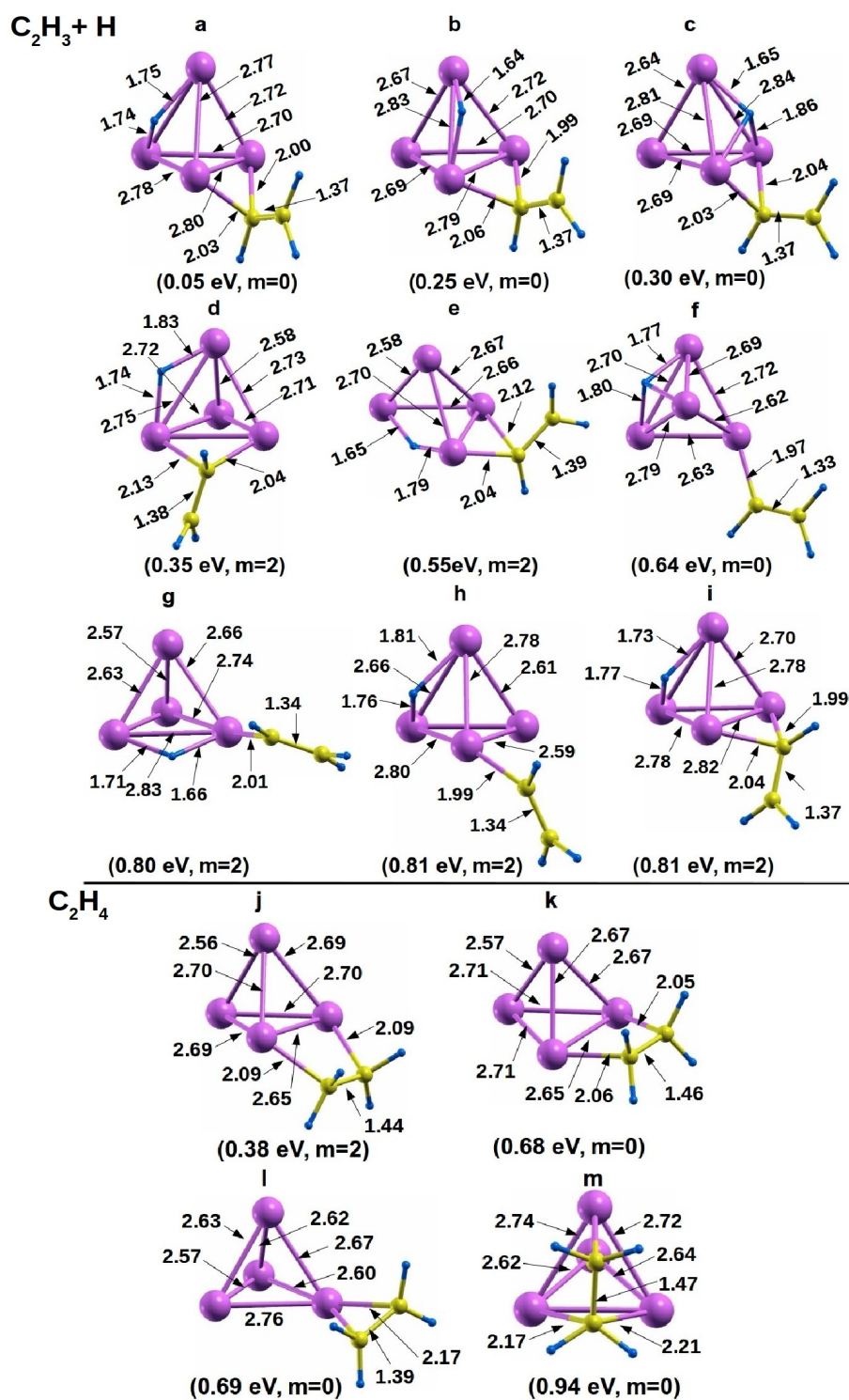


Figure C2: Various configurations of vinyl (C₂H₃) and ethylene (C₂H₄) adsorbed on the Pd₄ cluster. The magnetic moment is denoted by 'm' and the relative energies are represented by the numbers given in eV. The bond lengths are in Å.

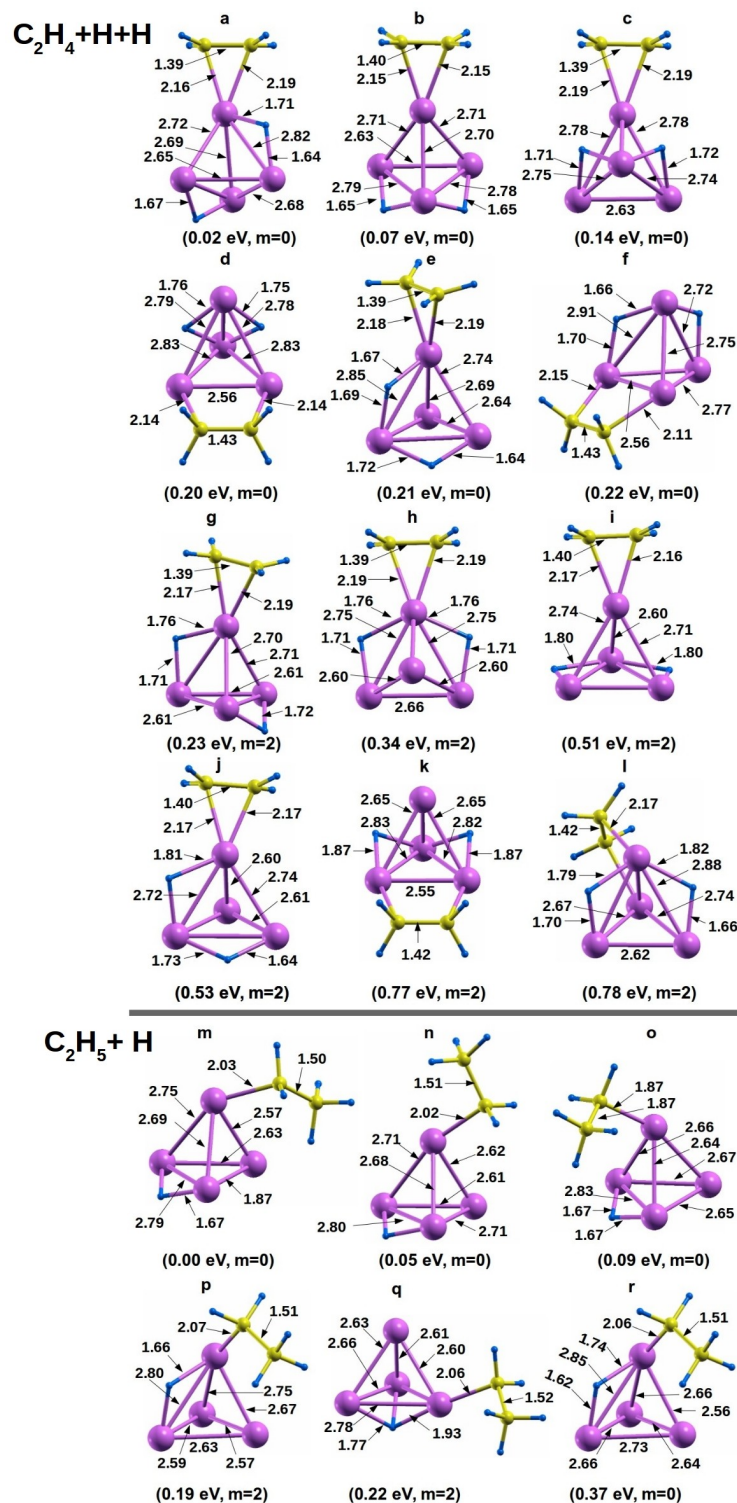


Figure C3: Various configurations of adsorption of ethylene (C₂H₄ + H* + H*) and ethyl (C₂H₅) on the Pd₄ cluster pre-adsorbed with hydrogen. The magnetic moment is denoted by ‘m’ and the relative energies are represented by the numbers given in eV. The bond lengths are in Å.

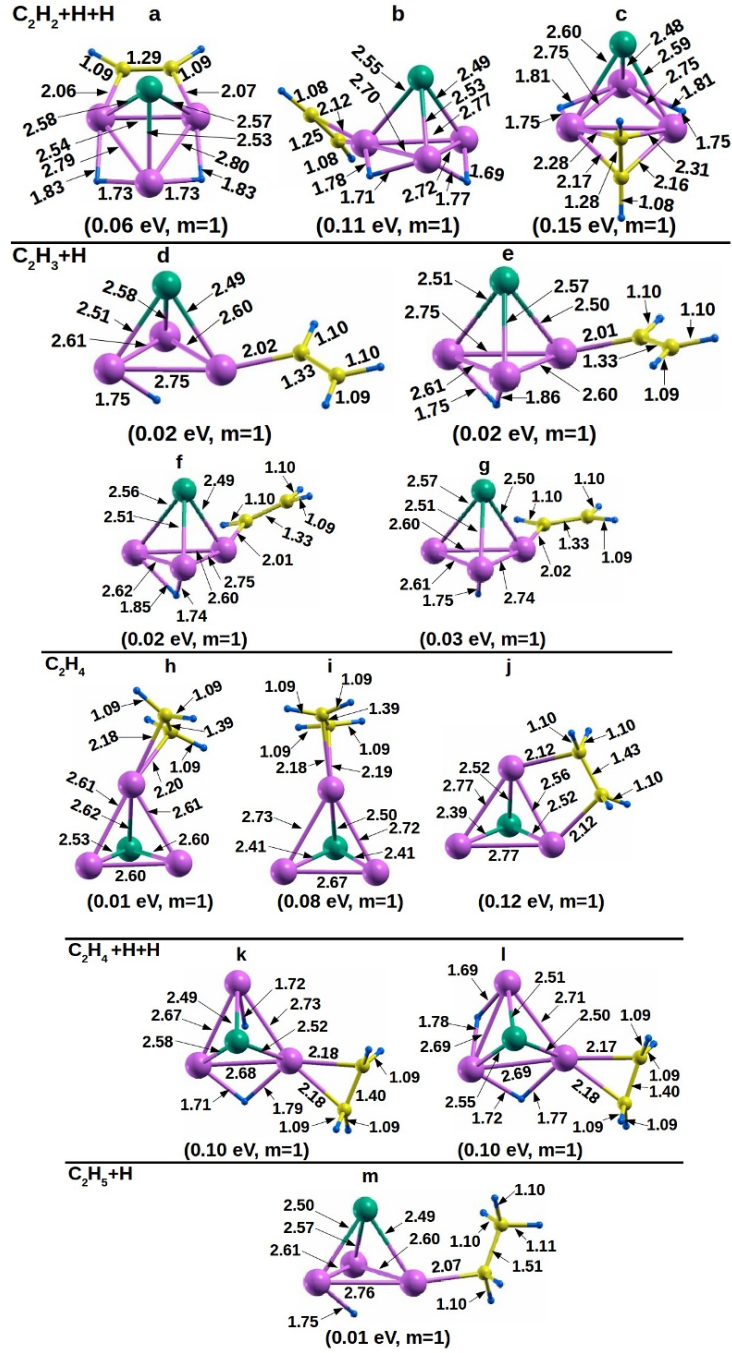


Figure C4: Various configurations for different adsorbates adsorbed on the Pd_3Ga cluster. The magnetic moment is denoted by ‘m’ and the relative energies of these structures are represented by the numbers given in eV. The bond lengths are in Å.

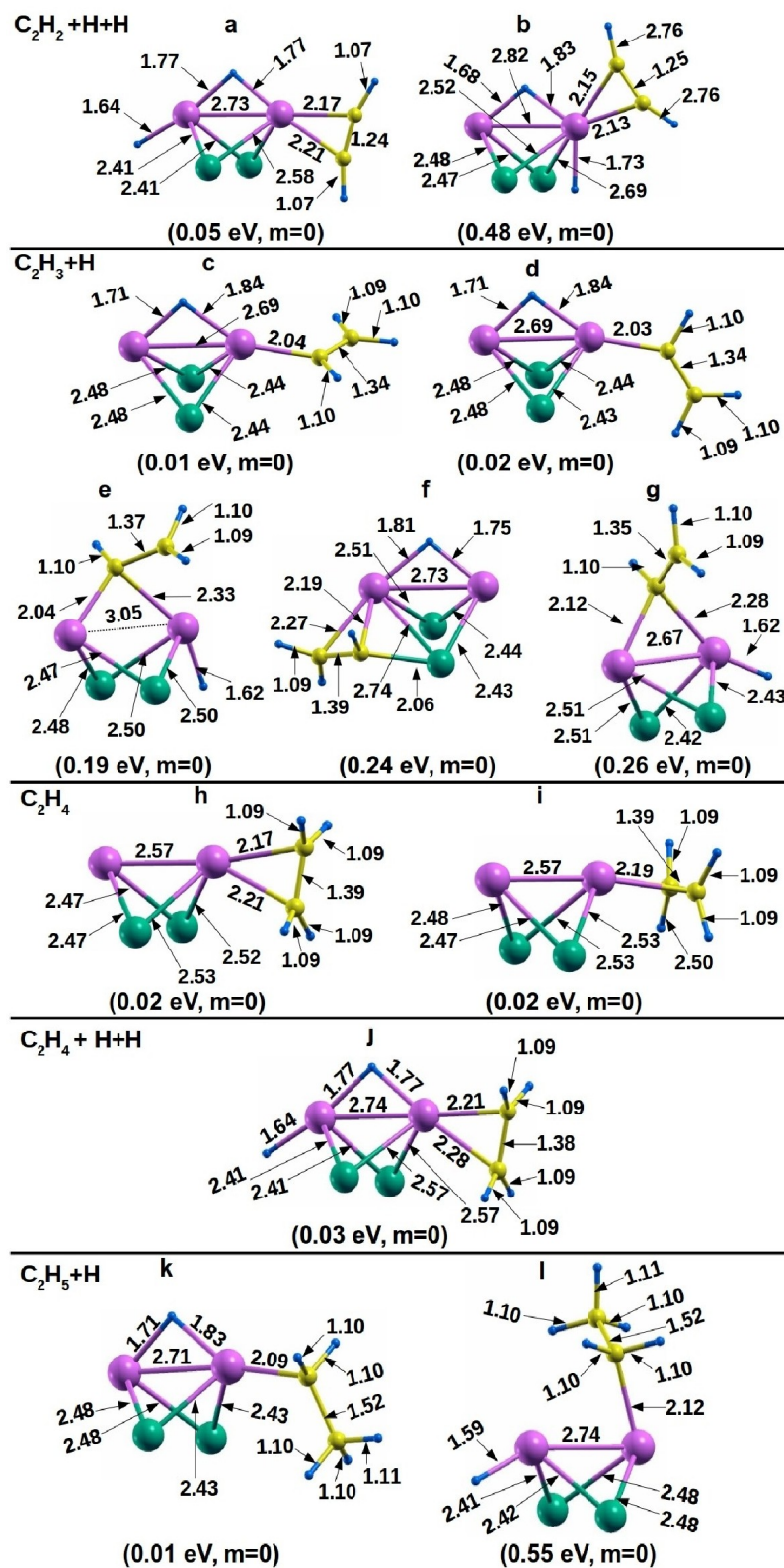


Figure C5: Various configurations for different adsorbates adsorbed on the Pd_2Ga_2 cluster. The magnetic moment is denoted by 'm' and the relative energies are represented by the numbers given in eV. The bond lengths are in Å. — [118] —

Appendix D: Adsorption of cyclododecadiene on clean and hydrogen covered Pd(100) surfaces

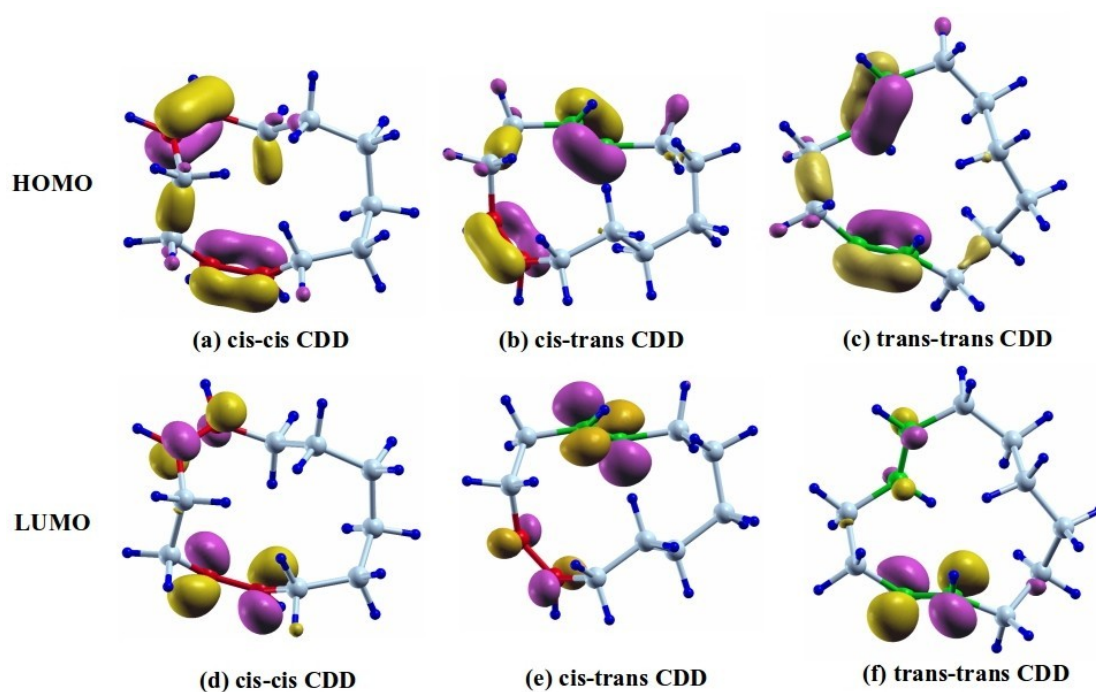


Figure D1: HOMOs and LUMOs of isomers of CDD in gas phase.

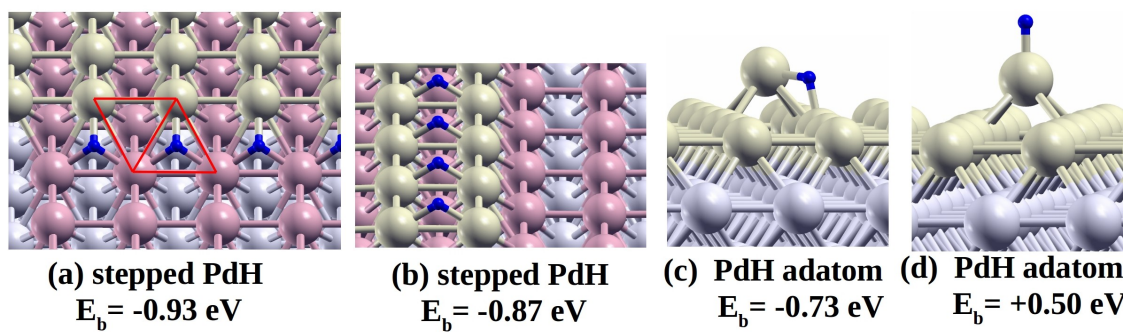


Figure D2: Different configurations of hydrogen adsorption on stepped Pd surface and Pd adatom.

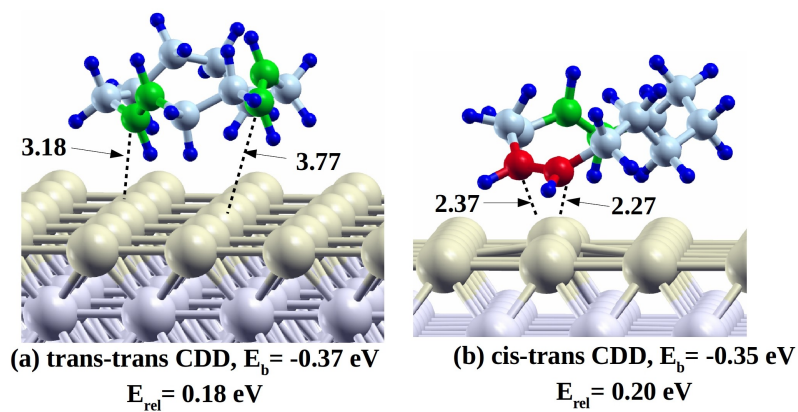


Figure D3: Relative energies and configurations of CDD isomers adsorbed on flat Pd surface. The bond lengths are in Å.

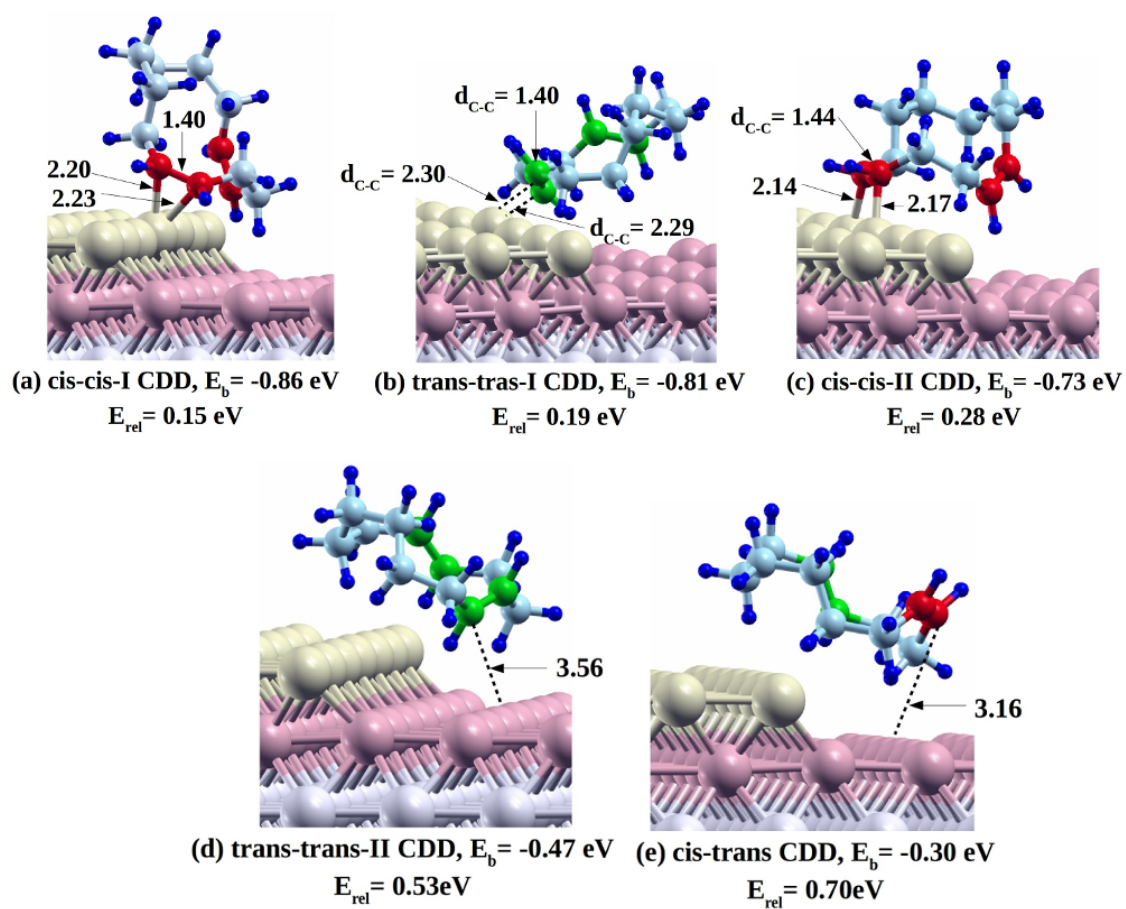


Figure D4: Relative energies and configurations of CDD isomers adsorbed on stepped Pd surface.

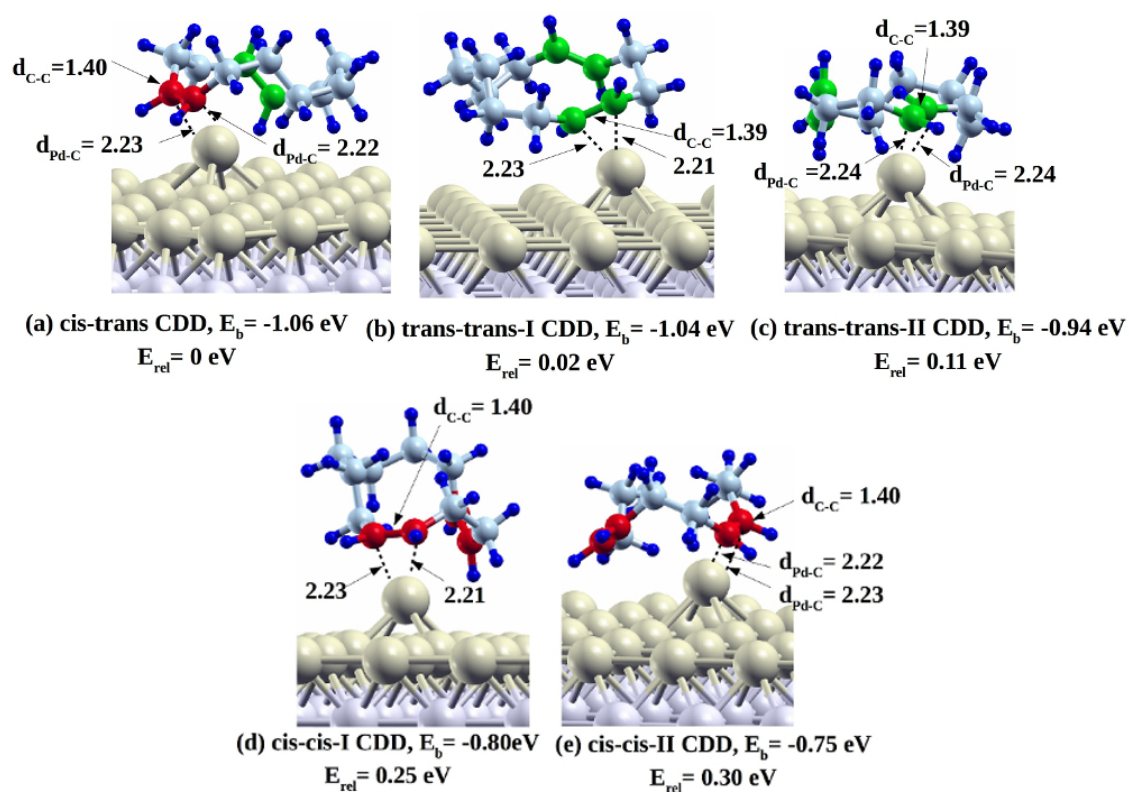


Figure D5: Relative energies and configurations of CDD isomers adsorbed on Pd adatom. The bond lengths are in Å.

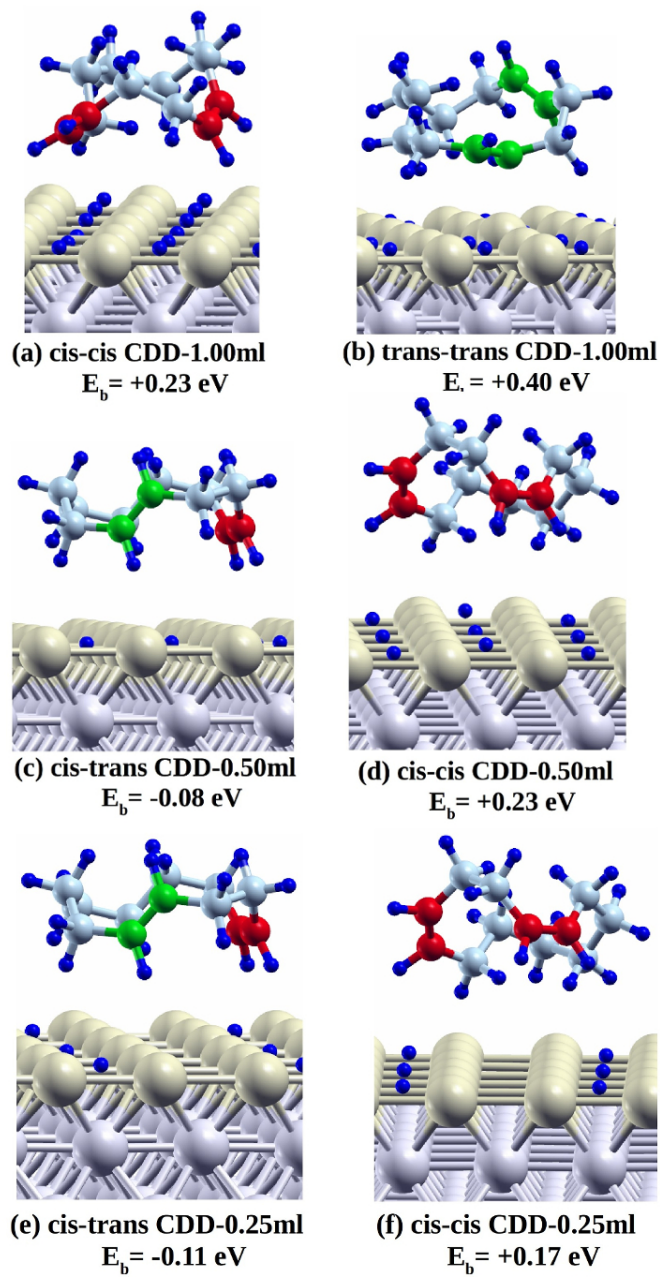


Figure D6: Relative energies and configurations of CDD isomers adsorbed on hydrogenated flat Pd surface. The bond lengths are in Å.

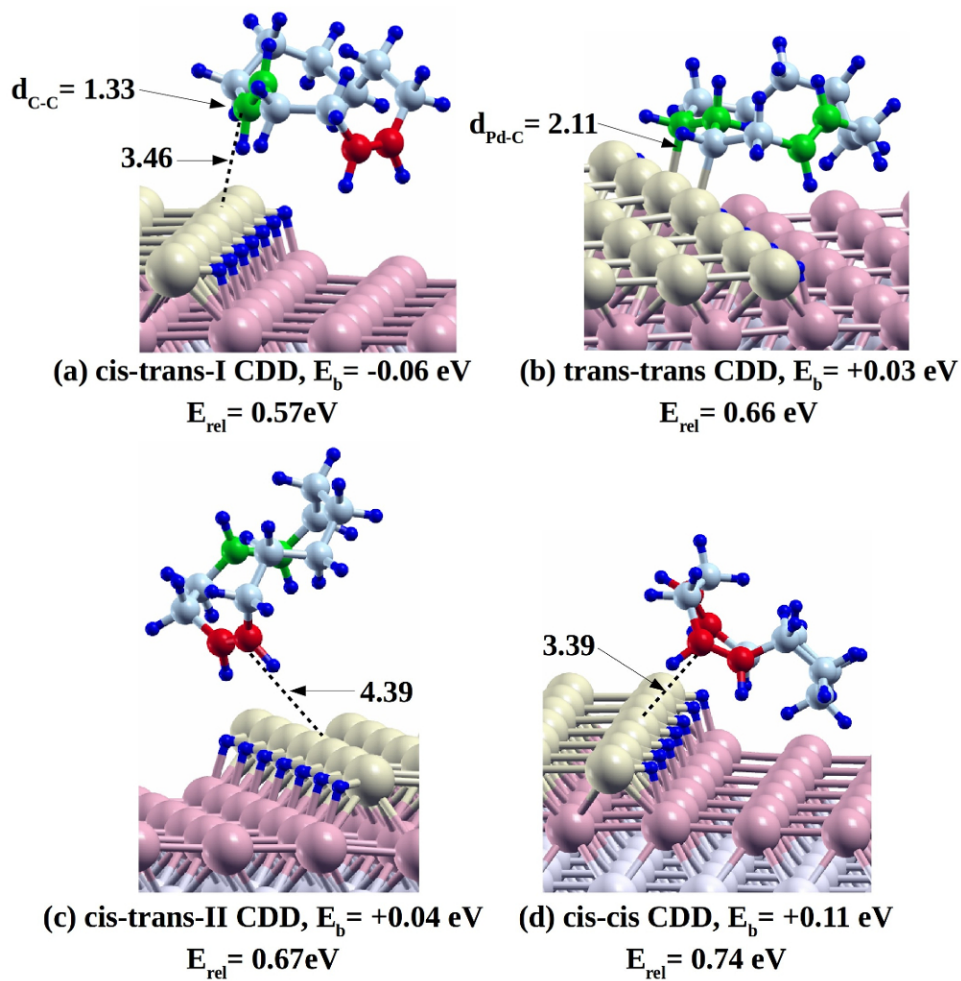


Figure D7: Relative energies and configurations of CDD isomers adsorbed on hydrogenated stepped Pd surface. The bond lengths are in Å.

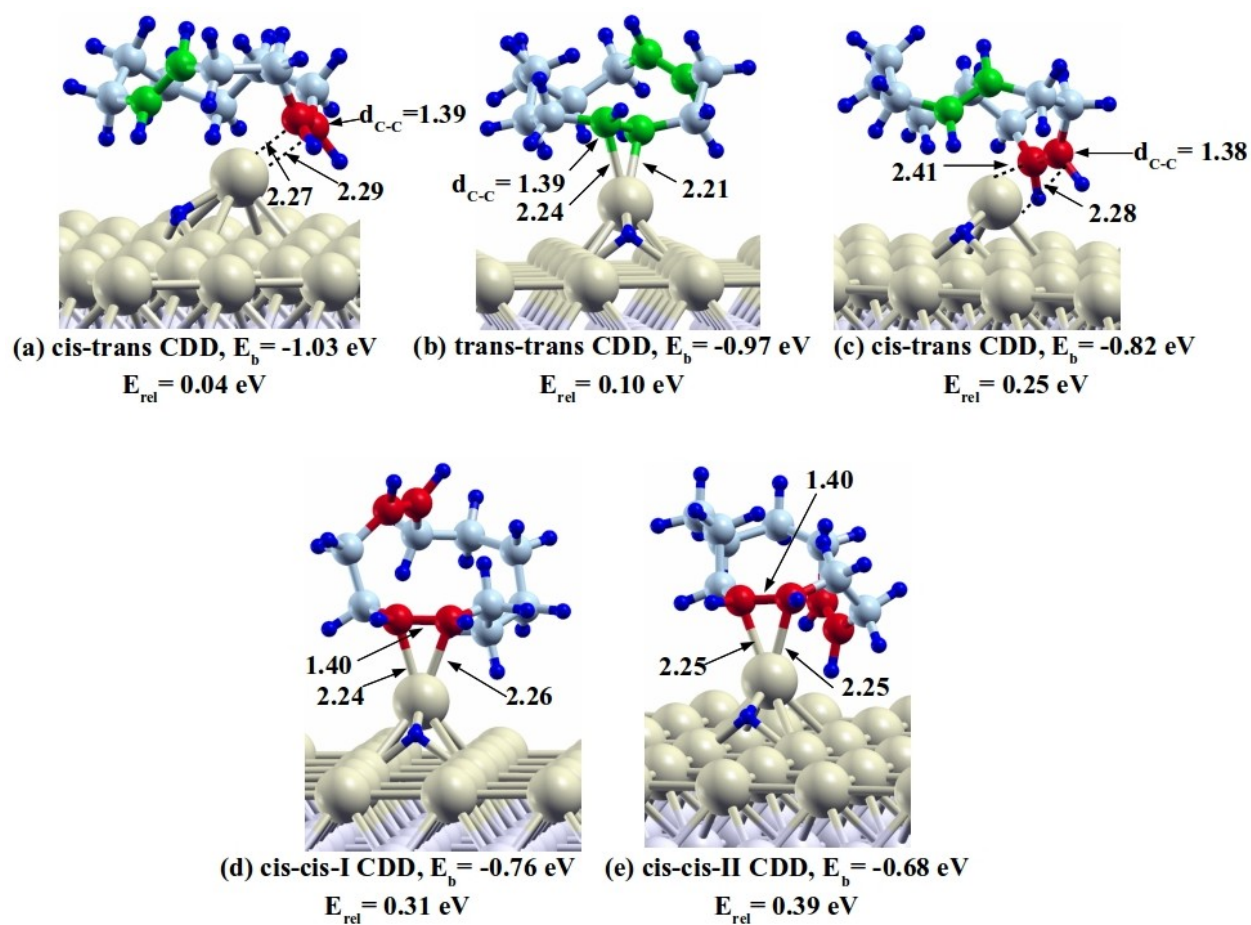


Figure D8: Relative energies and configurations of CDD isomers adsorbed on hydrogenated Pd adatom. The bond lengths are in Å.

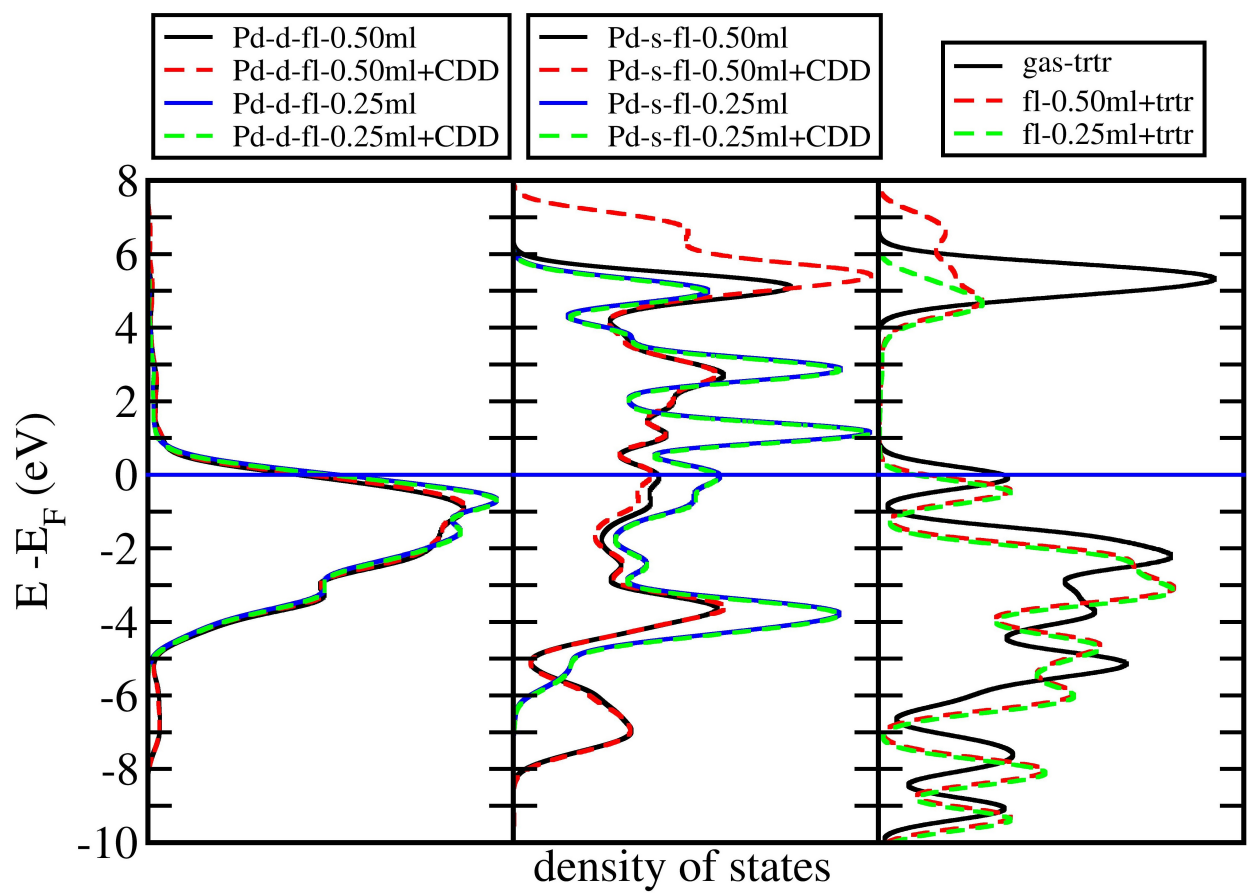


Figure D9: Density of states (DOS) plot for CDD adsorbed on hydrogenated flat Pd(100) surface.

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