

# Hydrogen Separation with Pd-Pt Membrane (DFT-Study)

BY

LAWAN MUHAMMAD ADAM

A Thesis Presented to the  
**COLLEGE OF GRADUATE AND INTERDISCIPLINARY STUDIES**  
**KING FAHD UNIVERSITY OF PETROLEUM & MINERALS**  
DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the  
Requirements for the Degree of

**MASTER OF SCIENCE**

In

**MATERIAL SCIENCE AND ENGINEERING**

MAY 2024

**KING FAHD UNIVERSITY OF PETROLEUM & MINERALS**

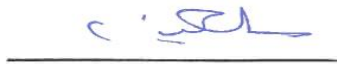
**DHAHRAN- 31261, SAUDI ARABIA**

**DEANSHIP OF GRADUATE STUDIES**

This thesis, written by **LAWAN MUHAMMAD ADAM** under the direction of his thesis advisor and approved by his thesis committee has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTERS IN MATERIAL SCIENCE AND ENGINEERING**.



**Dr. NAYEF MESNAD AL-SAIFI**  
Department Chairman



**Dr. SULIMAN SALEH AL-HOMIDAN**  
Dean of Graduate Studies

\_\_\_\_\_  
Date

 28/04/2024

**Dr. ABDULJABAR AL-SAYOUD**  
(Advisor)



**Prof. ABDULAZIZ A. AL-SAAD** |  
(Member)



**Dr. QASEM AHMED DMOOSH**  
(Member)



© Lawan Muhammad Adam  
2024

## *Dedication*

*This work is dedicated to my family, well-wishers, and the people who help during challenges while doing this work.*

# ACKNOWLEDGMENTS

I would like to begin by giving thanks to Allah for guiding me through all the challenges. In addition, I would like to thank KFUPM and the Department of Material Science and Engineering for this chance and the boundless knowledge I have gained while attending. I also appreciate my adviser, Dr. Abduljabar Al-Sayoud, for his help, inspiration, and direction. I also want to thank Prof. Abdulaziz A. Al-Saadi and Dr. Qasem Ahmed Drmosh of the committee for their thoughtful remarks and recommendations. My profound thanks are also extended to Ahmed Abuelyamen and Dr. Venkateswara R. Manga for their counsel, astute remarks, and recommendations.

Finally, but just as importantly, I want to thank my friends, coworkers, and everybody else who contributed.

# TABLE OF CONTENTS

|                                                           |             |
|-----------------------------------------------------------|-------------|
| <b>ACKNOWLEDGMENTS</b>                                    | <b>iv</b>   |
| <b>TABLE OF CONTENTS</b>                                  | <b>v</b>    |
| <b>LIST OF TABLES</b>                                     | <b>ix</b>   |
| <b>LIST OF FIGURES</b>                                    | <b>x</b>    |
| <b>LIST OF ABBREVIATIONS</b>                              | <b>xiii</b> |
| <b>ABSTRACT</b>                                           | <b>xv</b>   |
| <b>ملخص الرسالة</b>                                       | <b>xvii</b> |
| <b>CHAPTER 1</b>                                          | <b>1</b>    |
| <b>INTRODUCTION</b>                                       | <b>1</b>    |
| 1.1 Methods of Hydrogen Production                        | 3           |
| 1.2 Mechanism of Hydrogen Permeation through the Membrane | 4           |
| 1.3 Motivation and Significance of the Study              | 5           |
| 1.4 Research Objectives                                   | 5           |
| <b>CHAPTER 2</b>                                          | <b>7</b>    |
| <b>LITERATURE REVIEW</b>                                  | <b>7</b>    |
| 2.1 Pure palladium                                        | 7           |
| 2.2 Alloying effect                                       | 10          |

|                                                                                                             |                                                           |           |
|-------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------|-----------|
| 2.3                                                                                                         | Effect of Coverage .....                                  | 10        |
| <b>CHAPTER 3.....</b>                                                                                       |                                                           | <b>16</b> |
| <b>BACKGROUND AND RESEARCH METHODOLOGY .....</b>                                                            |                                                           | <b>16</b> |
| 3.1                                                                                                         | Methane Reforming of Natural Gas.....                     | 16        |
| 3.2                                                                                                         | Synthetic Gas or Syngas (Partial Pressure Reaction) ..... | 19        |
| 3.3                                                                                                         | Hydrogen Separation Techniques .....                      | 20        |
| 3.3.1                                                                                                       | Pressure swing adsorption (PSA) .....                     | 20        |
| 3.3.2                                                                                                       | Cryogenic distillation .....                              | 21        |
| 3.3.3                                                                                                       | Hydrogen selective membrane .....                         | 21        |
| 3.4                                                                                                         | Membrane Process Terminologies .....                      | 22        |
| 3.4.1                                                                                                       | Permeability .....                                        | 22        |
| 3.4.2                                                                                                       | Porous selective membranes .....                          | 24        |
| 3.5                                                                                                         | Dense Metal (Palladium) Membrane .....                    | 24        |
| 3.5.1                                                                                                       | Poisoning Mechanism.....                                  | 25        |
| 3.6                                                                                                         | The Density Functional Theory(DFT) and Method.....        | 25        |
| 3.6.1                                                                                                       | Calculation Procedure of DFT .....                        | 29        |
| 3.6.2                                                                                                       | DFT Parameter Optimizations .....                         | 34        |
| 3.6.3                                                                                                       | Optimization of ecutwfc and K-points.....                 | 35        |
| 3.6.4                                                                                                       | Pd-surface Preparation .....                              | 38        |
| <b>CHAPTER 4.....</b>                                                                                       |                                                           | <b>42</b> |
| <b>ADSORPTION AND DISSOCIATION OF HYDROGEN ON PALLADIUM SURFACE DOPED WITH PLATINUM-GROUP ELEMENTS.....</b> |                                                           | <b>42</b> |

|                                                            |                                                                                         |           |
|------------------------------------------------------------|-----------------------------------------------------------------------------------------|-----------|
| 4.1                                                        | H <sub>2</sub> Physisorption Process .....                                              | 42        |
| 4.2                                                        | Charge density difference analysis on H <sub>2</sub> dissociation. ....                 | 46        |
| 4.3                                                        | H <sub>2</sub> Dissociation Barrier Path.....                                           | 49        |
| 4.4                                                        | Catalytic Enhancement Analysis .....                                                    | 53        |
| <b>CHAPTER 5.....</b>                                      |                                                                                         | <b>59</b> |
| <b>HYDROGEN TRANSPORT PROCESSES ON Pd-Pt SURFACE .....</b> |                                                                                         | <b>59</b> |
| 5.1                                                        | Surface and Alloy Model .....                                                           | 59        |
| 5.2                                                        | Computational Cost Analysis .....                                                       | 60        |
| 5.3                                                        | H <sub>2</sub> Physisorption on Pd-Pt (111) surface .....                               | 61        |
| 5.4                                                        | H <sub>2</sub> Chemisorption and Dissociation on Pd-Pt (111) surface .....              | 67        |
| 5.5                                                        | Electronic Charge Density Difference Analysis of H <sub>2</sub> -PdPt Interaction ..... | 69        |
| 5.6                                                        | Adsorption of CO and H <sub>2</sub> S on Pd-Pt surfaces .....                           | 70        |
| 5.7                                                        | Effect of CO and H <sub>2</sub> S on H <sub>2</sub> Adsorption on Pd-Pt Surface .....   | 75        |
| 5.8                                                        | Comparative analysis of improvement between bare Pd and PdPt surfaces .....             | 78        |
| 5.9                                                        | Delta Analysis of H <sub>2</sub> adsorption in the presence of poisoning gases .....    | 80        |
| <b>CHAPTER 6.....</b>                                      |                                                                                         | <b>83</b> |
| <b>CONCLUSION AND RECOMMENDATION .....</b>                 |                                                                                         | <b>83</b> |
| 6.1                                                        | Conclusion.....                                                                         | 83        |
| 6.2                                                        | Future Recommendations.....                                                             | 83        |

|                        |           |
|------------------------|-----------|
| <b>APPENDIX.....</b>   | <b>85</b> |
| <b>REFERENCES.....</b> | <b>88</b> |
| <b>VITAE.....</b>      | <b>92</b> |

# LIST OF TABLES

|          |                                                                                                                                                      |    |
|----------|------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Table 1. | Maximum limit for components composition for pipeline natural gas quality [12]. .....                                                                | 19 |
| Table 2. | The characteristics of several kinds of hydrogen-selective membranes are taken directly from Al-Mufachi et al [8]. .....                             | 22 |
| Table 3. | Results summary of DFT calculation for Pd bulk .....                                                                                                 | 38 |
| Table 4. | The dissociation barrier and relaxed dissociative energy of H <sub>2</sub> on Pd-X surfaces.....                                                     | 51 |
| Table 5. | H <sub>2</sub> Binding Energy (eV) on bare Pd(11) and a Pd-Pt(111) Surface at 0.25ML Coverage.<br>67                                                 |    |
| Table 6. | Difference between H <sub>2</sub> adsorption energy with and without CO and H <sub>2</sub> S on Pd-Pt in comparison to that on bare Pd surface. .... | 81 |

# LIST OF FIGURES

|            |                                                                                                                                             |    |
|------------|---------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 1.  | Hydrogen gas passes through a highly selective membrane while impurities are blocked. ....                                                  | 2  |
| Figure 2.  | A schematic representation of a device used in a Pd-based membrane reactor for H <sub>2</sub> permeation and MSR reaction[12]. ....         | 18 |
| Figure 3.  | Palladium bulk material with a generated slab of six-layer surfaces. ....                                                                   | 27 |
| Figure 4.  | Energy-volume curve while varying the lattice parameter of the unit cell. ....                                                              | 30 |
| Figure 5.  | Crystal planes of Pd(111) plane at low-index surfaces. ....                                                                                 | 31 |
| Figure 6.  | Sites available for FCC structure. ....                                                                                                     | 31 |
| Figure 7.  | The orientation of gas molecule adsorption at the membrane surface. ....                                                                    | 32 |
| Figure 8.  | Dissociation of the gas molecule to gas atoms. ....                                                                                         | 33 |
| Figure 9.  | Convergence of total energy concerning ecutwfc. ....                                                                                        | 36 |
| Figure 10. | Convergence of total energy with respect to K-points ....                                                                                   | 36 |
| Figure 11. | Change of total energy with the cell volume. ....                                                                                           | 37 |
| Figure 12. | Interaction of 1 Pd atom due to periodic boundary conditions at different distances apart from each other. ....                             | 37 |
| Figure 13. | Atoms arrangement for surfaces (111). (a) Top view and (b) front view ....                                                                  | 39 |
| Figure 14. | The Pd unit cell is used for surface relaxation. ....                                                                                       | 40 |
| Figure 15. | (A) Dissociative adsorption energies of H <sub>2</sub> on Pd-X surfaces with (B) corresponding relaxed geometry and final bond length. .... | 43 |
| Figure 16. | The available adsorption sites on Pd(111) surface with T(top), B(bridge), FCC, and HCP are the hollow sites. ....                           | 44 |

|            |                                                                                                                                                                                                                                    |    |
|------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 17. | Electronic charge density difference (EDD) plots of relaxed H <sub>2</sub> interaction with the doped Pd surfaces.....                                                                                                             | 47 |
| Figure 18. | Mapping the CDD of the final state of H <sub>2</sub> initially at T0 sites on Pd-X surfaces with their corresponding dissociative energies. ....                                                                                   | 48 |
| Figure 19. | The initial and final geometrical configuration for nudge elastic band (NEB) calculation.....                                                                                                                                      | 50 |
| Figure 20. | The energy profile of H <sub>2</sub> dissociation on atop sites doping atoms (T0) of Pd-X surfaces (X <sub>i</sub> = Os, Ir, Pt, Ru and Rh).....                                                                                   | 52 |
| Figure 21. | Comparison of H <sub>2</sub> relaxation state on bare Pt-group surfaces and the Pd surface when doped with the atoms from the pure element. ....                                                                                   | 53 |
| Figure 22. | Electronic charge density difference (EDD) plots of relaxed H <sub>2</sub> interaction with the pure platinum group element surfaces. ....                                                                                         | 54 |
| Figure 23. | A combined graph of relaxed height (AdH), relaxed bond length (BL), and the relaxed energy of H <sub>2</sub> on pure (A) platinum-group surfaces and the doped Pd surfaces (B). ....                                               | 55 |
| Figure 24. | Combined energy profile for Comparison of all the doping materials to understand the catalytic enhancement in the Pd surface. ....                                                                                                 | 56 |
| Figure 25. | Analysis of the catalytic enhancement of H <sub>2</sub> adsorption energy by comparison of H <sub>2</sub> relaxed energy on pure and alloy of platinum-group elements. ....                                                        | 57 |
| Figure 26. | Surface Culmination of Pd-Pt Slab .....                                                                                                                                                                                            | 60 |
| Figure 27. | Hydrogen adsorption on the available sites of culminated 5layers, 3layers, and 2layers surfaces .....                                                                                                                              | 61 |
| Figure 28. | Alloy surface of Pd-Pt with designated sites available. ....                                                                                                                                                                       | 63 |
| Figure 29. | H <sub>2</sub> adsorption energy on Pd atoms in the presence of Pt with their corresponding final relaxed bond length and height of H <sub>2</sub> from the surface. ....                                                          | 65 |
| Figure 30. | The initial and final relaxed geometry of H <sub>2</sub> on Pd and Pt top sites of perfect PdPt(111) surface. Pd top layer atoms in dark-blue while the light-blue represents the first sub-layer atoms and Pt is grey color. .... | 66 |
| Figure 31. | Relationship between bond length, adsorption height and energy of H <sub>2</sub> on the available sites on Pd-Pt surface. ....                                                                                                     | 68 |

|               |                                                                                                                                                  |    |
|---------------|--------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 32.    | The H <sub>2</sub> geometry for dissociation barrier calculation. ....                                                                           | 69 |
| Figure 33.    | Dissociation barrier path of H <sub>2</sub> initially placed on T0 in (a) and on B1 in (b).....                                                  | 69 |
| Figure 34.    | Electronic charge density difference of H <sub>2</sub> interaction with bare Pt and Pd-Pt alloy surfaces. ....                                   | 70 |
| Figure 35.    | The initial and relaxed orientation of CO on the available site (T0, T1, B1, FCC1, and HCP1) in the dilute region on the Pd-Pt(111) surface..... | 71 |
| Figure 36.    | Adsorption energy of H <sub>2</sub> , CO, and H <sub>2</sub> S on (a) the available sites of bare Pd(111) and (b) Pd-Pt(111) surfaces.....       | 73 |
| Figure 37.    | H <sub>2</sub> S orientations with their respective relaxed energies.....                                                                        | 74 |
| Figure 38.    | The Initial and relaxed geometry of possible sites for H <sub>2</sub> S adsorption on Pd-Pt Surface<br>75                                        |    |
| Figure 39.    | H <sub>2</sub> adsorption on bare Pd surface, in the presence of CO and H <sub>2</sub> S .....                                                   | 76 |
| Figure 40.    | H <sub>2</sub> adsorption on PdPt surface, in the presence of CO and H <sub>2</sub> S.....                                                       | 77 |
| Figure 41.    | H <sub>2</sub> adsorption on Pd and PdPt surfaces.....                                                                                           | 78 |
| Figure 42.    | Comparison between the H <sub>2</sub> adsorption energy on Pd and PdPt in the presence of (a) CO and (b) H <sub>2</sub> S.....                   | 79 |
| Figure 43.    | Comparison between (a) CO and (b) H <sub>2</sub> S adsorption energy on Pd and PdPt .....                                                        | 80 |
| SL.Figure 44. | CO poisoning on H <sub>2</sub> adsorption and dissociation.....                                                                                  | 85 |
| SL.Figure 45. | Initial and relaxed state of H <sub>2</sub> S dissociation on Pd-Pt surface .....                                                                | 85 |
| SL.Figure 46. | Plots of adsorption energy of H <sub>2</sub> , H <sub>2</sub> S, and CO on the (a) bare Pd and (b) Pd-Pt surface<br>.....                        | 86 |

# LIST OF ABBREVIATIONS

|      |                                      |
|------|--------------------------------------|
| DFT  | : Density Functional Theory          |
| NEB  | : Nudge Elastic Band                 |
| CI   | : Climbing Image                     |
| PGEs | : Platinum Group Elements            |
| BL   | : Bond Length                        |
| AdH  | : Adsorption Height                  |
| B1   | : Bridge site                        |
| T1   | : Top site of Pd                     |
| T0   | : Top site of PGEs                   |
| HCP  | : Hexagonal Closed Packed            |
| FCC  | : Faced Centered Cubic               |
| HOMO | : Higher Occupied Molecular Orbital  |
| LUMO | : Lower Unoccupied Molecular Orbital |
| CDD  | : Charge Density Difference          |

|                               |                                                    |
|-------------------------------|----------------------------------------------------|
| $d$                           | : Distance between                                 |
| $X_{\text{Pd-PdPt}}$ (X=Site) | : Change from Pd to PdPt                           |
| $E$                           | : Energy                                           |
| $P, n$                        | : Positive and Negative Rotation in axis direction |
| $\delta$                      | : Difference in value                              |
| NGSR                          | Natural gas steam reforming                        |
| MSR                           | Methane steam reforming                            |

# ABSTRACT

Full Name : [LAWAN MUHAMMAD ADAM]  
Thesis Title : [Hydrogen Separation with Pd-Pt Membrane (DFTStudy)]  
Major Field : [Material Science and Engineering]  
Date of Degree : [May 2024]

The importance of hydrogen ( $H_2$ ) increases its demand daily. Fortunately, the Pd-based membrane method is promised to produce  $H_2$ . The adsorption and dissociation of hydrogen on the membrane surface are pivotal processes with profound implications on the  $H_2$  separation through the membrane. Understanding these phenomena is crucial for advancing the catalytic reactions and facilitating efficient  $H_2$  separation processes. In this research, we investigate the optimization of the adsorption and dissociation properties of Pd membrane surfaces by doping the Pd membrane surface with other platinum group elements (Pt, Ru, Rh, Ir, and Os). The main aim is to enhance the membrane's ability to selectively adsorb and dissociate  $H_2$  molecules, thereby increasing its efficiency in separating  $H_2$  from mixed gas streams. Density functional theory (DFT) is used to build a thorough process of hydrogen interaction over a Pd-based membrane. Atomic-level (quantum level) research was done on the hydrogen-Pd-based membrane interaction. This level of quantum analysis predicts factors associated with  $H_2$  flux through the membrane and provides insights into how the membrane feature would affect  $H_2$  penetration. Accordingly, the characteristics of Pd-based membranes such as binding energy and lattice parameters along with the binding energy of various gases ( $H_2$ , CO, and  $H_2S$ ) were estimated using DFT calculation and validated against data from the literature. Subsequently, the evaluation of the hydrogen gas adsorption process occurs at different locations on the membrane surfaces and different gas orientations on both bare Pd and

the dilute alloy surfaces of Pd-X (X=Pt, Ru, Rh, Ir, and Os). The adsorption energy of H<sub>2</sub> improved on all the surfaces with the minimum energy of -1.24eV which was achieved on the bridge site on the PdIr surface. The H<sub>2</sub> dissociation barrier path on top sites of all the surfaces is barrier-free except for bare Pd and PdPt where the barrier is observed to be -0.069eV and -0.057eV respectively. Moreover, we investigate the effects of pre-adsorbed gases on H<sub>2</sub> adsorption on the Pd-Pt surface. CO adsorption is dominant and follows uniform trends on all the surfaces with the minimum adsorption of -2.73eV on PdOs. Next is H<sub>2</sub>S which has -2.26eV as the minimum adsorption energy which was achieved on the bridge site of PdOs. The effect of CO on PdPt is almost like that on the bare Pd.

## ملخص الرسالة

الاسم الكامل: لاوان محمد آدم  
عنوان الرسالة: فصل الهيدروجين مع غشاء Pd-Pt (دراسة عن طريق نظرية الدالة الوظيفية للكثافة)  
المجال الرئيسي: علوم وهندسة المواد  
تاريخ الدرجة العلمية: مايو 2024

تزداد أهمية الهيدروجين والطلب عليه يوماً بعد يوم. ومن حسن الحظ أن طريقة الغشاء المعتمد على البلاديوم تعتبر واعدة لاستخدامها في إنتاج الهيدروجين. امتزاز الهيدروجين وتفككه على سطح الغشاء هما عمليتان حاسمتين ذات تأثيرات عميقة على فصل الهيدروجين من خلال الغشاء. فهم هذه الظواهر مهم جداً لتحسين التفاعلات المحفزة وتسهيل عمليات الفصل. في هذا البحث، نقوم بدراسة تحسين خصائص امتزاز وتفكك سطوح غشاء البلاديوم من خلال تطعيم سطح الغشاء باستخدام عناصر المجموعة النبيلة (Pt, Ru, Rh, Ir, and Os). الهدف الرئيسي في هذا البحث، هو تعزيز قدرة الغشاء على امتزاز وتفكك جزيئات الهيدروجين من أجل زيادة كفاءة فصل الهيدروجين من تدفقات الغاز المختلطة. من خلال استخدام برنامج نظرية الكثافة الوظيفية (DFT) لبناء عملية شاملة لتفاعل الهيدروجين على غشاء قائم على البلاديوم. تم إجراء بحث على مستوى ذري (مستوى الكم) حول تفاعل الهيدروجين مع غشاء قائم على البلاديوم. هذا المستوى من التحليل الكمي يتنبأ بالعوامل المرتبطة بتدفق بالهيدروجين خلال الغشاء ويقدم معلومات حول تأثير سمات الغشاء على اختراق الهيدروجين. وبناءً على ذلك، تم تقدير سمات الغشاء المعتمد على البلاديوم مثل طاقة الترابط وعوامل الشبكة البلورية بالإضافة إلى طاقات الترابط غازات مختلفة ( $H_2S$ ,  $H_2$  and  $CO$ ) حيث تم تقديرها باستخدام حسابات نظرية الكثافة الوظيفية (DFT) وتم التحقق منها ومقارنتها بقاعدة البيانات الموجودة في البرنامج. بعد ذلك، تم تقييم عملية امتزاز غاز الهيدروجين في مواقع واتجاهات مختلفة على سطح غشاء البلاديوم النقي Pd وأسطح البلاديوم التي تم تطعيمها بالعناصر النبيلة Pd-X (X= Pt, Ru, Rh, Ir, and Os). طاقة الامتزاز للهيدروجين تحسنت على كل الأسطح بتحقيق أقل طاقة بقيمة 1.24- إلكترون فولت والذي تم تحقيقه في موقع الجسر على سطح PdIr. مسار حاجز تفكك الهيدروجين في المواقع العلوية لجميع الأسطح لا يحتوي على حواجز، باستثناء البلاديوم الخالص Pd والبلاديوم البلاتيني PdPt حيث تم ملاحظة وجود حاجز بقيمة 0.069- إلكترون فولت و 0.057- إلكترون فولت على التوالي. بالإضافة إلى ذلك، تم التحقق من تأثير الغازات الممتزة مسبقاً على امتزاز الهيدروجين على سطح البلاديوم البلاتيني. يعد امتزاز أول أكسيد الكربون الأكثر سيطرة ويتبع اتجاهات متسقة على كل الأسطح بطاقة امتزاز تساوي 2.73- على

سطح PdOs. ويأتي بعده ثاني كبريتيد الهيدروجين S<sub>2</sub>H والذي يملك طاقة امتزاز تساوي 2.26- إلكترون فولت والذي تم تحقيقه على موقع الجسر لسطح PdOs. تأثير أول أوكسيد الكربون على سطح البلاديوم البلاتيني PdPt تقريبا مشابه لسطح البلاديوم الخالص Pd.



# CHAPTER 1

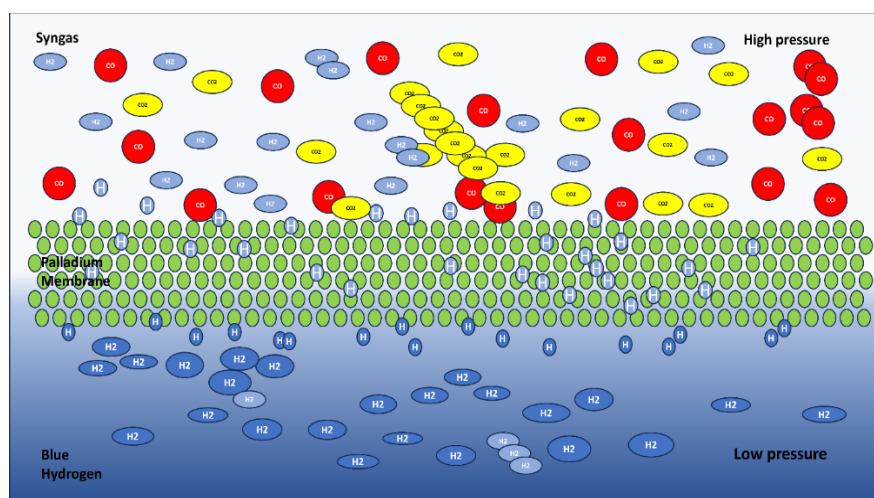
## INTRODUCTION

Energy direction changes now focus on renewable energy sources as per major to save the environment from the effect of CO<sub>2</sub> emissions [1]. CO<sub>2</sub> emission from fossil fuels has become a global concern due to the deterioration of ecosystems caused by the emitted gases. This motivates a search for supplements to the above-mentioned energy sources to achieve the goal of a greener future [2]. Among the target sources to replace fossil fuels, hydrogen gains more concern because of its unique qualities including zero carbon emissions [3,4]. Moreover, hydrogen is renewable which includes traditional biomass, made up 14% of the world's energy in 2016 [5,6,7]. An economy based on hydrogen can play a significant part in the transition. The hydrogen economy seems to be just around the corner because there is so much research being done to improve methods of manufacturing hydrogen using renewable sources [8,9].

Interestingly, hydrogen can be produced from various sources like water electrolysis, solar power, nuclear power, and steam methane reforming [10]. Depending on the method used to manufacture hydrogen, it is categorized as green, grey, blue, turquoise, or pink [11]. These describe the CO<sub>2</sub> process involved. Green hydrogen is commonly generated through water electrolysis, and no CO<sub>2</sub> is emitted. Coal, heavy oil, and natural gas used as feeds for methane reforming processes produce grey hydrogen which emits CO<sub>2</sub>. When this CO<sub>2</sub> released is captured and stored, blue hydrogen is obtained [12]. Turquoise hydrogen involves pyrolyzing methane (natural gas) to produce hydrogen. Heat is used in the pyrolysis process to transform methane into solid carbon and hydrogen gas. Then, like with blue hydrogen, the carbon is collected. When referring to hydrogen produced by nuclear power, the term "pink hydrogen" is occasionally used. The heat produced by nuclear reactors can be used to power water electrolysis, which

creates hydrogen. Although this process doesn't directly emit greenhouse gases, it has its own set of safety and waste management issues that are tied to nuclear power [13].

Among the methods, steam methane reforming turns out to be the most widely used method to produce hydrogen. Methane is a molecule that is difficult to activate, hence it is typically reformed at temperatures much higher than those of other hydrocarbons [14]. A mixture of gases is obtained from this method from which hydrogen can be separated. These gases are collectively called syngas which contain  $H_2$ ,  $CO_2$ ,  $CH_4$ , and  $CO$ , with respective percentages of 74, 18, 7, and 1 [8,15]. The techniques used in hydrogen extraction from the mixture include cryogenic distillation, pressure swing adsorption, dense metal membrane, etc. Comparatively, high purity levels can be achieved by separating hydrogen from a hot gas mixture using dense metal membranes, which are both energy-efficient and very selective [16,17]. A pressure gradient acts as the driving force for hydrogen separation in a membrane. In essence, one end of the airtight membrane receives a high-pressure feed gas mixture while the other side is kept at a comparatively low pressure as shown in Figure 1. Large hydrogen partial pressures will start the mass transfer mechanism. The impurity gases will be left behind when hydrogen moves through the membrane [6,8].



*Figure 1. Hydrogen gas passes through a highly selective membrane while impurities are blocked.*

The most promising and widely researched selective membrane is the palladium(Pd)-based membrane. This is because of their higher H<sub>2</sub> permeation rate as well as H<sub>2</sub> selectivity. Pd-based membrane separates H<sub>2</sub> with a purity of 99.99 percent [12,18]. However, there is a notable list of downsides to a Pure Pd membrane.

- (i) A pure Pd membrane in the presence of H<sub>2</sub> experiences embrittlement at temperatures below 300°C[8]. Similarly, deactivation occurs when carbonaceous contaminants settle at temperatures higher than 450 °C.
- (ii) Pure Pd foils made for commercial use are very expensive.
- (iii) Pure Pd membranes at high temperatures (over 300 °C) are prone to gaseous molecules, such as H<sub>2</sub>S, HCl, CO<sub>2</sub>, and CO, which can reduce their performance, especially H<sub>2</sub>S presence, which leads to great H<sub>2</sub> flux loss[8,12],
- (iv) There is a compromise between H<sub>2</sub> permeability and selectivity relative to the thickness of the membrane and in turn its mechanical stability.

All these challenges are bottlenecks. Using computational approaches many insights advance the understanding of H<sub>2</sub> transport mechanism through the membrane and the effect caused by the poisonous gases in the process. This information is relevant in choosing a better approach to improve the membrane. Therefore, advancement in computational analysis using density functional theory and classical Monte Carlo among many is highly needful to circumvent most of the challenges with Pd-based membranes.

## **1.1 Methods of Hydrogen Production**

There are various techniques for producing H<sub>2</sub> gas. Using alkaline water electrolysis is one of the simplest and easiest methods. Significant drawbacks, however, including those related to energy usage, security, robustness, and dependability, must be addressed. Steam-reforming methane is another technique

for producing hydrogen. Several gaseous components are used in this approach to extract hydrogen. Separating  $H_2$  from the hot gas mixture could be accomplished using a variety of methods, including membranes, pressure swing adsorption (PSA), and cryogenic separation. The temperature of the boiling point is used to determine the separation process in the cryogenic distillation procedure. All other impurity gases condense to produce a liquid phase, but  $H_2$  stays in a gaseous state since it has the lowest boiling point ( $-252.9\text{ }^{\circ}\text{C}$ ) [19]. This method separates  $H_2$  with 99% purity, although it is only practical on huge industrial sizes. PSA can be used to achieve high  $H_2$  purification (99 to 99.999%). The PSA separation process involves passing the gas mixture through an adsorber material, which adsorbs other impurities gases while allowing  $H_2$  to flow through. The partial pressure of the impurity gases between the exhaust and the feeding gas drives this process. Next, the system pressure is swung from the feeding pressure to the exhaust pressure value, eliminating the impurity gases. Using a hydrogen-selective membrane is the third method of separating  $H_2$  [20]. This method is likewise powered by a pressure gradient, in which one side of the membrane is fed with a high-pressure gas mixture while the other side is kept at a low pressure[19,21]. The membrane allows only  $H_2$  to flow through it. Up to  $900\text{ }^{\circ}\text{C}$  can be reached as high as an operational temperature and pressure range for the membrane separation process.

## **1.2 Mechanism of Hydrogen Permeation through the Membrane**

Under the influence of a pressure differential, a multi-stage process drives the hydrogen permeation mechanism through the membrane. The direction of flow is from high pressure to low pressure. (i) The first step involves the diffusion of hydrogen molecules to the membrane surface, (ii) followed by reversible dissociative adsorption on the Pd surface, (iii) the dissolution of atomic hydrogen into the bulk material, and finally the diffusion of hydrogen through the bulk material. As the atoms travel across the lattice of the bulk material, the electrons interact with the metal lattice until they cross the membrane and (iv) the hydrogen atoms re-associate on the palladium surface[12,22]. Following that, the

molecular hydrogen (v) desorbs from the membrane surface and (vi) diffuses away from it as shown in Figure 1.

### **1.3 Motivation and Significance of the Study**

As  $H_2$  emerges as a key player in the transition to sustainable energy systems, studying  $H_2$  adsorption and dissociation on Pd-based alloy membranes is motivated by the pressing need for efficient hydrogen separation and purification technologies. The significance lies in the unique properties of Pd-based alloys, such as high hydrogen permeability and selectivity, making them promising candidates for hydrogen purification and separation applications. Understanding the adsorption and dissociation behavior of  $H_2$  on these membranes is crucial for optimizing their performance in processes like hydrogen purification, fuel cell operation, and hydrogen storage. However, the species type and concentrations in the gas mixture, the membrane's Pd-alloy percentage, the operating temperature, the configuration of the system, etc., are some of the variables that affect the hydrogen purification process. Because so many tests must be performed and because different geometry of separation systems require different experimental setups, it is quite costly to investigate all these elements through experimentation.

### **1.4 Research Objectives**

The overall objective of this work is to develop insights into the interaction between  $H_2$  and Pd-based alloy surfaces to enhance the design and fabrication of advanced membrane materials with improved properties.

Accordingly, it can be divided into specific objectives as follows:

- (i) Investigate potential strategies for enhancing the catalytic activity and efficiency of Pd-based alloy membranes in  $H_2$  adsorption and dissociation processes.
- (ii) Carry out a series of calculations of density functional theory (DFT) on pure Pd- surface (111)

- and Pd-X (X=Pt, Ir, Os, Ru, and Rh) to identify the hydrogen adsorption energy and energy barriers during the dissociative-adsorption processes and identify their dependence on dopants.
- (iii) Study the impact of poisoning gases on the adsorption energy of hydrogen molecules on the most preferred Pd alloyed surface.

# CHAPTER 2

## LITERATURE REVIEW

### 2.1 Pure palladium

Due to the polycrystalline nature of Pd membranes, they have a variety of facets, with low-index faces (111), (100), and (110) receiving more research attention than high-index faces due to their higher prevalence [23]. Depending on the crystallographic orientation of the surface, in general, it has the following adsorption sites (i)top, (ii)bridge, and (iii)hollow through which the gases are adsorbed. H<sub>2</sub> and other gases are usually adsorbed at a certain distance from the Pd-based membrane surface which is known as the adsorption height. This height differs from one molecule to another, and it determines the reaction rate and mechanisms. When the gaseous molecules are too far away from the surface, their interaction with the surface becomes very weak. As the gases approach the surface, the interaction strengthens, and each type of gas is attracted to certain adsorption sites on the surface. In metals like Ag, Cu, Au, and Pt with (100) orientation surfaces, hydrogen may probably prefer to be adsorbed through hollow on FCC Ag(100) and Cu(100) and the bridge on FCC Au(100) and Pt(100) [24]. However, on the Pd surface, the hollow is probably the most stable for hydrogen adsorption. The variation in the atomic orientations of the Pd surface may affect the adsorption energy and even change the preferential adsorption site for H<sub>2</sub>[25]. It is interesting to know that the hollows in (111) and (211) surfaces are advanced compared to (100) with addition of hcp and fcc hollow sites and these sites could show different potentials toward hydrogen even though the adsorption energies between them were mostly reported to be slightly different if not equal as reported that hydrogen adsorption energy on Pd(211) of 0.52eV to be similar for hcp and fcc site [26]

Obviously, physisorption occurs due to the weak attractive Van der Waals force and as a result, the process is reversible. However, moving closer of the  $H_2$  molecules toward the Pd surface activates the chemisorption reaction which is a strong and more specific interaction between the  $H_2$  molecule and the Pd membrane surface. It involves the formation of a chemical bond between the  $H_2$  and the palladium atoms. The chemisorption is not easily reversible because it results in  $H_2$  molecules dissociating into individual atoms (H) on the surface and subsequently, the H atoms preferentially diffusing into the membrane lattice. Just as the adsorption site on the surface, the absorption site in the subsurface and other membrane layers exhibit preference as to whether H-atom to move onto or not. The most important to note is that hydrogen adsorption and dissociation occur on the surface. However, adsorption may also occur in the subsurface. Hydrogen adsorption in the subsurface of Pd(211) was reported and the octahedral site in the subsurface has an adsorption energy of 0.19eV which is slightly favorable compared to that of the tetrahedral site with 0.18eV [26]. Ironically, the octahedral and the tetrahedral are considered the bulk sites and should be associated with absorption instead of adsorption and the dissociated hydrogen atoms could not be adsorbed again on the subsurface since the diffusion process begins immediately after the H atom leaves the surface into the subsurface down to the bulk.

Although the conclusion that subsurface sites are energetically less favorable than surface adsorption sites has not yet been verified experimentally, and subsurface mechanisms have many scenarios that make it study more complex, it may be logical, since surface atoms are more unstable compared to subsurface atoms due to their missing neighbor atoms and this could favor more hydrogen adsorption reaction on the surface. However, the chemical composition, surface area, porosity, surface charge, and other factors can greatly alter the adsorption and subsequently the diffusion behavior of various surfaces [26].

While the Pd-based membrane allows H<sub>2</sub> passage, the case with other gases is different. CO<sub>2</sub>, CO, and H<sub>2</sub>S are present in the gas mixture from which H<sub>2</sub> is separated and their reaction processes on the membrane are crucial to the stability of the membrane as well as the H<sub>2</sub> process.

Jinfan Chen et al. analyzed the reaction processes of CO<sub>2</sub> and CO on (100), (110), and (111) surfaces of the Pd membrane [27]. The behavior of the surfaces when exposed to the gases reveals that the perfect Pd surface resists the inhibition from CO<sub>2</sub> and is inactive to CO<sub>2</sub>-CO catalysis which is limited by the formation and dissociation steps of COOH [28].

Hydrogen sulfide (H<sub>2</sub>S) is another gas of concern, and its decomposition on (111) Pd surface is easily achieved even when its adsorption on the surface is unstable[29,30]. When it decomposes into SH and H they prefer to respectively migrate and bind at the bridge adsorption sites and FCC adsorption sites instead of the original top site that is preferential for the H<sub>2</sub>S molecule. Alfonso et al. further claimed that the adsorption of H<sub>2</sub>S is non-active from the gas phase and exothermic [29]. Similarly, Hyman et al. move further to study the H<sub>2</sub>S dissociation on Pd(111), Cu(111), Ag(111), and Au(111) as well as Pd-alloys under the effect of lattice constraint and electronic ligand and reported that the adsorption energy of H<sub>2</sub>S, SH, and S are correlated with lattice constant. Accordingly, the Fermi level, d-state density at the Fermi level, and d-band center relative to the Fermi level are the determinants of H<sub>2</sub>S binding energy [31]. Also, they confirm the top site as the most favorable for H<sub>2</sub>S adsorption and the H<sub>2</sub>S dissociation reaction is exothermic as mentioned by Alfonso et al.

All these studies shed light on the adsorption, dissociation, and diffusion behavior of hydrogen and some of the gases(CO, CO<sub>2</sub>, and H<sub>2</sub>S) contained in the mixture produced from methane reforming on the Pd membrane. This will facilitate the design of efficient membranes for large-scale hydrogen production.

## 2.2 Alloying effect

The alloying effect could improve the adsorption and dissociation of  $H_2$  on the Pd membrane surface. Unlike pure Pd membranes, Pd-alloy membranes have collective properties from the individual elements participating in the alloying. Hence, their properties are more enhanced than the pure Pd membrane. PdCu is widely reported and considered one of the promising materials for hydrogen separation. When Pd(FCC) and copper(FCC) are alloyed, they can form a solid solution where the two elements are combined at the atomic level. If the content is within specified ranges, the resultant crystal structure can stay FCC.

Although alternative crystal forms, such as body-centered cubic (BCC) or even an amorphous structure, may be seen as the alloy's composition deviates from certain ranges. The precise composition and processing conditions will determine the crystal structure of a PdCu alloy. However, hydrogen adsorption and dissociation could be studied on any of the structures for a better understanding of the material's behavior to hydrogen separation.

Liu et. al studied the FCC(111) and BCC(110) surfaces of PdCu(50:50) and found the hydrogen( $H_2$ ) adsorption to be more favorable on BCC(110) compared to the FCC(111). This is a similar case with the dissociation where the hydrogen seems to dissociate more easily on BCC(110) than the FCC(111) which complies with the experimental findings [32].

## 2.3 Effect of Coverage

When compared to other membrane types, dense metal membranes function between 300 and 600 °C, have excellent hydrogen selectivity, and provide higher flux rates. Dense metal membranes may produce  $H_2$  that is 99.99% pure, which is suitable for PEFCs that employ Pt catalysts that can be contaminated by CO. The primary disadvantage is the high initial cost of the dense metal membranes,

which are frequently based on Pd. And since flux is a function of membrane permeability and thickness, efforts are being undertaken to deposit thin films of Pd onto porous substrates to decrease material costs and boost H<sub>2</sub> flux rates.

Although pure Pd membrane has a unique selective priority for H<sub>2</sub>, the process is always faced with challenges mostly with the poisoning effect from other gases(CO, CO<sub>2</sub>, H<sub>2</sub>S) present in the feed.

These gases can severely poison the Pd-based membrane and destabilize the hydrogen's transport mechanism [33]. The magnitude of the effect of the poisoning gases depends on how they interact with the hydrogen and the membrane, especially in competing for adsorption sites and the level of surface coverage formed by the poisonous gases on the membrane surface. This coverage and competition for an adsorption site affect the H<sub>2</sub> adsorption and permeation. These gases occupy most of the favorable sites for H<sub>2</sub> to be adsorbed and this metamorphoses into poisoning the membrane and subsequently declines the flux rate of H<sub>2</sub>. However, H<sub>2</sub> coverage is desirable, once H<sub>2</sub> molecules are adsorbed onto the Pd-membrane surface, they undergo surface reactions where higher H<sub>2</sub> coverage promotes the dissociation process of H<sub>2</sub>, and its permeation becomes more favorable.

Song et al. studied the adsorption, diffusion, and permeation of H<sub>2</sub> on Pd(100) covered with H<sub>2</sub>. They reported two permeation mechanisms of H<sub>2</sub> from the surface to the subsurface sites which were recognized as monomer and dimer permeation pathways. The former is favorable at low H<sub>2</sub> coverage and the latter at a saturated surface. The energy barrier of the dimer permeation pathway declines when the H-coverage reaches a monolayer (ML) and for the monomer pathway, the barrier appears low when the coverage is less than a ML [34]. In general, hydrogen coverage enhances its permeation. As the coverage increases the probability of H<sub>2</sub> to adsorb and later dissociate on the surface increases. This could be a favor for H<sub>2</sub> to dissociate diffuse into the bulk and desorbed from the other membrane's surface (where the H-atoms recombine to form pure H<sub>2</sub>).

Liang. et al.[35] extend the research by considering the effect of coverage from other adsorbed gases (OH, O<sub>2</sub>, and O) on the Pd(100) surface on the atomic mechanism for H<sub>2</sub> diffusion into the subsurface in addition to the H coverage. They calculate favorable pathways while varying the level of each coverage. At 0.5ML, O<sub>2</sub>, O, and H<sub>2</sub> coverages decrease the H<sub>2</sub> diffusion barrier into the subsurface of the Pd(100) while H<sub>2</sub> coverages of 0.25ML and 0.75ML increase the barrier for the forward process which is in conformity with the Song. et al. since the two monolayers here are less than 1ML like their report. The electro-properties, adsorption position at different orientations, as well as the spatial structure of the adsorption gases always have an influence on the diffusion barrier and the adsorption locations. Some orientations like horizontal are often reported to be more favorable to surface reactions compared to vertical even though there may be exceptional cases in which the reverse is the case.

In addition, an exothermic diffusion pathway is observed at 0.5ML which could be linked to the dissociation process of the gases as reported by Hayman et al. and Alfonso et al. Research on the choice of gases to prevent overheating reactors may be built upon this. Also claimed that the presence of O, OH, and CO<sub>2</sub> adsorption favors the subsurface sites for the chemisorption of hydrogen to be more stable, and at different coverages of OH, hydrogen prefers the bridge site on the surface.

Considering methane reforming as the main source of feed to the membrane and it supplies a mixture of gases(Syngas) hydrogen inclusive, Abuelyamen et al. cover the Pd membrane with H<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub> each at varying coverage and study the hydrogen adsorption on these coverages and reveal the effect of the carbon-bearing species on the adsorption process of the hydrogen. Findings exposed that hydrogen easily adsorbs at the top site on the Pd surface when it is horizontally aligned, CO has more poisoning effects than others, and its adsorption energy is the greatest.

Moreover, they confirmed the decrease in the physical adsorption barrier of hydrogen at its higher

coverage like the earlier report. When compared to CO which adsorbed (energy of  $-1.887\text{eV}$ ) close to the surface ( $1\text{--}1.5\text{\AA}$ ),  $\text{CO}_2$  and  $\text{CH}_4$  have low adsorption energy (respectively,  $-0.255\text{eV}$  and  $-0.194\text{eV}$ ) due to their long adsorption distance of  $3\text{\AA}$  and  $2.6\text{\AA}$  respectively from the surface. While performing adsorption calculations, it is important to have similar initial heights for all gases on the surface as a reference for easy comparison. It may sometimes be difficult to comprehend the results. Like in this case,  $\text{CO}_2$  and  $\text{CH}_4$  have energies that are higher in value but because of their distance when related to CO which has low energy in value, they are assumed to be the least obtained energies even though are higher in value however, the CO shows a high poisoning effect. Nevertheless, the chemisorption energy which is about 3 times that of physisorption increases with an increase in hydrogen coverage up to 1ML then decreases. When the chemisorption becomes more positive it might be unlikely to have extreme coverage, and the  $\text{H}_2$  extreme adsorption energy may appear at high coverage only if the covering hydrogen atoms (H) are well dispersed on the surface without blocking the  $\text{H}_2$  adsorption sites.

The fact that CO has the greatest poisoning effect compared to other gases is widely reported, and insights into its transport mechanisms are of paramount importance in understanding how it happens. Also, it may help to improve hydrogen permeability and selectivity through the Pd membrane in its presence. The CO adsorption sites might be competitive with that of hydrogen or a different thing that results in hindering the  $\text{H}_2$  transport in the presence of the CO. However, Abueelyamen et al. [27], and like experimental findings reveal 0.5ML CO coverage appears to form a surface reconstruction of the  $c(4\times 2)$  phase on Pd(111), Hooshmand et al. attempted to verify the exact site for which such adsorption happens. Using coverage up to 0.5ML with CO, the study showed that CO prefers only a particular type of site but not a combination. Either favorably adsorbs on (i) FCC or HCP hollow sites only or (ii) an intermediate site between FCC and bridge sites. [36] Meanwhile, any other site is unfavorable for CO molecules to adsorb and reconstruct the surface. Fortunately, those sites differ from the favorable sites where  $\text{H}_2$  is

absorbed. Many studies show that  $H_2$  prefers the top, and this is a clear indication that the effect of CO might come from a different cause but not certainly  $H_2$  adsorption site blockage. Furthermore, findings show that  $H_2$  adsorption decreases notably below 600K by CO, while the  $CO_2$  dissociation step above 750K shows the same effect on (100) and (110) Pd surfaces. Carbon deposition is seen on (100) Pd slab when the rate-limiting steps for  $H_2 + CO$  reactions on all the surfaces are associated with the COH species dissociation.[28]

Another most poisonous is  $H_2S$ . It was discovered to completely limit  $H_2$  penetration in pure Pd membranes at concentrations above 100 ppm [31]. The sulfur compound poisoning of metallic surfaces is a highly critical issue that affects several industrial operations.

Sulfur adsorption on surface sites can be used to explain how  $H_2S$  poisoning of palladium-based membranes results in a reduction in the active surface area of the membranes. For hydrogen separation, the procedure entails a few dissociative stages. Chemical reactions between the adsorbed sulfur and the membrane may result in palladium sulfide compounds on the surface which potentially clog the membrane's pores or active sites, depending on the amount of  $H_2S$  present and the surrounding circumstances. Through displacement of the crystalline lattice, this corrosion product can cause the membrane performance to deteriorate over time since PdS is less permeable to  $H_2$  than pure palladium [8,37,38]. Interestingly, this challenge is minimized to enhance the membrane performance in  $H_2$  separation and other applications. Among the prominent methods is Pd-based alloying, other methods include surface modification, nanostructuring, thin film deposition, membrane microstructure control, etc. [5,39].



## **CHAPTER 3**

# **BACKGROUND AND RESEARCH METHODOLOGY**

### **3.1 Methane Reforming of Natural Gas**

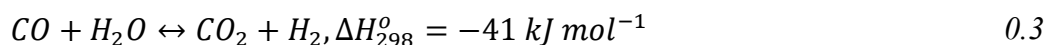
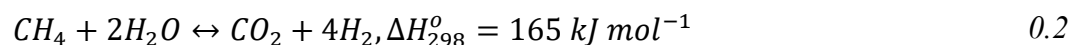
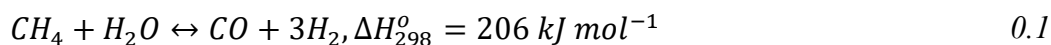
The process of turning hydrocarbons into hydrogen is known as steam reforming technology. Since natural gas is widely available, simple to use, and reasonably priced, it is the main feedstock [5]. A method for turning hydrocarbons into  $H_2$  in the presence of steam was first presented by Motay and Marechal in 1968 [40]. Later, Badische Anilin- & Sodafabrik (BASF) patented the industrial update of this method in 1912, while Dieffenbach and Moldenhauer patented it in 1909 [12,41]. On a smaller scale, the novel membrane reactor technique offers cost-effective hydrogen generation. Due to their potential for gas separation and their use in steam reforming, dense metallic membranes have received special attention. The low mechanical resistance and limited tolerance to sulfuric chemicals and unsaturated hydrocarbons of a Pd membrane are its drawbacks. Nevertheless, there has been a lot of interest in high  $H_2$  permeability, which results from high  $H_2$  purity and recovery.

More than 90% of the hydrogen produced in the World is generated using natural gas steam reforming (NGSR), one of the most popular ways for producing  $H_2$  [42]. Methane is a vital constituent of natural gas. However, the geology of the reservoir affects its composition. For this reason, the required purification procedures must be carried out to adhere to the specifications established by environmental agencies and pipeline corporations. Table 4 displays the specifications for pipeline-quality natural gas depending on the upper bound of its composition.

Since most of the research deals with catalyst deactivation, kinetics, and energy evaluation for industrial reforming, there have generally been less investigations on hydrogen generation in membrane reactors, particularly Pd-Ag membrane reactors [5].

Another popular industrial method for producing hydrogen is methane steam reforming (MSR), which was first presented in 1930 [14]. MSR is a cost-effective process whose feedstocks include gases and liquid hydrocarbons. It produces 40–50% of the world's hydrogen. The process is carried out at pressures of 13–20 bar and temperatures between 800 and 1100 °C. Since this type of reaction is endothermic, it must be conducted at extremely high temperatures. However, to maintain the reaction and obtain a high methane conversion, a significant heat flux must also be applied to the reaction system. Consequently, a substantial portion of fixed and running expenses were identified because of the necessity of transferring heat from an external source to a high-temperature catalytic system, setting a crucial goal for process intensification.

Pretreatment of the raw feedstock, reforming to produce synthesis gas, conversion to a hydrogen-rich gas, and purification to gather hydrogen are the several processes that make up the MSR process. The following are the three primary reactions occurring:

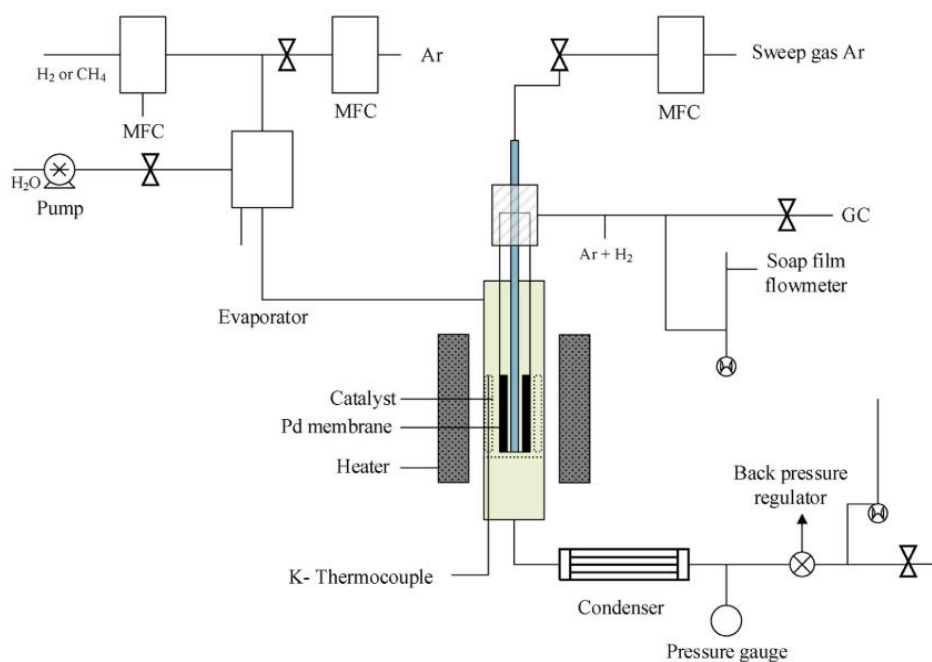


0.1 and 0.2 are endothermic processes. Better efficiency might be attained via (i) The endothermic process might be powered by steam produced by a reformer burner powered by the pressure swing adsorption of purge gas. (ii) Reusing raw resources [43].

This kind of reaction requires catalysts, which are necessary to speed up the process. As previously said for the MSR processes, catalyst sizes and shapes play a significant role in ensuring that the catalysts can function at high operating temperatures and pressures. Furthermore, catalysts made of

noble metals, such as Pd, Rh, Ir, Ni, and Ru, are very effective in this process [43,44].

The architecture of reactors is equally important in MSR procedures. For example, pressure is a crucial design parameter since, in most cases,  $H_2$  pressure requirements are as high as 20 bar. Reformers are therefore designed to operate between 20 and 26 bars [12,14]. For this kind of high-pressure application, a compact design is therefore seen to be very appropriate, which lowers the cost of materials. To further guarantee a decrease in energy loss, materials that withstand heat should be carefully chosen.



**Figure 2.** A schematic representation of a device used in a Pd-based membrane reactor for  $H_2$  permeation and MSR reaction[12].

Reactor tubes, for instance, are constructed of materials resistant to heat (Ni alloy). An annulus is formed between the tube and the membrane in **Figure 2**, which shows a detailed membrane reactor in which the Pd membrane is fitted within the stainless-steel tube reactor. The inner volume functions as the permeate side and the annular chamber as the retentate side. Using a K-thermocouple, the temperature of the catalyst and the reactor are closely monitored. In general, Ni-based catalysts are chosen

because they are less expensive than other types. A catalyst like Ru is employed in a membrane reactor as opposed to a traditional equilibrium reactor. While hydrogen is eliminated from the reaction area, the typical equilibrium reactor's low operating temperature increases the likelihood of coke production [45].

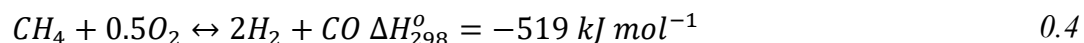
### 3.2 Synthetic Gas or Syngas (Partial Pressure Reaction)

Through an oxidation process with steam and oxygen, a variety of carbon feedstocks, including natural gas, oil products, and biomass, may be converted into synthetic gas, or syngas, which is primarily composed of hydrogen, carbon monoxide, and carbon dioxide.

In the industry, MSR is widely utilized for syngas production. Carbon decomposition, catalyst sintering, and explosion danger can all arise from standard operating circumstances. **Table 1** displays the maximum component composition for natural gas pipelines.

Consequently, a different approach called partial oxidation of methane with oxygen is suggested. However, using pure oxygen has its major disadvantages. Because a membrane reactor's membrane is oxygen-perm-selective, air is used as a substitute within one. The engineering of membrane reactors combines the normal features of catalytic reactions with the membrane's separation qualities. As a result, since a greater methane conversion at low temperatures is obtained, they are recommended as a viable path toward the manufacture of syngas.

The following is the exothermic partial oxidation process that yields syngas.



**Table 1. Maximum limit for components composition for pipeline natural gas quality [12].**

| Component   | Butane | Nitrogen | Carbon-Dioxide | Propane | Ethane | Methane |
|-------------|--------|----------|----------------|---------|--------|---------|
| Max. (mol%) | 2      | 4        | 4              | 5       | 10     | >96     |

### 3.3 Hydrogen Separation Techniques

The syngas gas produced through the methane reforming process, primarily ( $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{S}$ ), do not chemically react easily with one another because of the higher reaction barrier. For this reason, syngas remains as a mixture of gases that could be separated into individual gases, a chance that warrants  $\text{H}_2$  separation. Three commercial processes now available provide different levels of purity; some are employed on large industrial sizes, while others may be scaled down for portable purposes.

#### 3.3.1 Pressure swing adsorption (PSA)

PSA is a process in which a gas combination is passed through a large surface area adsorber that permits hydrogen to flow through the material while adsorbing impurities gases. At high gas partial pressures, impurity gas species are adsorbed onto an adsorbent material and, conversely, desorbed at lower partial pressures. Zeolite is a prominent adsorbent substance. By adjusting the system pressure from the feed to the exhaust (tail gas) pressure and performing a high-purity hydrogen purge, the contaminants may be eliminated. To provide a steady flow of feed, product, and tail gas, several adsorbers are employed in this cyclic process. Every adsorbent material goes through an identical swinging process, although the stages are spaced apart throughout. The partial pressure differential between the feed and tail gas of impurity gases is what powers PSA. Generally, a 4:1 pressure ratio between the feed and tail gas is needed for hydrogen separation.

PSA has two primary benefits: it can generate hydrogen with high purity levels, up to 99.999 percent, and remove contaminants down to parts per million (ppm). The PSA unit's tail gas is often used as fuel at low pressures, which offers an inexpensive advantage. Nevertheless, compressing the tail gas results in significant expenses that are equal to or greater than the unit's purchase price.

Therefore, it is crucial to choose a tail gas pressure. An important trade-off arises between tail gas

compression costs and hydrogen purity when the tail gas pressure of the PSA system is increased [13]. The infrastructure and operational scope are further disadvantages. PSA can be applied on medium to large industrial scales; however, smaller portable scales are not practicable for its application.

### 3.3.2 Cryogenic distillation

Due to the low temperatures used during the whole process, this approach is extremely energy-intensive. Because the constituents of the gas have different boiling points, cryogenic distillation may also separate a feed gas combination, just like other distillation methods do. As the impurity gases cool down, a liquid phase forms. Since  $H_2$  has the lowest boiling point of the mixture— $-252.9\text{ }^{\circ}\text{C}$ —it stays in a gaseous condition. The extracted hydrogen's low purity levels, at about 99 percent, are a significant drawback [46]. Additionally, the expense of gas compression to keep the process running at cryogenic temperatures is significant; that being said, the collected  $H_2$  is easily stored in a liquid state [47]. Cryogenic distillation is perfect for big industrial scales, much like PSA, it is not fit for small-scale applications.

### 3.3.3 Hydrogen selective membrane

A pressure gradient is what propels  $H_2$  separation in a membrane. In essence, a hermetically sealed membrane has a high-pressure feed gas combination delivered to one end while the pressure on the other side is kept comparatively low. Massive partial pressures of hydrogen will start a process called mass transport. As hydrogen starts to move over the barrier, the impure gases are left behind. The performance and applications of each of the six primary types of hydrogen-selective membranes may be ascertained by determining certain characteristics [47,48].

**Table 2. The characteristics of several kinds of hydrogen-selective membranes are taken directly from Al-Mufachi et al [8].**

|                                                                                                                  | Dense polymer                                       | Micro-porous ceramic                                                                                            | Dense metallic                                                                | Porous carbon                                                                                    | Dense ceramic                                                                                                        |
|------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------|-----------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|
| Temperature range (°C)                                                                                           | < 100                                               | 200–600                                                                                                         | 300–600                                                                       | 500–900                                                                                          | 600–900                                                                                                              |
| H <sub>2</sub> selectivity                                                                                       | Low                                                 | 5–139                                                                                                           | > 1000                                                                        | 4–20                                                                                             | > 1000                                                                                                               |
| H <sub>2</sub> flux<br>( $\times 10^{-3} \text{ mol m}^{-2} \text{ s}^{-1}$ )<br>at $\Delta P = 100 \text{ kPa}$ | Low                                                 | 60–300                                                                                                          | 60–300                                                                        | 10–200                                                                                           | 6–80                                                                                                                 |
| Stability issues                                                                                                 | Swelling, compaction, mechanical strength           | Stability in H <sub>2</sub> O                                                                                   | Phase transition                                                              | Brittle, oxidising                                                                               | Stability in CO <sub>2</sub>                                                                                         |
| Poisoning issues                                                                                                 | HCl, SO <sub>x</sub> , CO <sub>2</sub>              |                                                                                                                 | H <sub>2</sub> S, HCl, CO                                                     | Strong adsorbing vapours, organics                                                               | H <sub>2</sub> S                                                                                                     |
| Materials                                                                                                        | Polymers                                            | Silica, alumina, zirconia, titania, zeolites                                                                    | Pd alloy                                                                      | Carbon                                                                                           | Proton conducting ceramics (mainly SrCeO <sub>3-<math>\delta</math></sub> , BaCeO <sub>3-<math>\delta</math></sub> ) |
| Transport mechanism                                                                                              | Solution/diffusion                                  | Molecular sieving                                                                                               | Solution/diffusion                                                            | Surface diffusion; molecular sieving                                                             | Solution/diffusion (proton conduction)                                                                               |
| Development status                                                                                               | Commercial by air products, linde, BOC, air liquide | Prototype tubular silica membranes available up to 90 cm. Other materials only small samples (cm <sup>2</sup> ) | Commercial by Johnson Matthey; prototype membrane tubes available up to 60 cm | Small membrane modules commercial, mostly small samples (cm <sup>2</sup> ) available for testing | Small samples available for testing                                                                                  |

For easy comparison, **Table 2** lists all the challenges, and qualities linked to each kind of membrane. Because the membranes have no moving components and can function at a wide variety of pressures and temperatures, they are highly scalable on both industrial and portable sizes, preventing system wear [49].

### 3.4 Membrane Process Terminologies

A membrane's feed or upstream side is the side with high gas pressure, whereas the opposite side is referred to as the downstream or permeate side (see Figure 1 in Chapter 1). Although permeation can happen in both directions, it will favorably occur in the direction of low pressure. The stream of gas onto the gas flow that remains on the feed side after permeation occurs is referred to as the retentate flow, and it is appropriately titled feed flow. The input flow is referred to as the sweep flow on the opposite side, and the term "permeate flow" refers to the outflow.

#### 3.4.1 Permeability

There are several meanings for the term "permeability." However, for this research, it refers to the assessment of a gas's ability to penetrate a solid material. Permeability is mathematically described and discussed in terms of Fick's diffusion laws. One crucial consideration for H<sub>2</sub> separation is the hydrogen

flow over the membrane. The quantity of hydrogen moles that diffuse along a perpendicular unit cross-sectional area in a unit of time is defined as flux in this context. A variation of Fick's first rule may be used to describe steady-state gas fluxes across a thick solid membrane, as shown by the following equation.

$$J = -D \frac{\partial C}{\partial x} \quad 0.5$$

where D is the diffusivity, or diffusion coefficient, J is the flux of the diffusing species, and  $\partial C/\partial x$  is the concentration gradient. In this derivation, the negative sign, which specifies the direction of gas diffusion, can be ignored. It should be highlighted that variations in a system's chemical potential can be the root cause of all common driving forces, including gradients in concentration, pressure, temperature, and electromotive force. As a result, flux is ultimately determined by a gradient in chemical potential.

Furthermore, permeability is a material constant that is unaffected by the thickness of the membrane. Moreover, the following Arrhenius-type equation expresses permeability, a temperature-dependent characteristic.

$$\varphi = \varphi_0 \exp\left(\frac{-E_\varphi}{RT}\right) \quad 0.6$$

where T is the absolute temperature, R is the gas constant,  $E_\varphi$  is the activation energy for permeation, and  $\varphi_0$  is the maximum permeability at infinitely high temperatures. In the same way, diffusivity Equations. 0.7 and 0.8, respectively, demonstrate how an Arrhenius-type connection controls (D) and solubility (S).

$$D = D_0 \exp\left(\frac{-E_D}{RT}\right) \quad 0.7$$

$$S = S_0 \exp\left(\frac{-E_S}{RT}\right) \quad 0.8$$

where  $E_S$  is the hydrogen enthalpy of solution,  $E_D$  is the activation energy for hydrogen diffusion, and  $D_0$  and  $S_0$  are the diffusivity and solubility, respectively, at infinite temperature. Furthermore, figure 0.9 defines  $E_\phi$ , the activation energy for hydrogen permeation, as the total of the activation energies for solubility and diffusivity.

$$E_\phi = E_D + E_S \quad 0.9$$

### 3.4.2 Porous selective membranes

Many porous materials are currently available for separating hydrogen, usually by a procedure known as molecular sieving. Zeolites, Vycor glass, sintered metals like nickel, and a variety of ceramics including alumina and zirconia are examples of commercially accessible porous materials.

## 3.5 Dense Metal (Palladium) Membrane

It's critical to comprehend the rationale behind the widespread use of metals like Pd in the hydrogen separation industry. Many different metals may dissolve hydrogen to form metal hydrides or interstitial solid solutions. While certain metals can produce stable hydrides at ambient temperature, others can only absorb hydrogen at extreme temperatures and pressures [8,50].

The Pd metal is perfect for separating hydrogen because it can break down molecules of hydrogen into atomic forms that can diffuse quickly through its lattice. In addition, Thomas Graham found in 1866 that this metal can absorb hydrogen up to 600 times its volume while retaining its physical characteristics and structural integrity [51]. Pd membranes were not scaled up from laboratory settings for the nuclear fission industry until the 1950s due to a rising need for hydrogen isotope separation. Since then, Pd membranes have increasingly often been utilized in the semiconductor industry for highly pure hydrogen synthesis [8,51].

Pd, discovered by William Hyde Wollaston in 1803, is a malleable, easily worked silvery white metal with a melting point of 1555°C and a density of 12.023gcm<sup>-3</sup> [8] . It is widely used in the automotive industry for catalytic converters. It possesses a total of 46 electrons, and ionic configurations of [Kr]4d<sup>8</sup> and [Kr]4d<sup>6</sup> when they form ions with a +2 or +4 charge respectively. Between the 4d and 5s energy bands, there are overlapping energy bands that are typical of transition metals. This results in Pd's strong affinity for donor electrons coming from other atoms. Pd's unique chemical and metallurgical interactions with other elements are because its 5s band is filled first before the high energy 4d [8,52].

### 3.5.1 Poisoning Mechanism

Poisonous gases including CO, H<sub>2</sub>S etc. have the potential to bind to the active sites on the surface. Most of the sites are favorable for H<sub>2</sub>. When these sites are occupied by the poisonous gases, H<sub>2</sub> could not be able to adsorb again on the surface because of the unavailability of active site. This is how the poisonous gases compete with H<sub>2</sub> for binding sites and decline the separation of H<sub>2</sub> over time [27].

## 3.6 The Density Functional Theory(DFT) and Method

DFT is a quantum mechanical method used to investigate the electronic composition and behavior of atoms, molecules, and solids. The electron density, which completely describes the electronic system, is the key idea in DFT. The ground-state electron density is the sole factor that affects the external potential and total energy of the system, according to the Hohenberg-Kohn theorems, which form the basis of DFT. A crucial part of DFT is the Kohn-Sham equations, which divide the complicated many-electron systems into hypothetical, non-interacting electrons traveling in an effective potential [53]. We can write the equations as follows:

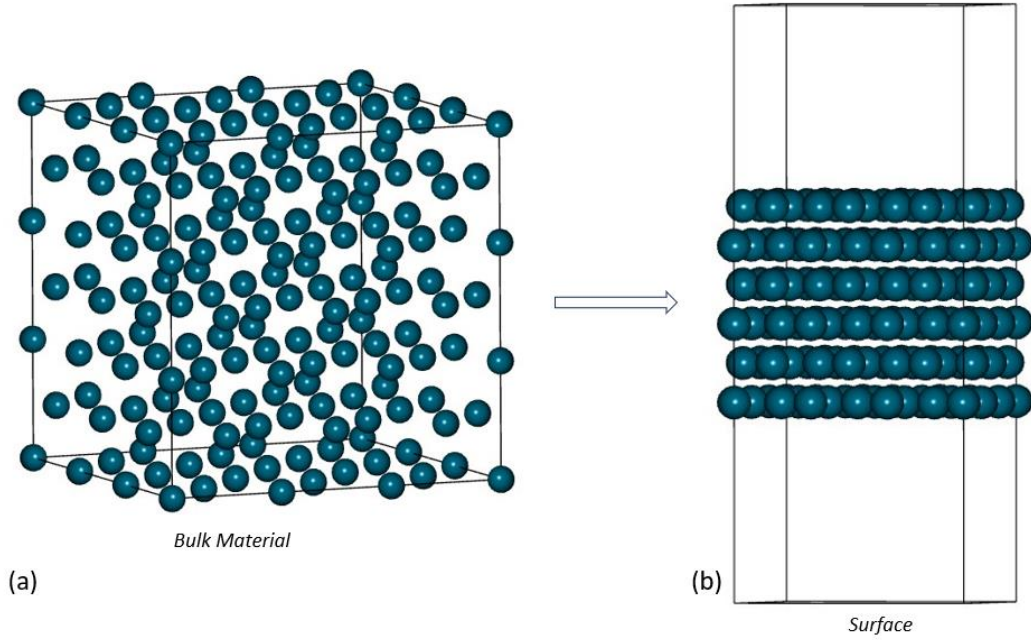
$$H_{KS}\psi_i(r) = \left( -\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(r) \right) \psi_i(r) = \varepsilon_i \psi_i(r) \quad 0.10$$

Here,  $H_{KS}$  is the Kohn-Sham Hamiltonian,  $V_{eff}(r)$  is the effective potential,  $\varepsilon_i$  are the orbital energies, and  $m$  is the electron mass.

DFT has been extensively used to predict properties including electronic structure, energy gaps, vibrational frequencies, and reaction routes. However, it depends on the choice of exchange-correlation function, which approximates the elusive exchange and correlation terms found in the real many-body wave function.

Another important technique that is mostly used together with the DFT is the Nudged Elastic Band (NEB). NEB is a technique for examining how atoms and molecules change during chemical reactions and structural transformations, as well as their transition states and reaction routes [54,55]. The goal of NEB is to identify the most likely transition state and the corresponding reaction pathway by concentrating on the energy landscape along a reaction path. To determine the lowest energy pathway that connects the start and final states of a reaction, the approach first defines an "elastic band" of images between them. This "elastic band" is then iteratively adjusted to discover the lowest energy pathway. NEB aids in the understanding of the energetics of reactions and the movement of molecules between various configurations.

As powerful computational tools, they are extensively used in the study of Pd-based membranes. The mentioned limitations to the Pd-based membrane are systematically studied [23]. One of the early research projects in hydrogen separation and storage was conducted by Kelly M. et al., which confirmed the potentiality of DFT in fastening materials discovery when they used its calculations to screen large metal-based systems with favorable capacities and thermodynamics for hydrogen storage in metal hydrides with application in hydrogen separation [56].



**Figure 3. Palladium bulk material with a generated slab of six-layer surfaces.**

In the density functional theory (DFT), a system that involves the interaction of several bodies is described through its particle density rather than the wave functions of these bodies. The theorem of Hohenberg-Kohn (HK) is considered the basis for DFT. Where the system properties are taken to be functionals of ground state density only. With the help of the Born- Oppenheimer (BO) approximation and Kohn-Sham (KS), the DFT calculation becomes available employing so-called exchange-correlation (XC) potential. For a system involving nuclei and electrons, the time-independent Schrodinger equation and Hamiltonian equation can be written as:

$$H_{tot}\psi(\{R_i\}, \{r_i\}) = E\psi(\{R_i\}, \{r_i\}) \quad 0.11$$

$$H_{tot} = -\sum_I \frac{\hbar}{2M_I} \nabla_{R_I}^2 - \sum_i \frac{\hbar}{2m_e} \nabla_{r_i}^2 + \frac{1}{2} \sum_{I,j} \frac{Z_I Z_j e^2}{|R_I - R_j|} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|r_i - r_j|} - \sum_{I,i} \frac{Z_I e^2}{|R_I - r_i|} \quad 0.12$$

where  $\Psi(\{R_I\},\{r_i\})$  is the total wave function of the system and  $E$  is its total energy. The first two terms of the right-hand side of equation 0.12 represent kinetic energy for the nuclei and electrons, respectively. The other terms represent the potential energy of Coulomb interaction of nucleus-nucleus, electron-electron, and nucleus-electron, respectively. If the Schrodinger equation is solved, then every piece of information about the system would be known, nevertheless, it is impossible to do so practically. Considering that nuclei have a much heavier weight than electrons, thus, they move much slower compared to electrons. Accordingly, Born and Oppenheimer made an approximation of separating the nuclei and electrons movements. Where the nuclei are fixed when the electrons are moving. This leads to two separate Schrodinger equations:

$$H_e \phi(\{r_i\}; \{R_I\}) = V(\{R_I\}) \phi(\{r_i\}; \{R_I\}) \quad 0.13$$

$$\left[ -\sum_I \frac{\hbar}{2M_I} \nabla_{R_I}^2 + V(\{R_I\}) \right] \phi(\{R_I\}) = E \phi(\{R_I\}) \quad 0.14$$

$$H_e = -\sum_i \frac{\hbar}{2m_e} \nabla_{r_i}^2 + \frac{1}{2} \sum_{I,j} \frac{Z_I Z_j e^2}{|R_I - R_j|} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|r_i - r_j|} - \sum_{I,i} \frac{Z_I e^2}{|R_I - r_i|} \quad 0.15$$

The movement of the nuclei can be obtained by solving equation 0.14 after obtaining eigenvalues of the energy  $V(E)$  from equation 0.13. This approach is considered the starting point for the DFT, where the nuclei are considered to form an external potential field in which electrons are moving. KS replaced the interacting system with an auxiliary non-interacting system whose particle number density is the same as the interacting system. Accordingly, the auxiliary Hamiltonian is reduced to equation 0.16. For a system of  $N$ -non-interacting electrons, the Schrodinger equations of  $N$ -electrons (**equation** 0.17) should be solved to obtain the ground state. The density of the auxiliary system can be written in terms of the single-electron orbitals as in equation 0.18. Then the KS one-particle potential can be considered as the sum of external potential, Hartree potential, and an exchange potential as expressed in 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup> terms of

equation 0.19, respectively. Since the KS potential and the energy density are connected, these equations must be solved in a self-consistent manner. After that various quantities can be calculated such as electron density of states, total energy, band structure, forces, etc.

$$\hat{H}_{KS} = \left[ -\frac{1}{2} \nabla^2 + V_{KS}(r) \right] \quad 0.16$$

$$\hat{H}_{KS} \psi_i(r) = \varepsilon_i \psi_i(r) \quad 0.17$$

$$n(r) = \sum_{i=1}^N |\psi_i(r)|^2 \quad 0.18$$

$$V_{KS}(r) = V_{ext}(r) + \frac{\partial E_H[n(r)]}{\partial n(r)} + \frac{\partial E_{XC}[n(r)]}{\partial n(r)} \quad 0.19$$

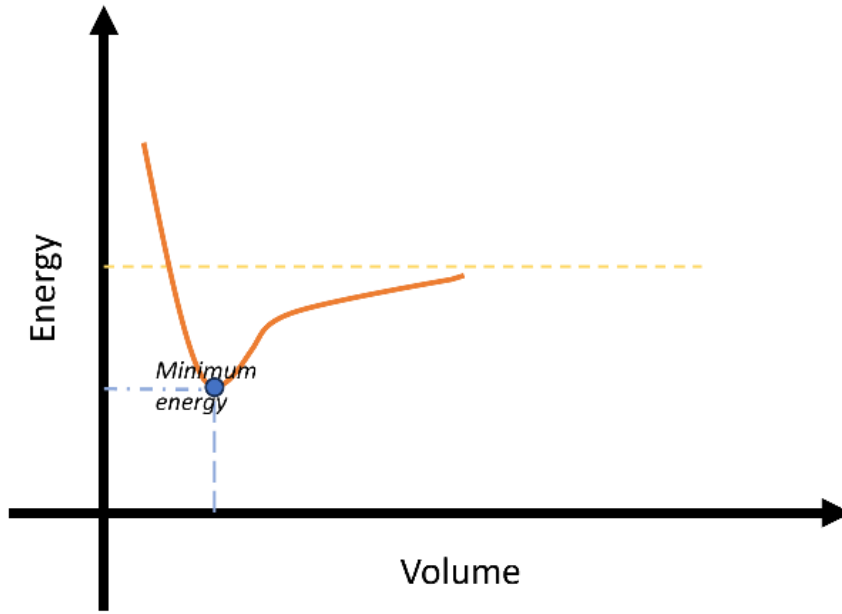
### 3.6.1 Calculation Procedure of DFT

In this work, a numerical model is developed using DFT calculation to study the H<sub>2</sub> separation through a solid Pd-membrane. The characteristic features of the H<sub>2</sub> permeation through the membrane would be obtained by conducting a series of DFT calculations using a plane wave-based program (Quantum ESPRESSO software) where the interaction of H with the Pd-based membrane would be studied. The steps required to complete the work can be summarized as follows:

**(a) Calculate the correct unit cell volume of the solid membrane:**

The membrane is built starting from the atom level by structuring the atoms at a unit cell of FCC. Then, the unit cell volume is calculated by varying the lattice parameter until we get the volume that has minimum equilibrium energy (as shown in **Figure 4**) which will be used for the study of hydrogen interaction with

the membrane, so the hydrogen will diffuse through this volume.

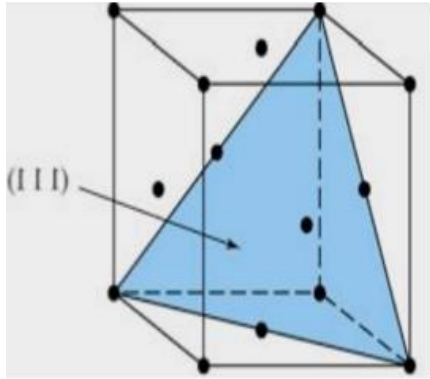


*Figure 4. Energy-volume curve while varying the lattice parameter of the unit cell.*

**(b) Construct the actual surface of the membrane:**

The FCC unit volume will be cut to the low-index surfaces (111) as shown in **Figure 5** or a supercell cut to slab of (111) surface(**Figure 3**) to study the adsorption and dissociation of  $H_2$  on these surfaces. The atoms on the surface will be relaxed so their location will change to minimize energy. Accordingly, the surface energy can be obtained as:

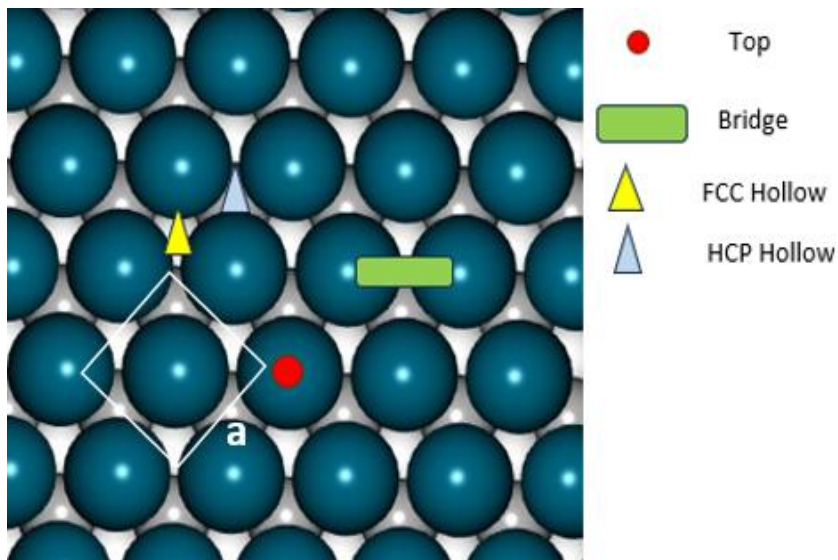
$$E_{surface} = E_{relaxed-surface} - E_{bulk} \quad 0.20$$



*Figure 5. Crystal planes of Pd(111) plane at low-index surfaces.*

**(c) Determine the sites for gas adsorption and dissociation:**

At the top layer of the membrane surface, the hydrogen molecule may sit at different sites, at the top of the Pd-atom, on the bridge between two Pd-atoms, or at the hollows (i.e. in the center between Pd-atoms). **Figure 6** shows the four available sites of surface (111). The site type, at which the hydrogen will sit, affects the adsorption process because there is different energy for each site. So, the site with the low state of energy will be the one that  $H_2$  would prefer to be adsorbed on it.



*Figure 6. Sites available for FCC structure.*

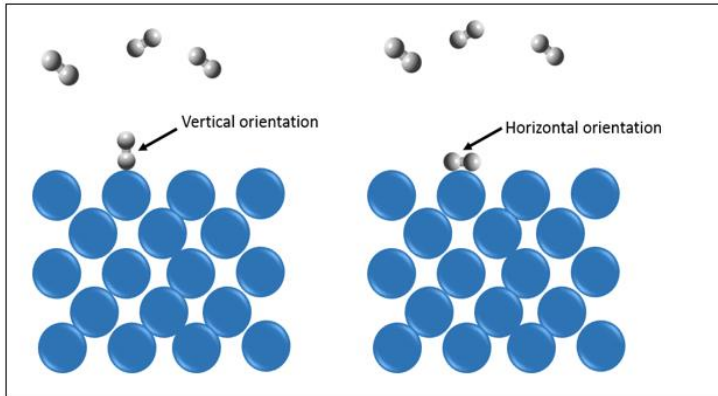
The adsorption energy of the molecule gas on the surface can be defined as:

$$E_{ads} = E_{slab+nX} - E_{slab} - yE_{H_2} \quad 0.21$$

where  $E_{slab+nX}$  is the total energy of the simulated cell which contains the membrane slab and gases, and  $E_{slab}$  is total energy of the system without the gas of interest which we want to get its adsorption energy,  $yE_{H_2}$  is the energy of gas alone, and  $y$  is several molecules. Thus,  $X$  can be  $H_2/CO_2/CO/CH_4$  or H-atom. In the case of  $X$  representing H-atom, the value of  $y$  is equivalent to half of the total number of H-atoms, and in that case,  $E_X$  is multiplied by  $y$ . To calculate  $E_{ads}$  of  $H_2$  at co-adsorption with poisoning gases ( $CO_2/CO/CH_4$ ) or to the presence of various coverage of H-atoms that have dissociated from previous steps,  $E_{slab+nX}$  represents the energy of the all system including the slab and any molecule of H-atoms except  $H_2$  molecule.

**(d) Specify the adsorption orientation.**

The hydrogen molecule may stick to the membrane surface at different orientations, hence, the orientation that makes the minimum energy of the state will be the preferred orientation. Accordingly, this step represents how the  $H_2$  molecule will sit on the available sites of the Pd-surface (**Figure 7**).



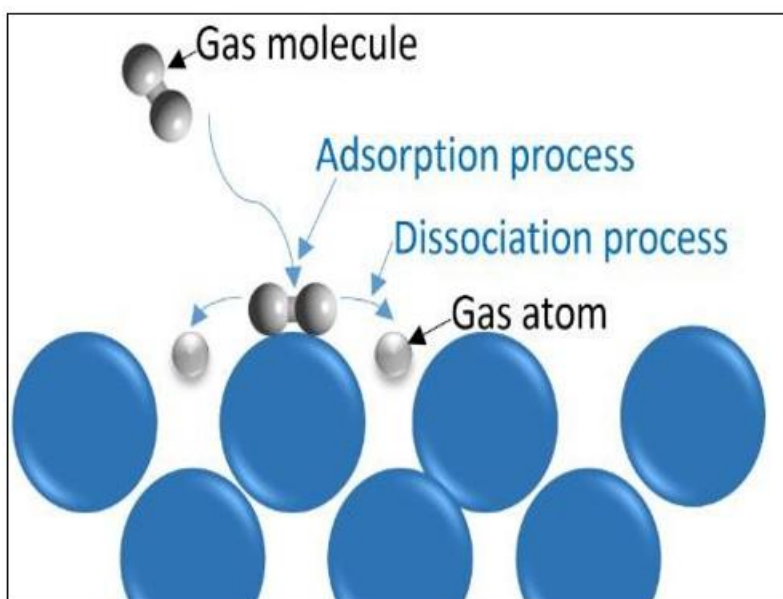
**Figure 7. The orientation of gas molecule adsorption at the membrane surface.**

Determine the lowest adsorption energy for the different combinations of steps c and d (orientation and

sites) to define where the  $H_2$  will sit on the membrane surface. Investigate the location where the dissociated H-atoms will site: After the hydrogen molecule sits on the membrane surface it will dissociate, hence, it is required to define the location where the H-atoms will sit on the surface (it is the location where the hydrogen atoms will have the lowest energy). The H-atoms will also have favorable sites like the case of the  $H_2$  molecule. This location is the final state of the dissociation process.

**(e) Finding the barrier of  $H_2$  dissociation to hydrogen atoms:**

After the  $H_2$  molecule gets adsorbed at the surface, the  $H_2$  atoms may take different paths to reach a minimum state of energy on the membrane surface (i.e. final state of dissociation which is obtained from step f). This could happen on different paths, so it is required to specify the path with minimum energy. Accordingly, the barrier will be decided according to the path that gives minimum energy by using NEB.



*Figure 8. Dissociation of the gas molecule to gas atoms.*

**(f) Obtaining the hydrogen diffusion path:**

Once the dissociation process is complete, the  $H_2$  atoms start to diffuse through the bulk material. Similarly, there may be different paths that the atoms may take to diffuse and maneuver through bulk

membrane atoms. Consequently, it is required to determine the diffusion path that has the lowest energy using the NEB method. This method is used to obtain saddle points and minimum energy pathways between two known states (reaction and product states). It was conducted by optimizing several intermediate reaction coordinates to their lowest possible energy. It is conducted by adding spring forces along the band between intermediate states and by projecting out the component of the force due to the potential perpendicular to the band.

### 3.6.2 DFT Parameter Optimizations

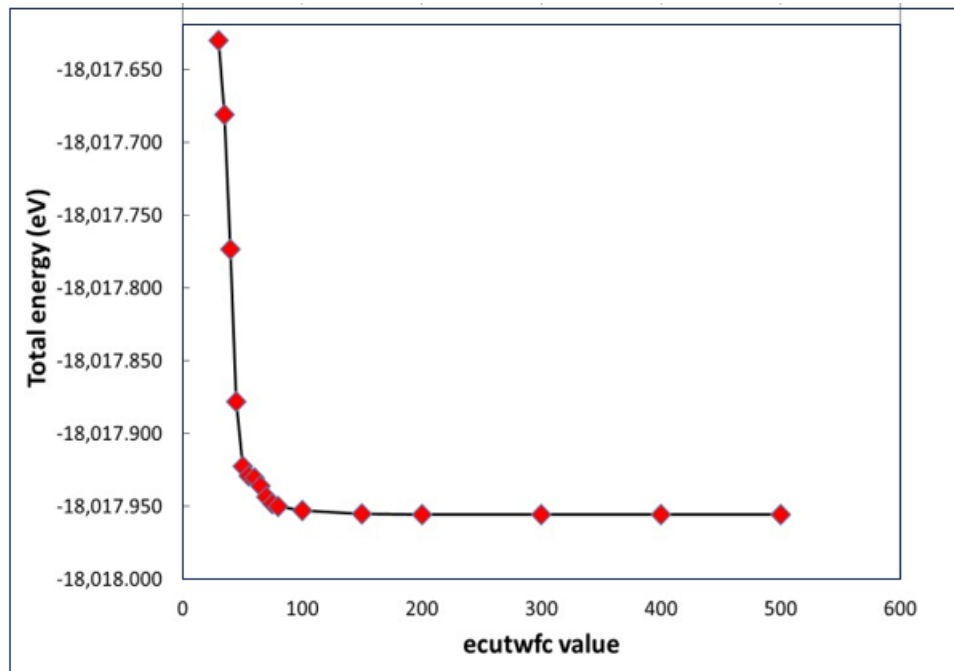
At the beginning, a vc-relax model is used to optimize the lattice constant. The vc-relax model brings the system to its ground state by allowing both cell size and atomic position to relax. The obtained lattice constant is used for the optimization of kinetic energy cutoff for wave functions (*ecutwfc*) and *K-points* (the sampling points in the first Brillouin zone of the material, i.e. the specific region of reciprocal space which is closest to the origin (0,0,0)). The optimization of *ecutwfc* and *K-points* is conducted using the self-consistent field (SCF) calculation method which solves the electronic structure at fixed atoms position. After that, scf calculation is performed for different lattice constants. There are 4 Pd atoms per unit cell representing the periodic repetition of the atoms to form the FCC structure. The length of the cubic cell represents the lattice constant value. The results (i.e. lattice constants and their corresponding total energies) are fit to the equation of state to obtain the equilibrium-lattice constant and the bulk modulus. A 2<sup>nd</sup> order Birch equation of state is used for the fitting. Then, the equilibrium-lattice constant is used to calculate the total energy of the bulk material. The binding energy is obtained by taking the energy difference when the Pd-atoms are gathered in the bulk and the state where the atoms are far away from each other, so they no longer interact with each other. The later state (i.e. the Pd-atoms are far away from each other) is considered a reference state for the energy-volume curve.

### 3.6.3 Optimization of *ecutwfc* and *K*-points

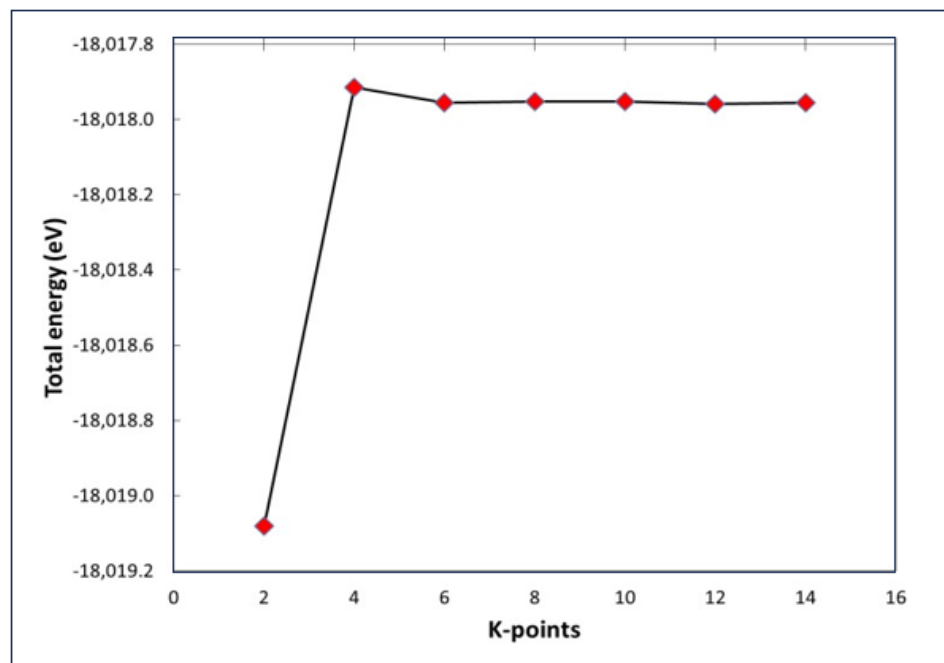
The calculation of the vc-relax model reveals that the lattice constant of the Pd is around 3.937 Angstrom. This value is used for the *ecutwfc* and *K*-points optimization. The *ecutwfc* ranged between 30 and 500 examined. The total energy concerning each *ecutwfc* is shown in **Figure 9**. The total energy stabilizes around (-18017.96 eV) after *ecutwfc* value of 200. The *K*-points are investigated for a range of 2 to 14 where it was shown that the total energy stabilizes after *K*-points equal 6 at -18017.96 eV (**Figure 10**). Accordingly, *ecutwfc* and *K*-points of 200 and 6 are used to optimize the lattice constants. Lattice constants ranging between  $\pm 10$  percent of the initial value (3.937 Angstrom) are calculated and used as fitting data for the equation of state. It turns out that a lattice constant of 3.948 Angstrom leads to the smallest total energy as depicted in **Figure 11**, and hence it is considered as the lattice constant for the Pd (FCC). Furthermore, the fitting data of the equation of state indicates that the material has a bulk modulus of 169.375 GPa/atom.

**Figure 11** shows the total energy at different lattice-constant along with the binding energy. An energy reference value is considered where the atoms of the Pd bulk material are far away from each other, so they do not interact together. Accordingly, a DFT calculation is performed for 1 Pd atom at a unit cell. Due to the periodic boundary conditions, the atom will interact with the next cell's atom, so different cell lengths are examined until enough distance between Pd atoms prevents any interaction between the periodic atoms. The results are summarized in **Figure 12**. At a distance greater than 7.5 Angstrom the energy of the Pd-atom fixed at -4500.556 eV and does not change which indicates that the Pd atoms are no longer interact with each other. This value is for 1 Pd atom, so it is multiplied by 4 to compare it with the energy of bulk Pd material which has 4 periodic atoms in the unit cell of FCC structure. Accordingly, all represented data in **Figure 11** are shifted by the energy of the Pd bulk when the atoms are far away from each other (i.e.  $4500.556 \times 4 = -18002.217$  eV). So, the reference energy at large lattice-

constant is replaced by zero eV instead of having a value of -18002.217 eV. **Table 3** summarizes the results for this part of the calculation. The lowest total energy of the Pd<sub>FCC</sub> bulk (with 4 periodic atoms) is 3.935 eV/atom and it also represents the binding energy.



*Figure 9. Convergence of total energy concerning ecutwfc.*



*Figure 10. Convergence of total energy with respect to K-points*

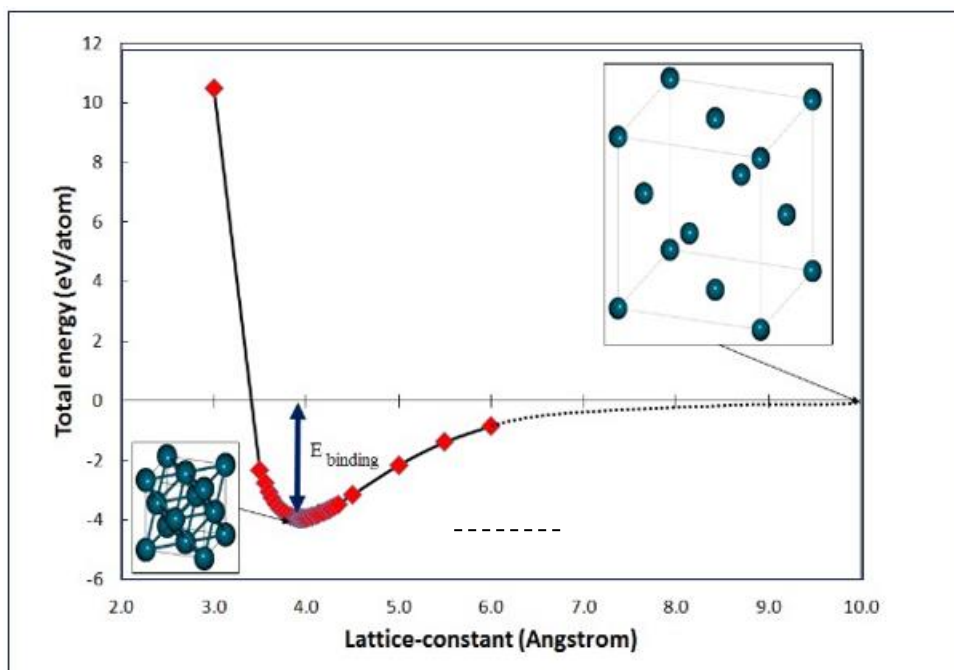


Figure 11. Change of total energy with the cell volume.

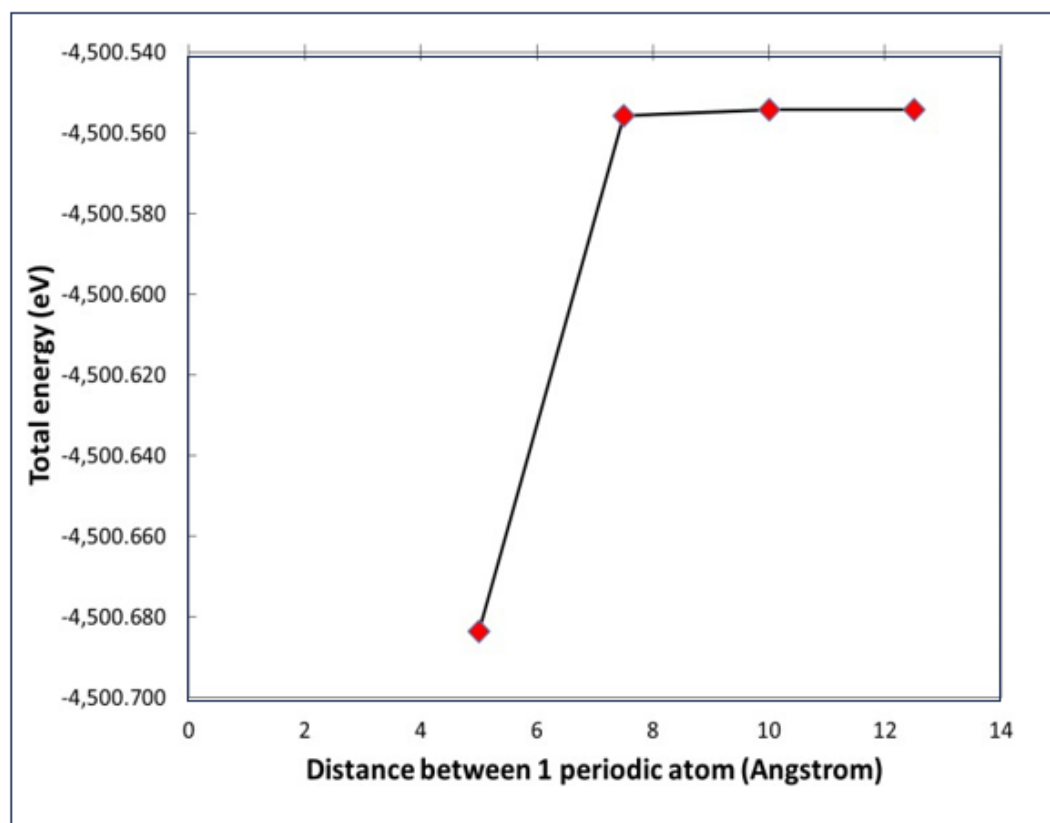


Figure 12. Interaction of 1 Pd atom due to periodic boundary conditions at different distances apart from each other.

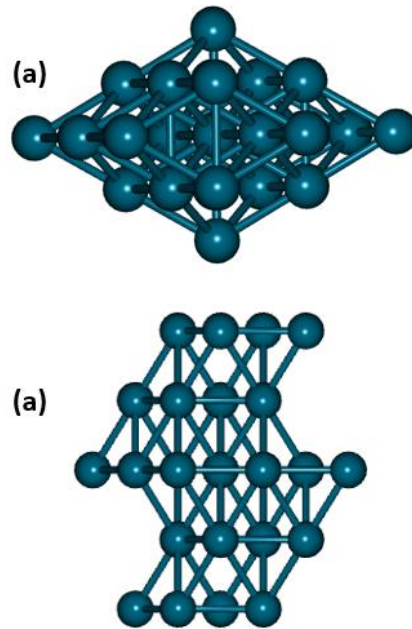
*Table 3. Results summary of DFT calculation for Pd bulk*

| Parameter                | Value   |
|--------------------------|---------|
| ecutwfc                  | 200     |
| K-point                  | 6       |
| Lattice-constant (Å)     | 3.948   |
| Binding energy (eV/atom) | 3.935   |
| Bulk modulus (GPa/atom)  | 169.375 |

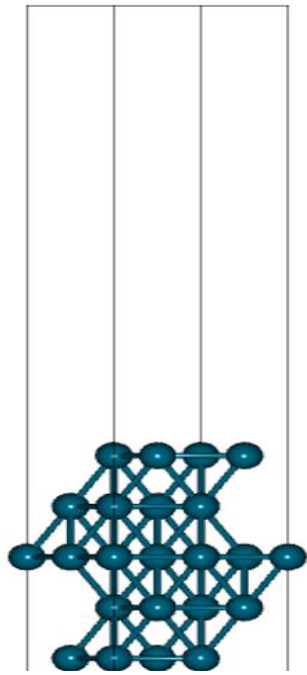
#### 3.6.4 Pd-surface Preparation

This part aims to relax the atoms at the Pd surface (111) and get the surface energy and final positions of the atoms. Once the bulk Pd (FCC) is prepared, it cuts at the plane surfaces(111) as shown in **Figure 3** and **Figure 5**. Accordingly, atoms at the surface become only bonded from one side. Thus, those atoms at the surface of the Pd-membrane move to reduce their energy. Consequently, a relaxed model of DFT calculation is required to find the new position of those atoms. To model the atoms at the surface, a vacuum area is made above the surface to prevent the interaction of atoms at the surface with the others due to the periodic boundary condition of the calculation. A relaxed model is used for calculation as it allows the atoms to move, and it also solves the electron structure. A similar pseudopotential file of Pd material applied in the bulk calculation is used for the surface relaxation calculation. Also, similar parameters of ecutwfc and K-points are applied so the results of both bulk and surface calculation are comparable. The unit cell representing surface 111 is hexagonal with dimensions of 5.52x5.52x25 Å and it has 12 Pd atoms. The resulting geometry out of the plane cut is represented in **Figure 13**. Five layers of

atoms, in the z-direction, are considered for the surface relaxation as shown in **Figure 13b**. The three bottom layers are fixed to represent the bulk atoms, while the two top layers of atoms are set free to relax in a new position to represent the surface. A large vacuum area is introduced above the top layer of atoms to ensure that there is no interaction of atoms at the top surface layer with the bulk atoms (i.e. fixed atoms at the bottom) reflected at the top of the unit cell as depicted in **Figure 14**. Compared to the bulk system, the binding energy of atoms after surface cutting becomes small because the atoms are bonding from one direction only. The bulk Pd<sub>FCC</sub> has a binding energy of -4.935 eV/atom. This value becomes less negative when bulk material is cut through the plane (111) (-4.631 eV/atom). This binding energy is normalized by the total number of atoms in the unit cell. For instance, the unit cell for the surface relaxation of 111 has 12 atoms, so the total energy of that unit cell is divided by 12(no. of atoms). Then, the binding energy (eV/atom) is obtained by taking the difference between the normalized cell total energy and the energy of the normalized unit cell that has atoms apart enough from each other to prevent any interaction between them.



**Figure 13. Atoms arrangement for surfaces (111). (a) Top view and (b) front view**



**Figure 14. The Pd unit cell is used for surface relaxation.**

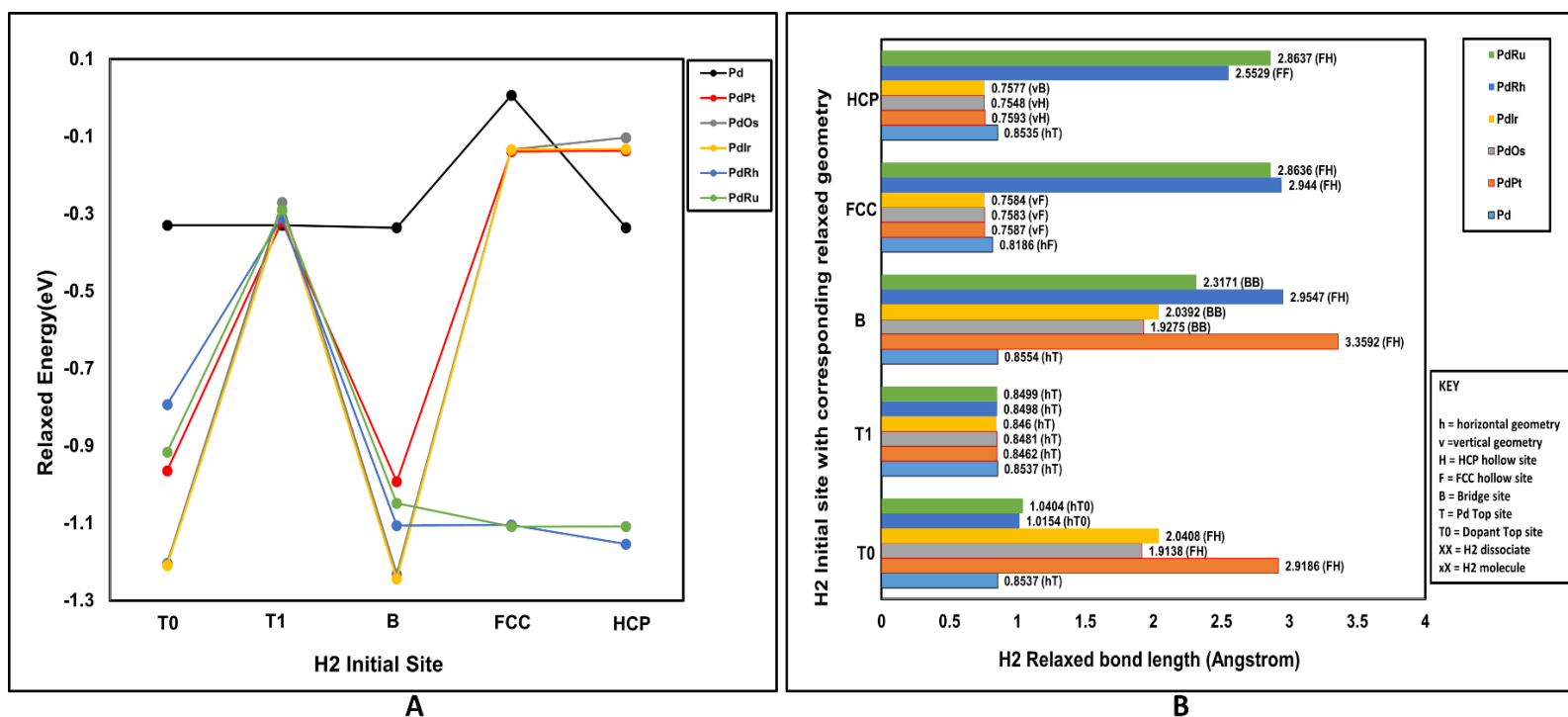


# **CHAPTER 4**

## **ADSORPTION AND DISSOCIATION OF HYDROGEN ON PALLADIUM SURFACE DOPED WITH PLATINUM-GROUP ELEMENTS**

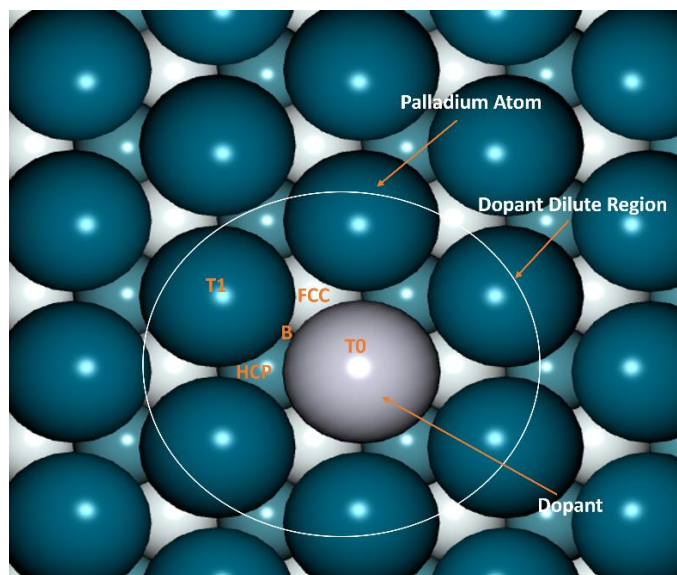
### **4.1 H<sub>2</sub> Physisorption Process**

Most H<sub>2</sub> applications on metal surfaces require hydrogen molecules to easily adsorb and dissociate on the metal surface. A good instance is in the H<sub>2</sub> separation and purification via a Pd-based membrane [27,57]. Reference always gives a better image of any study. Accordingly, we include the bare Pd among other doped surfaces while studying the two primary surface processes(adsorption and dissociation) of H<sub>2</sub> on the metals. For most applications, the H<sub>2</sub> surface process begins with the physisorption of the H<sub>2</sub> molecule onto the surface thus, we begin by studying the energetics of H<sub>2</sub> adsorption on bare Pd, PdPt, PdIr, PdOs, PdRu, and PdRh surfaces through the careful determination of the most favorable physical binding sites, the orientation of the molecule relative to the surface, the reactive separation distance between the molecule and the surface, and the related binding energies. These were achieved considering all the surfaces while treating each at a time through the following: (i) Firstly, the available sites were defined as T0, T1, B, FCC, and HCP on each surface, though all the surfaces were built base on a similar facet (111), the only difference is the T0 a top site of a dopant which originally replaced a Pd atom on a bare Pd surface at the doping process.



**Figure 15. (A) Dissociative adsorption energies of H<sub>2</sub> on Pd-X surfaces with (B) corresponding relaxed geometry and final bond length.**

Unlike the basic homo atomic metal system, two different top sites (Pd and the dopant) are also available on the (111) perfect Pd-X surface, which was previously defined as T1 and T0 respectively. In a similar vein, B represents the bridge location that develops between a Pd atom and a Pt atom. The surface features two types of hollow sites in addition to the top and bridge sites: both hollow sites are produced by two Pd atoms and a Pt atom, however, one of the hollow sites (shown by HCP) is covered below by the first sub-layer (atoms in light grey) while the other hollow site (shown by FCC) is covered by the second sub-layer atom (atoms in lightest grey). In **Figure 16**, every location is displayed. (ii) These sites were utilized and H<sub>2</sub> molecules were arranged across each of the well-defined adsorption sites to determine the best stable adsorption orientation for H<sub>2</sub> on the perfect Pd-X (111) surfaces.



**Figure 16.** The available adsorption sites on Pd(111) surface with T(top), B(bridge), FCC, and HCP are the hollow sites.

There are 15 Pd atoms and one Pt atom summing up to 16 atoms on the uppermost layer of the ( $2 \times 2$ ) supercell. Surface  $H_2$  coverage ( $\theta_{H_2}$ ) is defined as the quantity of  $H_2$  molecules that bond to one surface Pd atom per surface. A single  $H_2$  molecule on a ( $2 \times 2$ ) supercell is equivalent to  $\theta_{H_2} = 0.06$  ML using the above definition. (i) **Pd-top site (T1):** The results from Kumar et al. and Abuelyamen et al. concur that at this coverage, in the most stable adsorption geometry, the  $H_2$  molecule bonds on top of Pd (T1 site) in an activated state with an H–H bond length of 0.85 Å [27,32,57]. Irrespective of the Pd-X surface, all the  $H_2$  molecules that were initially located at the Pd top sites, including those that are far and near the doping atom gave almost the same value (0.85 Å) of bond length for the bonded  $H_2$  (see T1 in **Figure 15B**). In this configuration of adsorption,  $H_2$  attaches itself to the Pd surface in such a way that the palladium-hydrogen distance ( $d_{Pd-H}$ ) is 1.72 Å, and the molecular axis is parallel to the surface. For this configuration, the H–H bond length ( $d_{H-H}$ ) is around 0.85 Å, and the adsorption energy is determined to be  $-0.32$  eV. This is a general observation on all the surfaces and based on such energy, the  $H_2$  molecule could only bind to the Pd atom despite the presence of a dopant and adsorbed but not dissociated.

(ii) **Dopant site (T0):** however, apart from the geometry given above, a noteworthy instance is noted; H<sub>2</sub> may dissociate easily on top of Pt, Ir, and Os (T0-sites) in their respective Pd-X surfaces. This is observed due to the respective minimum energies -0.96eV, -1.21eV, and -2.20eV identified from the relaxed H<sub>2</sub> molecules. These energies are enough to enable the H<sub>2</sub> molecule to dissociate easily and were achieved when H<sub>2</sub> was initially placed at T0 sites of PdPt, and PdIr and PdOs surfaces. After the dissociation, the H-atoms move to the hollow sites; on PdPt, the atoms separated 2.9 Å with positions at FCC and HCP hollow sites(FH), similar positions were utilized by the dissociate atoms on PdIr and PdOs with d<sub>H-H</sub> of 2 Å and 1.9 Å respectively. However, in a similar situation, the energies obtained for the relaxed H<sub>2</sub> molecules on PdRu and PdRh could be categorized as transitional energy instead of dissociative energy because the H<sub>2</sub> is still in molecular form though the d<sub>H-H</sub> elongate to 1 Å on the two surfaces. Moreover, the H-atoms in all the dissociative cases move very close to the surface with d<sub>X-H</sub> of approximately 0.98 Å.

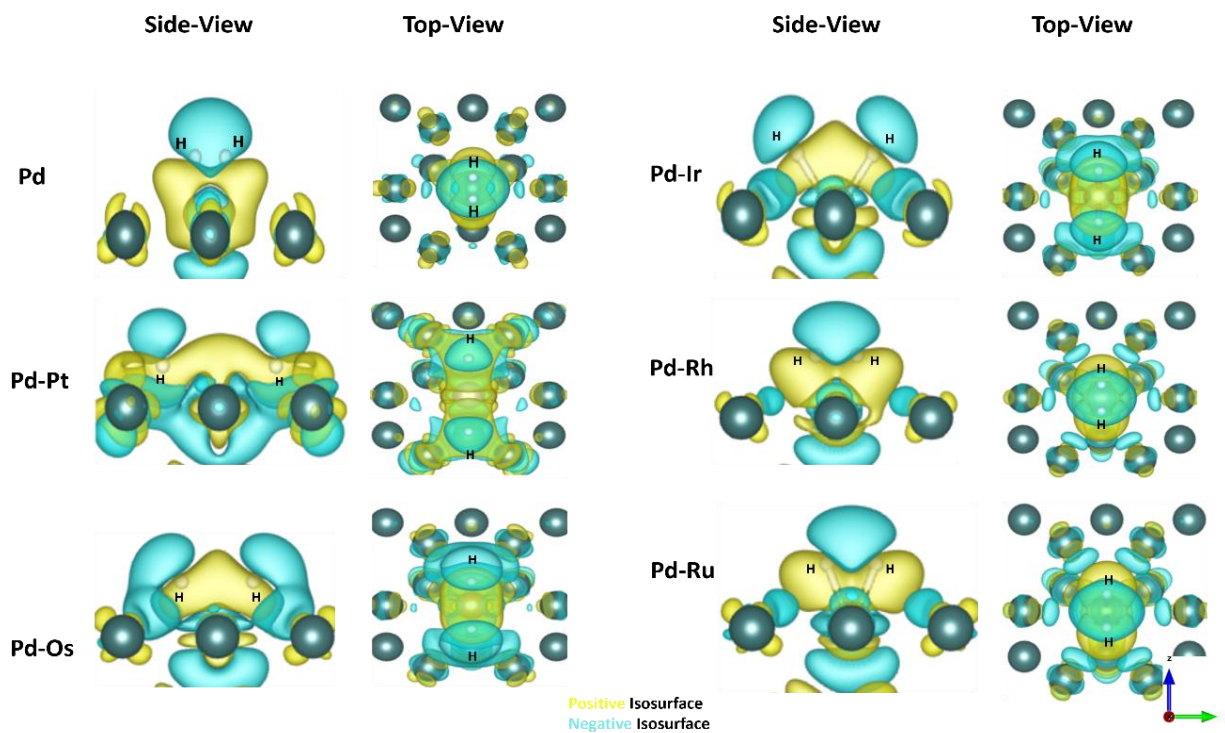
(iii) **Bridg site (B):** Apart from the dissociation notice on top of some dopant above, a great one is seen virtually on the bridge sites on all the doped surfaces. H<sub>2</sub> molecule dissociates clearly on this site with each H-atom moving to again the opposite bridges(BB) on PdRu, PdIr, and PdOs after separating with a distance (d<sub>H-H</sub>) 2.32Å, 2 Å and 1.93 Å respectively. In addition, the dissociated atoms on PdRh and PdPt are located at FCC and HCP hollow sites(FH). In hydrogen separation and purification using Pd-based membranes and in a hydrogen fuel cell, dissociation of H<sub>2</sub> is highly desired.

(iv) **HCP and FCC hollow sites:** The H<sub>2</sub> molecule elongates and finally dissociates into H-atoms, one atom remains at the FCC hollow site while the other relocated to the nearest FCC hollow site on PdRu(d<sub>H-H</sub> = 2.86Å). This is the geometry with final H-atoms which were initially placed at the FCC site on PdRu and PdRh with the H-atoms separation(d<sub>H-H</sub>) of 2.86Å and 2.9Å respectively. Except for H-atoms on PdRh originally at the HCP site dissociated by taking both FCC hollow sites opposite to each other(FF) and separated(d<sub>H-H</sub>) 2.55Å apart. All other sites adsorbed H<sub>2</sub> in its molecular form with a geometry either horizontally(h) or

vertically(v) where  $H_2$  rotates to vertical orientation and moves far above the surface with  $d_{X-H} = 2.75 \text{ \AA}$  and the bond length remains almost like the initial ( $0.75 \text{ \AA}$ ). The proximity of the bridge site to the dopant could be the reason for such a similar effect on  $H_2$ . Since the  $H_2$  molecule moves away from most of the FCC and HCP hollow sites on the perfect Pd-X(111) surfaces then, there is a probability that H-atoms are more favorable only in their atomic form but not the molecule. **Figure 15** shows the details of the explanation above. These surfaces present enough sites where  $H_2$  dissociation becomes more favored.

## 4.2 Charge density difference analysis on $H_2$ dissociation.

To further confirm the occurrence of  $H_2$  dissociation on the Pd-X surfaces, an analysis of the electronic charge density difference (EDD) was carried out to observe the interaction of the H-atom with the surface at their final relaxed states through the concept of high occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) spaces. To summarize the situation, the cases at T0 were selected and charged density analysis was performed on the final relaxed states of H-atoms on the Pd-X surfaces as shown in **Figure 17**. The idea for this selection is because the observation on T0 sites could be used to judge the events on the other site based on the energy relations. Thus, the electron density difference isosurface maps were carefully studied and used to depict the electron transport between the transition  $H_2$  molecule and the Pd-X surfaces. The HOMO-LUMO concept can be understood as follows; when an atom loses electrons it moves to the LUMO envelope, whereas if an atom gain electrons it goes to the HOMO. Based on this concept, if the  $H_2$  molecule dissociates into its atoms or remains as a molecule after interacting with the Pd-X surface can easily be confirmed. As seen in **Figure 17**, the green and blue areas, respectively, reflect electron accumulation (HOMO) and depletion (LUMO). Usually, hydrogen takes charge from the surfaces generating a strong covalent interaction, but in the same line, electron interaction allows hydrogen to move on metal surfaces in each case [24].



**Figure 17 Electronic charge density difference (EDD) plots of relaxed H<sub>2</sub> interaction with the doped Pd surfaces.**

Starting with an investigation of the H<sub>2</sub> interaction with the bare Pd surface as a reference, it is observed that the two H-atoms are still within the HUMO envelope after their relaxation on the surface. A scenario that signifies that the H-atoms do not give away their electrons (no charge transfer) and are still bonded with each other, hence remaining in their molecular form. On the other hand, the H<sub>2</sub> molecules on PdPt, PdOs, and PdIr are in the LUMO envelope this means the H-atoms lose their electrons during the dissociation reaction process, disintegrate into H-atoms, and move down to interact more with the surfaces because they become more reactive (H<sup>+</sup>). These three surfaces record a clear potential to dissociate H<sub>2</sub> molecules available on their top sites. However, the H-atoms on PdRu and PdRh lie between the HOMO and the LUMO envelopes. These atoms do not completely release their electrons, though the portion into the LUMO is more compared to the part that remains in the HUMO. This indicated that the H<sub>2</sub> molecules are at the transition state to dissociate into H-atoms but not yet fully dissociated. Additional energy, though

very little may be required for the  $H_2$  molecule to disintegrate completely at the T0 site on these two surfaces.

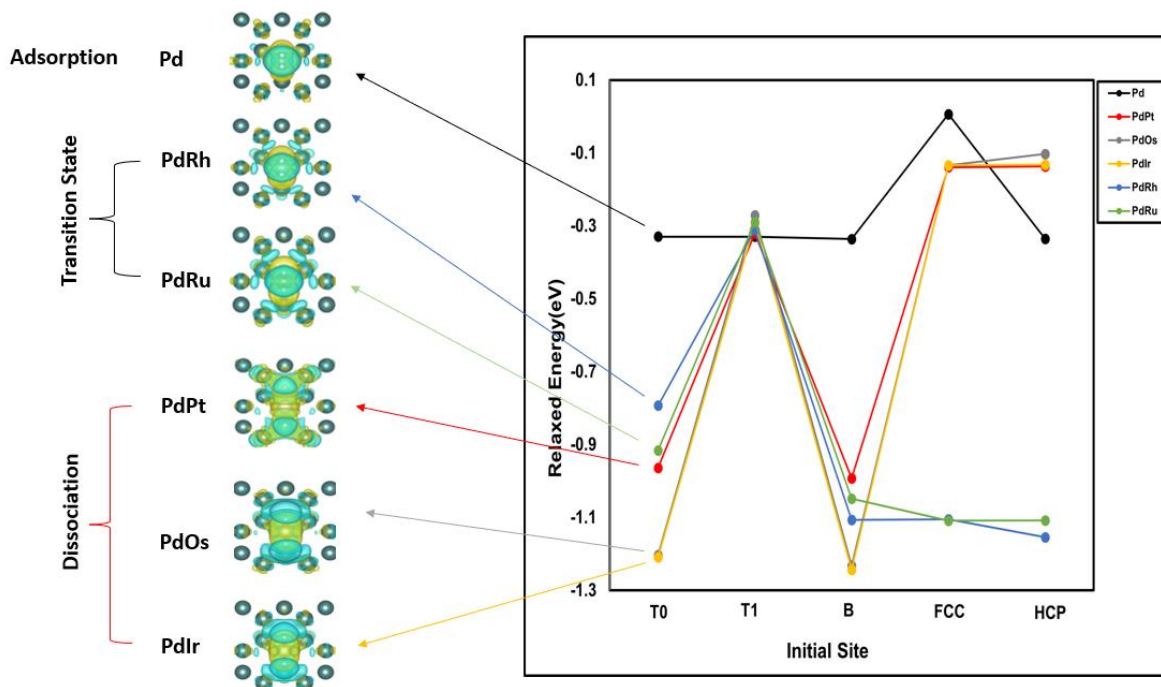
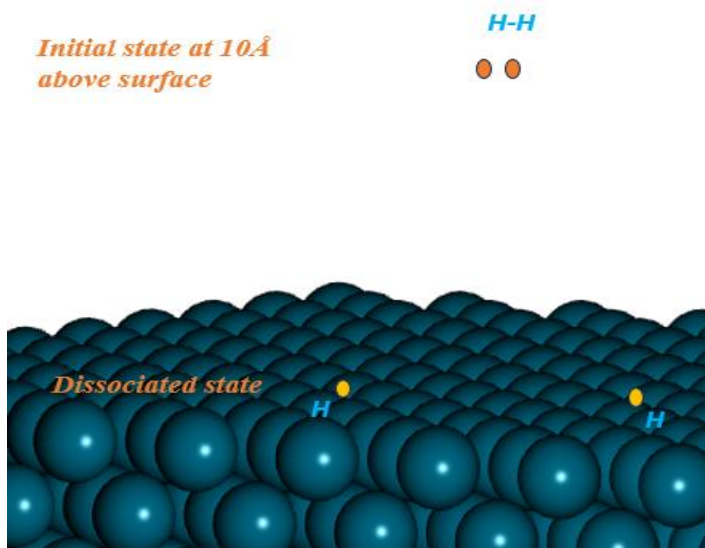


Figure 18. Mapping the CDD of the final state of  $H_2$  initially at T0 sites on Pd-X surfaces with their corresponding dissociative energies.

Now, that the events that occur at the relaxed states of the  $H_2$  molecule which were initially located at the top of the doping atoms designated as T0 are known, we map the CDD with their respective energies in **Figure 17** and discuss the rest of the events on the other sites (T, B, FCC, and HCP). Since the CDD of final relaxation of  $H_2$  on PdRu and PdRh surfaces with respective final energies -0.79eV and -0.92eV confirms that the  $H_2$  molecules are at the transition state to dissociation, then all the states where the final energies are minimum than those in the case of PdRu and PdRh surfaces should be enough for  $H_2$  molecule to dissociate into H-atoms readily. These include the  $H_2$  molecules which were originally located at the bridge sites on all the Pd-X surfaces, followed by those at FCC and HCP hollow sites on PdRu and PdRh. All other geometry results only in the physisorption of the  $H_2$  molecule. **Figure 17** demonstrates the events through the mapping between the CDD and the final state energies of  $H_2$ .

### 4.3 H<sub>2</sub> Dissociation Barrier Path

Dissociation is barrier-dependent. When the barrier leading to dissociation cannot be overcome, the reaction will be hindered and hence, dissociation will not take place [58]. This is the reason why some energies need to be supplied to the system to facilitate the reaction by lowering or removing the activation barrier. Because of the importance of understanding the H<sub>2</sub> activation barrier for the dissociation to occur, the dissociation barrier of H<sub>2</sub> for the cases studied above was determined using the NEB. The NEB is a potential method used to calculate the activation barrier path for a reaction. We maintain the same selection as those considered for CDD analysis. It focused on all the Pd-X surfaces while limiting the scope of the H<sub>2</sub> dissociation for the H<sub>2</sub> molecules that were initially located on the T0 which may later dissociate. Usually, the physisorption stage of H<sub>2</sub> is considered the initial state, and the dissociated stage is the final to perform the activation barrier calculation. However, it is more accurate to start from far beyond the physisorption stage. Because it will provide the whole picture of the process right before the physisorption, down to the point where the H<sub>2</sub> completely dissociates. Considering the top sites as earlier mentioned, H<sub>2</sub> is located on the top site on each Pd-X surface at 10 Å above the surface as the initial state. Furthermore, H-atoms were positioned at their most favorable dissociative sites as the final and then, the reaction path was determined. **Figure 19** demonstrates the configuration in a graphical view.



**Figure 19** The initial and final geometrical configuration for nudged elastic band (NEB) calculation.

The investigation of the activation barrier path reveals that H<sub>2</sub> molecules diffusing to the Pd surface will begin to experience the effects of the surface at image 4 due to the influence of energy around (-0.0035eV). These molecules will continue to move closer to the surface minimizing the energy of interaction until they are physisorbed, in a situation in image 8. Due to the presence of a little activation barrier of -0.069eV, the H<sub>2</sub> molecules could not directly proceed with the dissociation process. The barrier is the limitation to the H<sub>2</sub> dissociation that accounts for extra external energy. In hydrogen separation and purification application, this could reduce the number of dissociated atoms which is in direct proportion to the flux achieved through a Pd-based membrane. Syngas diffused to the membrane at high pressure and extreme temperature. The temperature will serve as extra energy to overcome the barrier present on a bare Pd surface and the pressure drives the dissociated H-atoms based on its gradient. Similarly, a barrier (-0.057eV) to H<sub>2</sub> dissociation was observed on the PdPt surface when the H<sub>2</sub> molecule physisorbed with an energy of -0.06eV at image 7. After overcoming the barrier, the H<sub>2</sub> molecule will dissociate into H-atoms with energy -0.94eV(image 10). Although the barriers on both the bare Pd and PdPt are low, the extra energy of an equal amount (Conservation law of matter) must be added to overcome it [59].

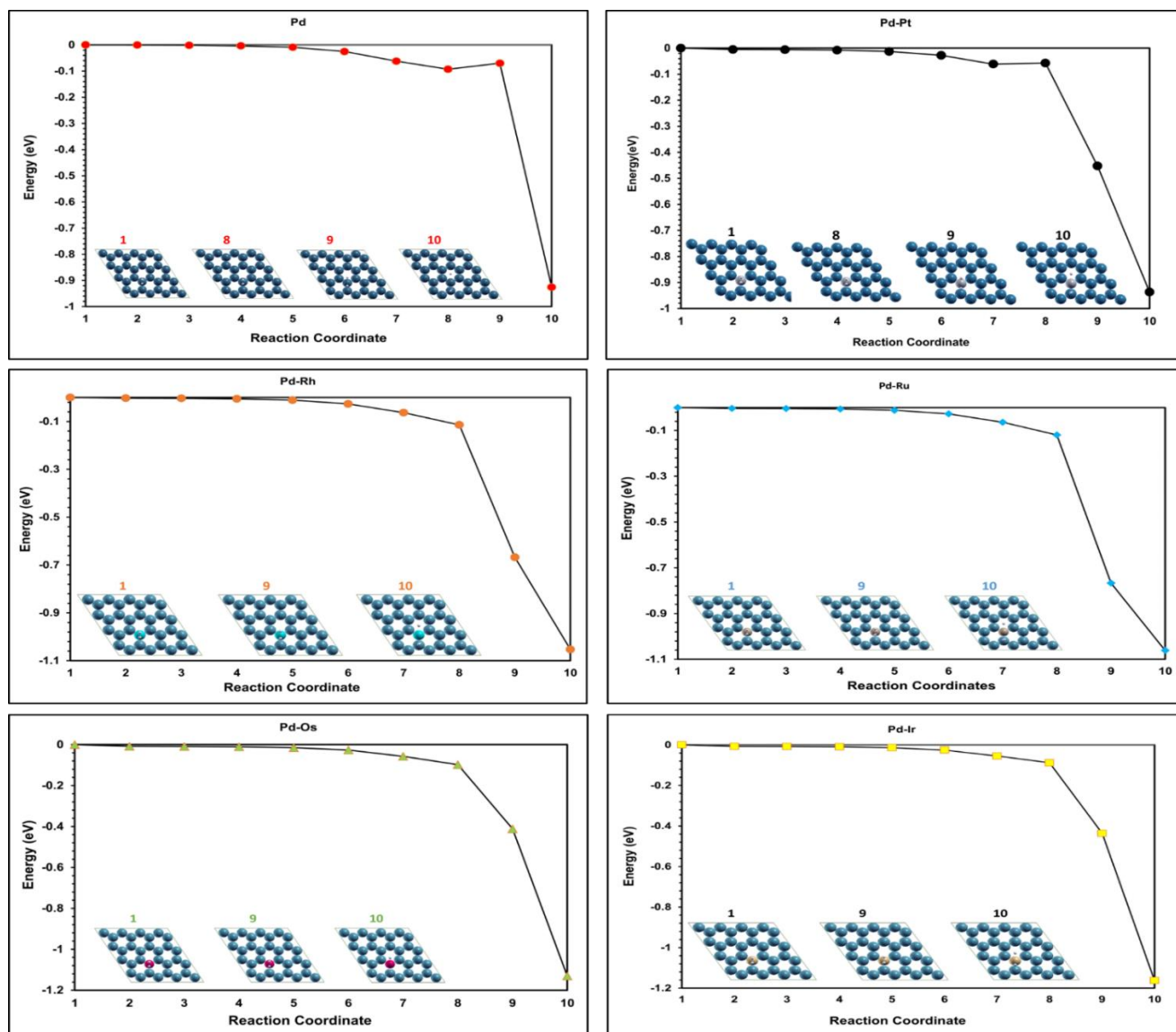
**Table 4. The dissociation barrier and relaxed dissociative energy of H<sub>2</sub> on Pd-X surfaces**

| Material | Dissociation Barrier | Final Dissociative Energy |
|----------|----------------------|---------------------------|
| Pd       | -0.07eV              | -0.93eV                   |
| Pd-Pt    | -0.06eV              | -0.94eV                   |
| Pd-Os    | -                    | -1.13eV                   |
| Pd-Ir    | -                    | -1.16eV                   |
| Pd-Rh    | -                    | -1.05eV                   |
| Pd-Ru    | -                    | -1.06eV                   |

However, the H<sub>2</sub> molecule on PdOs, PdIr, PdRu, and PdRh dissociated directly without a barrier. The H<sub>2</sub> molecules diffused toward these surfaces and began to feel the influence of these surfaces right from as low energy as -0.0089eV, -0.0079eV, -0.006eV, and -0.0055eV respectively. These energies continuously decrease without any jump up or down the last final dissociation state (see image 10 of each concerned reaction coordinate in **Figure 20**). Interestingly, for H<sub>2</sub> applications where H<sub>2</sub> dissociation is desirable, these surfaces are the best candidates because no extra energy is required for the H<sub>2</sub> molecule to readily dissociate into its atomic form. Unlike the bare Pd and PdPt surface, H<sub>2</sub> molecules might not have to be physisorbed at any point before dissociating. The physisorption, which is considered the starting point for the H<sub>2</sub> surface process on Pd-based membrane is no longer valid regarding the doped surfaces (PdOs, PdIr, PdRu, and PdRh). Moreover, in hydrogen fuel cells where H<sub>2</sub> dissociation is one of the main drivers that supply the charges (H<sup>+</sup>) needed to the output, additional catalysts are usually added to the electrodes to foster the H<sub>2</sub> dissociation process. Fabricating electrodes covered with these kinds of surfaces will greatly enhance the H<sub>2</sub> dissociation on the electrode, thereby improving the yield of the cell. **Table 4** presents the Dissociation activation barrier along its energy for final relaxed state of the dissociated atoms.

On a general note, the dissociation of H<sub>2</sub> on PdRu, PdRh, PdOs, and PdIr surfaces reveals a distinctive characteristic – the absence of a dissociation barrier along the reaction path. This distinctive feature points towards a "barrier-free" reaction, indicating that H<sub>2</sub> can potentially undergo dissociation on

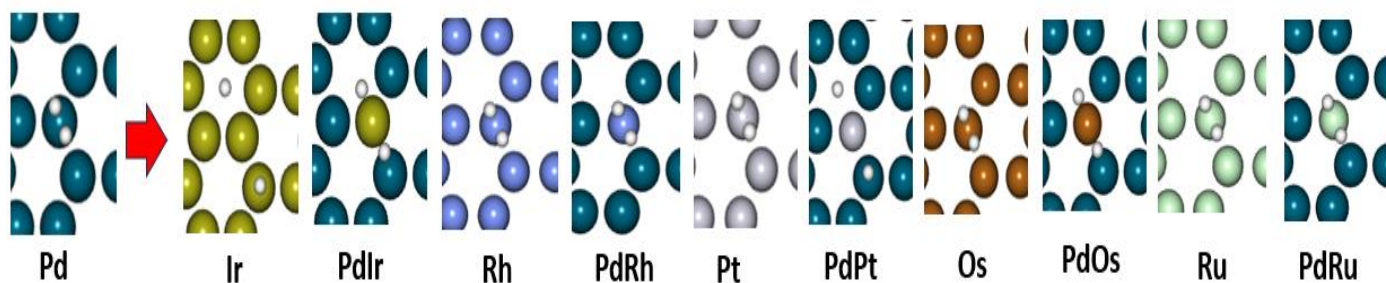
these surfaces without the need for external energy inputs. Combining PGEs creates surface alloys that allow surface electrical and geometric structures to be modulated, hence controlling the catalytic processes that take place on the catalyst surface [25]. This phenomenon challenges the conventional expectations of energy barriers in dissociation reactions, suggesting a unique reactivity on these doped Pd surfaces. This novel's insight into the reaction dynamics of  $H_2$  on specific doped Pd surfaces opens avenues for further exploration and application in catalysis and material science.



**Figure 20** The energy profile of  $H_2$  dissociation on atop sites doping atoms (T0) of Pd-X surfaces ( $X_i = Os, Ir, Pt, Ru$  and  $Rh$ )

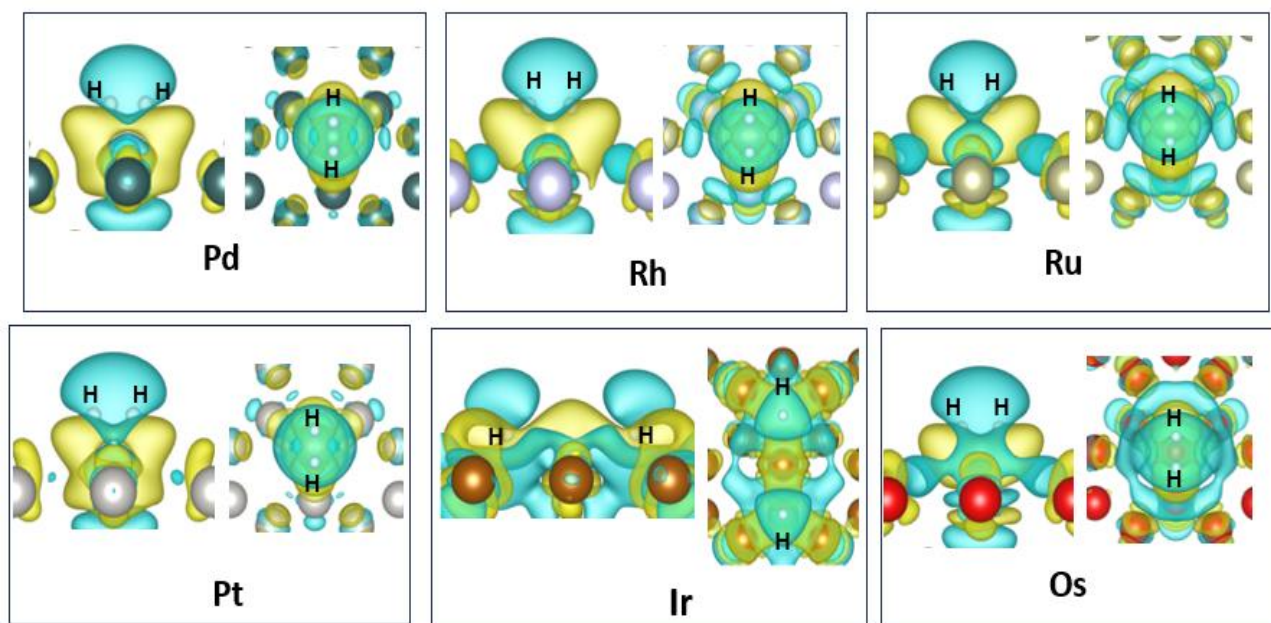
## 4.4 Catalytic Enhancement Analysis

To better analyze the general enhancement in the catalytic property of all the surfaces above, we investigated the interaction of the  $H_2$  molecule with the bare surfaces of Pt, Ir, Os, Ru, and Rh and related to the alloy surfaces. We focus on the T0 site only since the aim is to have a comparison between the bare surfaces and the Pd-X surfaces. The relaxed  $H_2$  molecules on these surfaces were visualized in **Figure 21**. Except for the bare Ir surface where the  $H_2$  molecule relaxed by dissociating into atoms, all other pure surfaces could not favor the direct dissociation  $H_2$ . The  $H_2$  molecule was only physisorbed, which is the tendency for the existence of a barrier to the dissociation. Furthermore, a charge density analysis was carried out on the bare surfaces to have clear information on how the  $H_2$  molecule finally relaxed on them. The CDD reveals that the  $H_2$  on the bare Ir surface greatly dissociated into H-atoms separated by a distance ( $d_{H-H}$ ) of about donating their electrons and moving to the LUMO and becoming more activated. However, the  $H_2$  on Pd and Pt are more in their molecular form with the H-atoms bonded within the HUMO envelope. However, Rh, Ru, and Os surfaces almost dissociate the  $H_2$  molecule though not absolutely because the H-atoms do not completely leave the HUMO into the LUMO(see **Figure 22**). This means that the  $H_2$  molecules on these surfaces are in a transition state to final dissociation. Compared to the Pd-X surfaces, it is obvious that the surface alloy effect contributes to the dissociation of  $H_2$ . Since all the Pd-X surfaces studied earlier presented greater potential for  $H_2$  dissociation than just the bare surfaces.



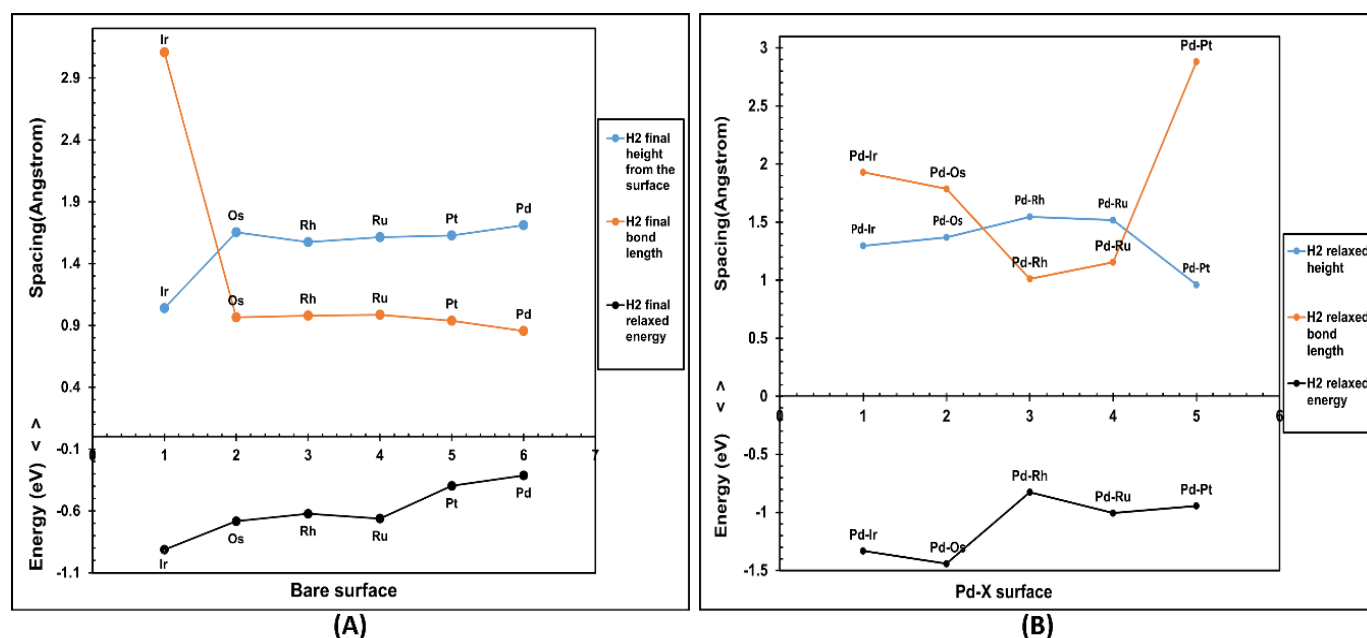
**Figure 21.** Comparison of  $H_2$  relaxation state on bare Pt-group surfaces and the Pd surface when doped with the atoms from the pure element.

In addition, we compare the details of H<sub>2</sub> adsorption on bare surfaces with their relaxed bond length (BL) and final relaxed height (AdH). The minimum H<sub>2</sub> adsorption energy on bare surfaces is -0.91 eV which was achieved on the Ir surface followed by the other energies in ascending order of magnitude -0.68 eV < -0.66 eV < -0.62 eV < -0.4 eV < -0.31 eV respectively obtained on Os < Ru < Rh < Pt < Pd. The change in the bond length from the initial (0.75 Å) which is the H-H bond length in gaseous form, on Os, Rh, and Ru is almost equal between 0.97-0.99 Å whereas, it elongates to 0.94 Å and 0.85 Å on Pt and Pd surfaces respectively. In a similar vein, the H<sub>2</sub> moved near the surfaces from the initial height of 1.8 Å and relaxed at 1.65 Å, 1.57 Å, 1.61 Å, 1.63 Å and 1.7 Å above bare Os, Rh, Ru, Pt, and Pd surfaces. The H<sub>2</sub> molecules moved a little from their original height toward the surfaces and relaxed, signifying that the molecules were adsorbed. However, the H<sub>2</sub> molecule moves from the initial 1.8 Å down to 1.04 Å; closer to the surface and dissociated as confirmed by the CDD analysis above.



**Figure 22. Electronic charge density difference (EDD) plots of relaxed H<sub>2</sub> interaction with the pure platinum group element surfaces.**

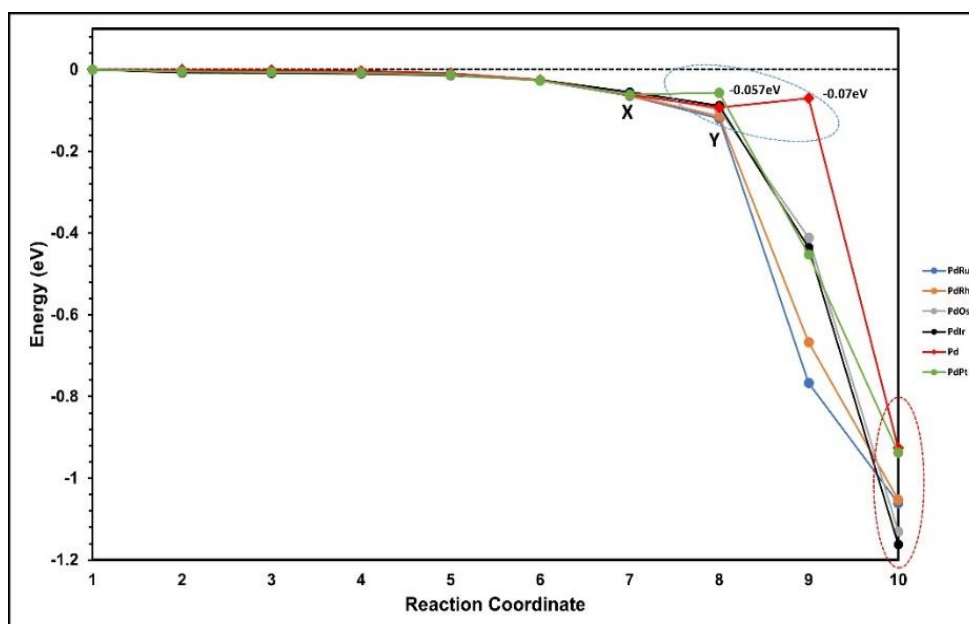
On the other hand, the H<sub>2</sub> molecules relaxed at 1.3 Å, 1.37 Å, 1.55 Å, 1.52 Å, and 0.96 Å above PdIr, PdOs, PdRh, PdRu, and PdPt after the H-atoms are separated a distance( $d_{H-H}$ ) of 1.93 Å, 1.79 Å, 1.01 Å, 1.15 Å, and 2.88 Å respectively. **Figure 23** shows the relationship between the relaxed energy of H-atoms when dissociated or H<sub>2</sub> molecule to the relaxed height and the H-H separation(BL). Although the H<sub>2</sub> molecules on Pd-X surfaces were weakly attracted to the surface; meaning they did not move far from the initial height closer to the surfaces, still the H<sub>2</sub> molecule readily dissociated on the surfaces. This could demonstrate how strong the potential of the Pd-doped surfaces is to dissociate H<sub>2</sub> molecules even a bit far above the surface. Hence, doping the Pd surface with the PGEs would massively enhance the catalytic property of the Pd surface.



**Figure 23. A combined graph of relaxed height (AdH), relaxed bond length (BL), and the relaxed energy of H<sub>2</sub> on pure (A) platinum-group surfaces and the doped Pd surfaces (B).**

Additionally, the reaction barrier plots were combined to facilitate a clear analysis of the intriguing enhancement in the catalytic ability of the Pd surface shown in **Figure 24**. The plot showcases distinct energy scales at which H<sub>2</sub> dissociates and relaxes, as indicated by the red circles. Furthermore, the

dissociation of  $H_2$  on PdPt is highlighted with a barrier energy of 57meV, potentially suggesting a less favorable dissociation compared to the 70meV barrier on a bare Pd surface. Except for the PdPt surface, all the other Pd-X surfaces have no barrier. This nuanced comparison underscores the subtle yet impactful differences in the catalytic behavior of Pd surfaces when doped with other Pt-group elements.



**Figure 24.** Combined energy profile for Comparison of all the doping materials to understand the catalytic enhancement in the Pd surface.

Unlike the bare surfaces, the adsorption of  $H_2$  on Pd-X surfaces becomes more favorable (see **Figure 25**). The energies required for  $H_2$  to adsorb and possibly dissociate decrease upon the alloying of these surfaces. The minimized energy for  $H_2$  to physisorption on the surface is a great indication that the Pd-membrane surface could be extremely active in terms of catalysis when the surface is carefully decorated by the dopant. The effect that enhances such property could be attributed to the dilute region where the dopant where surrounded by the host Pd-atoms. Based on this note, the minimization of  $H_2$  adsorption energy on doped-Pd surfaces suggests a more efficient utilization of the catalyst. Lower adsorption energies imply that  $H_2$  molecules can adsorb and desorb more readily, promoting turnover rates

in catalytic reactions. This increased turnover rate is crucial for the overall efficiency of catalytic processes, making doped-Pd surfaces promising candidates for various applications, such as hydrogenation reactions in chemical synthesis or fuel cell technologies[25].

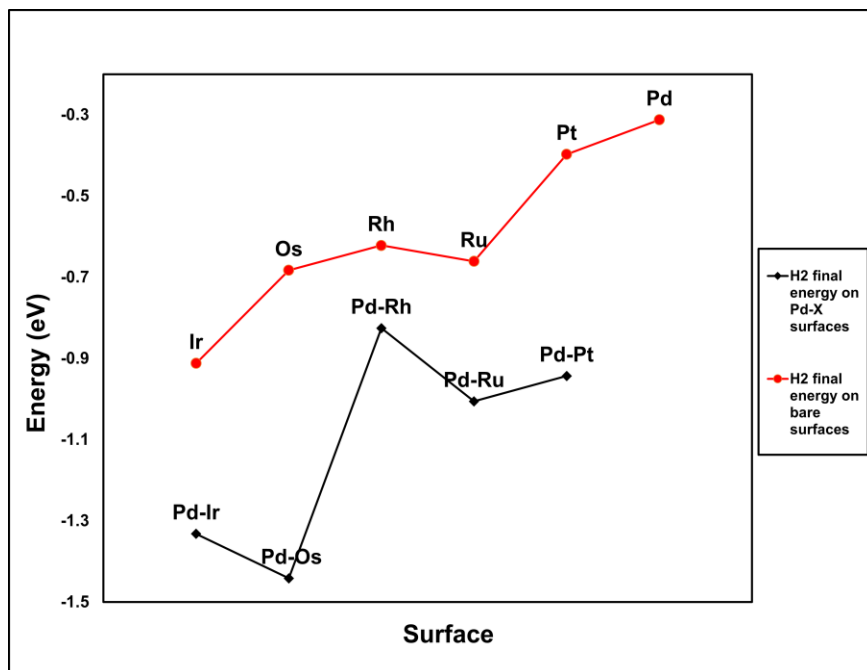


Figure 25. Analysis of the catalytic enhancement of H<sub>2</sub> adsorption energy by comparison of H<sub>2</sub> relaxed energy on pure and alloy of platinum-group elements.



# CHAPTER 5

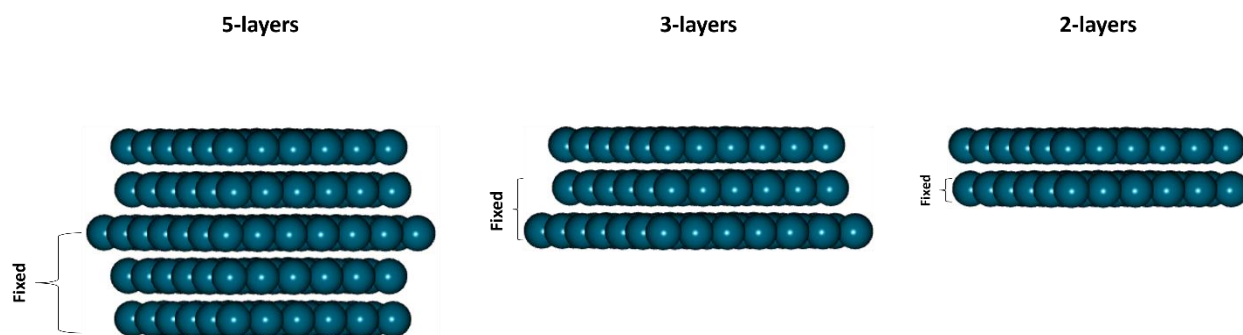
## HYDROGEN TRANSPORT PROCESSES ON Pd-Pt SURFACE

### 5.1 Surface and Alloy Model

We model a slab that represents a crystallographic plane (111) to study the surface chemistry happening on the Pd-Pt. We considered a (3x3) supercell of (111) surface to investigate the adsorption, dissociation, and hydrogen [60]. A five-layer-thick slab is used to maintain a balance between the precision of the calculations and the computational cost, with the atoms in the bottom three layers fixed at their bulk interplanar distances and the remaining atoms free to relax. The super-cell has a size of 11.85 x 11.85 x 45.92, periodic boundary conditions in all directions, and the analysis considers a 2x2x1 Monkhorst-Pack grid. The slab system would contain 180 atoms due to the FCC crystal structure of the membrane. To prevent interaction between periodic images, a vacuum size of 20Å along the slabs' vertical axes was established [61]. To find the most favorable adsorption sites in terms of energy, several positions for reaction intermediates on the surfaces were considered. Regarding the alloying, we consider the computational cost again at the same time accuracy of our calculation and added only one Pt atom on the surface to represent the alloying percentage keeping in mind a justification from statistical mechanics. The presence of one alloy atom in the calculation is enough to observe the effect of alloying because we consider the influence of the alloy atom on the adsorption and dissociation behavior on its neighboring Pd atoms and vice-versa [62]. Therefore, adding many alloy atoms (Pt) makes no difference instead increases the cost of the calculations because of the many interactions between other Pd and Pt atoms within the slab.

## 5.2 Computational Cost Analysis

The challenges associated with the cost of Density Functional Theory (DFT) calculations in analyzing gases on a metal surface stem from the computational demands of accurately modeling the electronic structure and interactions within the system [63,64]. DFT is a powerful method for studying molecular interactions, but its application to gas-metal surface systems requires extensive computational resources [63,65]. The complexity of the metal surface, the number of atoms involved, and the intricate nature of gas adsorption processes increase the computational cost substantially. Achieving high-level accuracy often necessitates employing advanced methods and larger basis sets, further escalating the computational expenses [64]. These challenges highlight the trade-off between computational accuracy and feasibility, underscoring the need for innovative approaches to enhance the efficiency of DFT calculations while maintaining a fair cost.



**Figure 26. Surface Culmination of Pd-Pt Slab**

Indeed, employing surface culmination strategies helps strike a balance between computational accuracy and cost in DFT calculations for gas-surface analyses. These methods often focus on representing the metal surface through simplified models or employing periodic boundary conditions to simulate a finite portion of an extended surface, reducing the number of atoms considered. This allows for a more efficient treatment of electronic interactions while maintaining the essential features of the metal surface. Furthermore, using specialized functionals or basis sets tailored for surface calculations can enhance

accuracy without significantly escalating computational expenses. However, we performed an analysis of  $H_2$  adsorption on three different surfaces we culminated. The culmination started with a five-layer slab with three bottoms fixed and the top two were allowed to relax. Next the last two bottom layers were removed to form the three-layer slab. Later the remaining fixed bottom layer was removed leaving the top relax two which forms the two-layer slab with the lower layer fixed and the upper relaxed as shown in **Figure 26**.  $H_2$  was located on all the sites at  $1.8 \text{ \AA}$  height above the surface. The relaxed energy where estimated and plotted in **Figure 27**. On T1, FCC1, and HCP1,  $H_2$  are adsorbed but dissociated on T0 and B1. However, all energies computed considering each case of the three culminated slabs (5-layer, 3-layer, and 2-layer slabs) virtually show the same result. This indicated all three slabs can ensure accurate results and drag the computational cost while using slabs with fewer atoms. Therefore, we continue the calculations using the 3-layer slab after these estimations.

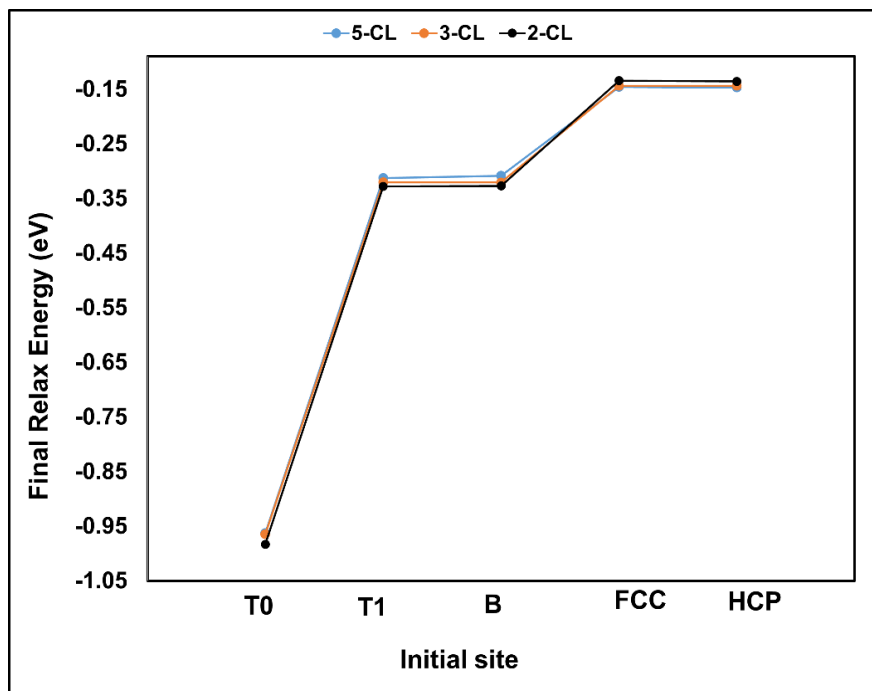
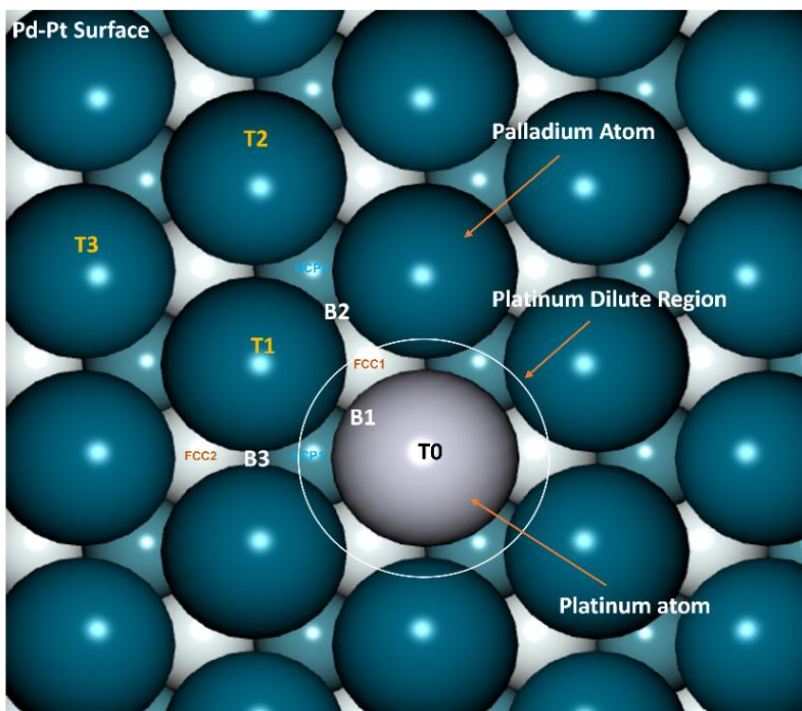


Figure 27. Hydrogen adsorption on the available sites of culminated 5layers, 3layers, and 2layers surfaces

### 5.3 $H_2$ Physisorption on Pd-Pt (111) surface

H<sub>2</sub> separation membrane performance is usually weighed based on the membrane's ability to easily adsorb and dissociate hydrogen molecules on the surface and allow its permeation through it[35,66]. The first two steps in the H<sub>2</sub> transport mechanism on the surface of the membrane are adsorption and dissociation. Hence, the adsorption and dissociation processes of H<sub>2</sub> molecules on the Pd-Pt(111) surface are reported here. We position H<sub>2</sub> on all the available adsorption sites on the surface with different orientations (vertical and horizontal) to calculate the most favorable location and orientation of H<sub>2</sub> on the surface. Unlike the pure Pd surface with lowest index Pd(100) and Pd(110), two hollow sites (FCC and HCP) and two types of atop sites are present, which are denoted as T1, T2, and T3 for Pd-atoms and T0 for Pt-atom respectively. The reason for considering three different Pd atop sites is to study the influence of the added Pt-atom on both the near and far Pd-atoms. Also, there are three bridge sites defined by B1, B2 and B3. B1 sites are between a Pd and Pt atop sites, while B2 and B3 are bridge sites located between two pairs of Pd atoms opposite to the Pt atom across FCC1-Hollow and HCP1-Hollow sites respectively. Additionally, two types of hollow sites are present on the surface: one located just above the first subatomic layer in light blue (designated as HCP1 and HCP2) and the other above the second subatomic layer in white (designated as FCC1 and FCC2). In **Figure 28**, all the sites mentioned are presented.

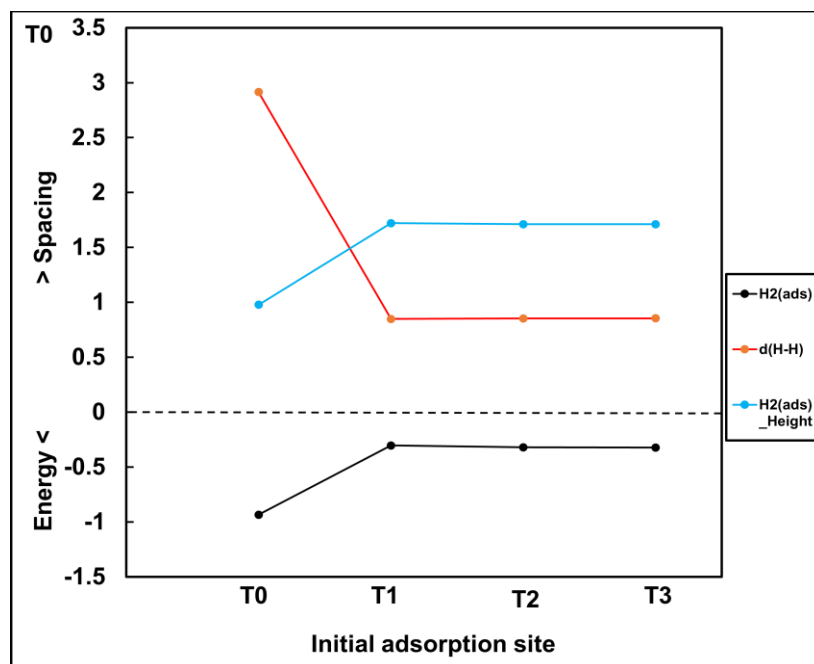


**Figure 28. Alloy surface of Pd-Pt with designated sites available.**

The total number of atoms on the upper layer of the (3x3) supercell with (111) index is 36 atoms (35-Pd atoms and 1-Pt atom ). The amount of  $H_2$  molecules that bind to the surface for each surface Pd atom is how we define the surface hydrogen coverage ( $\theta_{H_2}$ ). According to this definition, one  $H_2$  molecule translates to  $H_2 = 0.16$  ML on a (3 x 3) supercell. The  $H_2$  molecule attaches to Pd (T1, T2, and T3) at this coverage in the most stable adsorption orientation (Horizontal) in an activated state with an H–H bond length of 0.75 Å. With a  $d_{Pd-H}$  of 1.80 Å,  $H_2$  binds to the surface of Pd (T1, T2, and T3) in this adsorption configuration, keeping the molecule axis parallel to the surface. The H-H bond length ( $d_{H-H}$ ) in all the three Pd atop sites(T1, T2 and T3) is determined to be around 0.85 Å, and the adsorption energies for this configuration are found to be about -0.303 eV, -0.321 and -0.323 respectively (see Figure 29). Similar H-H bond length was reported by Kumar et. al with a little difference in the adsorption energy of (-0.35eV) compared to T1 while studying the  $H_2$  adsorption on a top site of Pd on PdCu. The slight difference could be attributed to the presence of Cu instead of Pt on the surface [57]. Moreover, the  $H_2$  adsorption on each

top site of Pd atoms occurs at 1.71 Å ( $d_{\text{Pd-H}_2}$ ) above the surface irrespective of the atom's location except for T1 where H<sub>2</sub> is adsorbed at 1.72 Å just 0.01 Å above the height in the cases on T2 and T3. Although H<sub>2</sub> was adsorbed on the Pd atom (T1) next to the Pt atom doped on the surface at slightly higher height and energy compared to the rest Pd tops, however, this signifies the effect of the doped Pt on the adsorption H<sub>2</sub> on Pd.

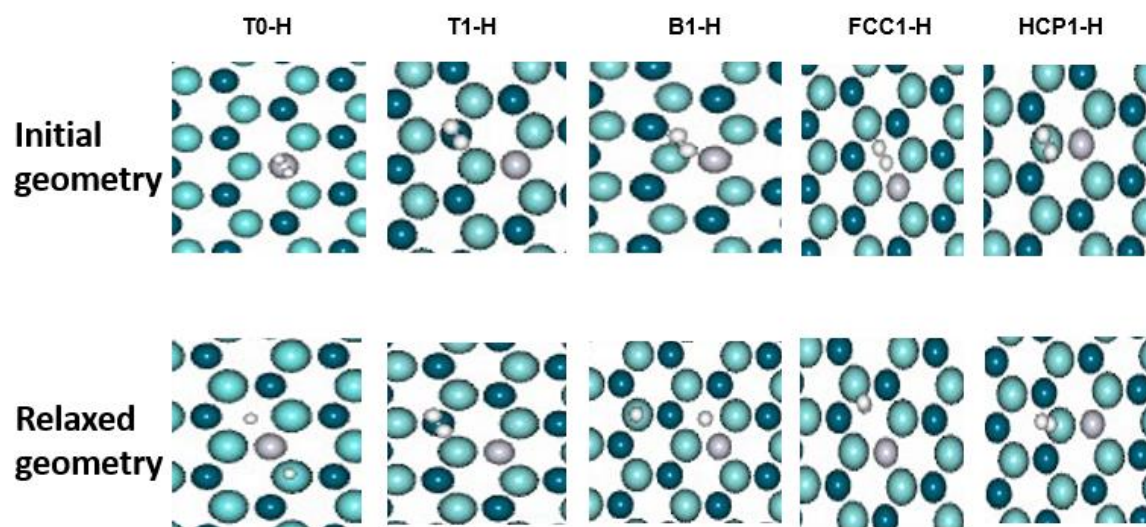
In addition, at similar H<sub>2</sub> geometry and its adsorbed height ( $d_{\text{Pd-H}_2}$ ) on T1, T2, and T3, H<sub>2</sub> dissociated directly into individual atoms on T0 (Pt-atom) as shown by energy in Figure 29 and visually in Figure 30 (T0). with the minimum dissociative adsorption energy (-0.93eV). An interesting dissociation happens when H<sub>2</sub> descends from its initial height of 0.8 Å to 0.98 Å very close to the surface. The H<sub>2</sub> molecule dissociates into its atoms. One H-atom relaxes on the FCC site and the other on the HCP as shown in Figure 30. The Pt atom (T0) on the surface demonstrated high affinity to H<sub>2</sub> molecule and this may be the justification why the adsorption energy of H<sub>2</sub> on T1 is higher. Unlike H<sub>2</sub> on the top site of Pd (T2 and T3) atoms that are far away from the doping Pt atom, the forces pulling H<sub>2</sub> on Pd top (T1) from the doping Pt (T0), must be compensated by the pushing forces to sustain the adsorption of H<sub>2</sub> on the T1. This results in the increase of adsorption energy on T1. However, the presence of Pt on the surface minimized the overall adsorption energy of H<sub>2</sub> on all the available sites on the surface. This is observed from the change in the adsorption energy of H<sub>2</sub> on bare Pd surface in the absence of Pt and with the Pt doped on the surface in the following manner: at T1<sub>Pd-PdPt</sub> ( $E_{\text{H}_2}$  = -0.024eV to -0.320eV), at B1<sub>Pd-PdPt</sub> ( $E_{\text{H}_2}$  = -0.025eV to -0.993eV), at FCC1<sub>Pd-PdPt</sub> ( $E_{\text{H}_2}$  = 0eV to -0.139eV) and at HCP1<sub>Pd-PdPt</sub> ( $E_{\text{H}_2}$  = 0eV to -0.139eV). Compare the H<sub>2</sub> adsorption energies of H<sub>2</sub> on all the corresponding sites in Figure 31 and **Figure 33**.



**Figure 29.** H<sub>2</sub> adsorption energy on Pd atoms in the presence of Pt with their corresponding final relaxed bond length and height of H<sub>2</sub> from the surface.

Similarly, the dissociation of H<sub>2</sub> molecules was observed on the bridge site (B1) next to the Pt atom (T0) as shown in Figure 30 (B1-H). H<sub>2</sub> is also dissociated into H-atoms, and the relaxed position taken by the dissociated atoms is still the FCC and HCP but different from those occupied when the dissociation happens on the Pt. The atoms relaxed with a dissociative energy of (-0.99eV), which is more minimum than the previous energy when dissociated on the Pt(see Figure 31). It became interesting when we observed that sizes of FCC and HCP hollow sites could only accommodate an H-atom at a time. This observation came when H<sub>2</sub> molecules were initially placed on the FCC and HCP site at 1.8 Å above the surface. Remember that the dissociated H-atoms on T0 and B1 preferentially relaxed on FCC and HCP sites, however, now that the whole H<sub>2</sub> molecule instead of just the H-atom was placed on these sites, each of the H<sub>2</sub> molecules rotates vertically while maintaining the same sites to allow one head of the H-atom in the molecule to relax first into the site with the other H-atom on top(Figure 30, *FCC1-H and HCP1-H*). Unlike the relaxation of H-atom which happens near the surface, the rotation of the H<sub>2</sub> molecules occurs

far above these sites with  $d_{fcc-H_2}$  and  $d_{hcp-H_2}$  of  $2.8\text{\AA}$  and  $2.7\text{\AA}$ , and bond length between the H-atoms( $d_{H-H}$ ) of approximately  $0.75\text{\AA}$  and  $0.62\text{\AA}$  respectively. This shows how the two sites prefer to accommodate an H-atom at a time, be it a single H-atom or a head of H-atom in its molecule. Also, this clearly proves the claim that metals adsorbed hydrogen in their atomic form and thereby act as hydrogen “sponges” [59]. **Table 5** has the summary of  $H_2$  adsorption and dissociative adsorption energies with the height and bond length for the relaxed  $H_2$  molecules or H-atoms. The  $H_2$  molecules placed on all other adsorption sites end up in any one of the above-mentioned top sites. Therefore,  $H_2$  molecules on Pd-Pt surface must dissociate before they can enter the subsurface and begin permeation into the membrane. This is consistent with the  $H_2$  transport process on the palladium (Pd) membrane, which is the breakdown of molecular  $H_2$  into individual hydrogen atoms (H) on the membrane's surface. On the other side of the membrane, these hydrogen atoms recombine to create  $H_2$  molecules after diffusing through the Pd lattice. Sieverts' law of hydrogen permeation describes this process[32,67,68].



**Figure 30.** The initial and final relaxed geometry of  $H_2$  on Pd and Pt top sites of perfect PdPt(111) surface. Pd top layer atoms in dark-blue while the light-blue represents the first sub-layer atoms and Pt is grey color.

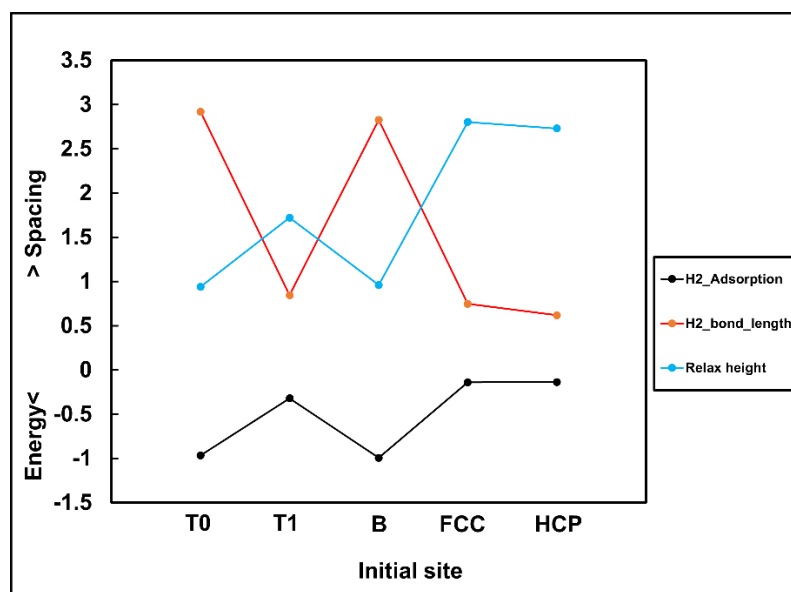
**Table 5. H<sub>2</sub> Binding Energy (eV) on bare Pd(111) and a Pd-Pt(111) Surface at 0.25ML Coverage.**

| Adsorption Site | Bare Pd |       |       | Adsorption Site | Pd-Pt |       |       |
|-----------------|---------|-------|-------|-----------------|-------|-------|-------|
|                 | H2      | CO    | H2S   |                 | H2    | CO    | H2S   |
| <b>T0</b>       | -       | -     | -     | <b>T0</b>       | -0.96 | -1.91 | -1.11 |
| <b>T1</b>       | -0.33   | -1.54 | -1.03 | <b>T1</b>       | -0.32 | -1.52 | -1.04 |
| <b>B1</b>       | -0.34   | -1.82 | -1.01 | <b>B1</b>       | -0.99 | -1.91 | -1.12 |
| <b>FCC1</b>     | -0.01   | -1.99 | -0.95 | <b>FCC1</b>     | -0.13 | -2.01 | -1.11 |
| <b>HCP1</b>     | -0.33   | -1.99 | -1.04 | <b>HCP1</b>     | -0.13 | -2.00 | -1.73 |
|                 |         |       |       |                 |       |       |       |

## 5.4 H<sub>2</sub> Chemisorption and Dissociation on Pd-Pt (111) surface

It was seen that H<sub>2</sub> dissociates on T0 and B1, with relaxed energy of the H-atoms being far minimized than when on other Pd sites, then, we can say that the presence of Pt as a dopant has a great influence on the dissociation of H<sub>2</sub> molecule on the surface. Since the adsorption of H<sub>2</sub> on top of Pd top sites(T1, T2, and T3) is fair compared to the dissociative adsorption of T0 and B1, though, we could not easily capture the physisorption of H<sub>2</sub> on T0 and B1 even after so many careful adjustments of the initial height( $d_{T0-H_2}$  and  $d_{B1-H_2}$ ), the H<sub>2</sub> molecule keeps dissociating until at about 2.4 Å height above the surface where the H<sub>2</sub> molecules move away, signifying that the H<sub>2</sub> molecule is no longer feeling or interacting with the surface. We therefore consider placing H<sub>2</sub> molecules at 10Å height on T0 and B1 sites above the surface (to capture all the events behind and through the challenging adsorption stage till the point of dissociation as shown in Figure 32) as the initial configuration to study the H<sub>2</sub> dissociation (marked as **1** in Figure 8(a) and demonstrated in Figure 7 as initial state). To find the final configurations, two H are placed at various possible adsorption sites like bridge and hollow sites. We found that in the most stable geometry, the two H atoms are adsorbed on two adjacent hollow sites (fcc1 and hcp1) for both cases (T0 and B1 tops) which are formed by two Pd atoms and a Pt atom (marked as **10** in Figure 8(a) for T0 only). This agrees with the final relaxed state of the H<sub>2</sub> molecule observed while studying the H<sub>2</sub> physisorption as explained earlier and shown in Figure 5. The dissociative adsorption of two H atoms is about -0.96eV and

-0.99eV for dissociation on T0 and B1 respectively, which are thermodynamically more stable than that of adsorption of molecular hydrogen. A reaction pathway was established for H<sub>2</sub> dissociation starting from the above-mentioned initial and final configurations, and the minimum energy path obtained from the CI-NEB calculation is presented in **Figure 33** (a) and (b). The  $d_{\text{H-H}}$ , which is about 0.75 Å in the initial state, is stretched to 1.56 Å at the transition state and finally to 2.9 Å at the final relax state of the H-atoms. The dissociative adsorption goes through a precursor state and the classical barrier for H<sub>2</sub> dissociation is estimated to be 57meV on T0 and no barrier was observed for the dissociation of H<sub>2</sub> that was initially on B1.



**Figure 31.** Relationship between bond length, adsorption height and energy of H<sub>2</sub> on the available sites on Pd-Pt surface.

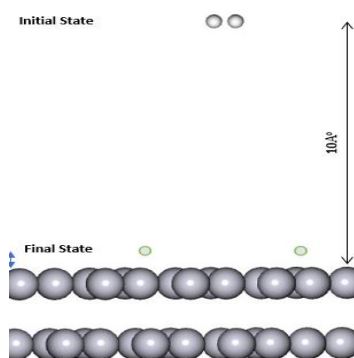


Figure 32. The H<sub>2</sub> geometry for dissociation barrier calculation.

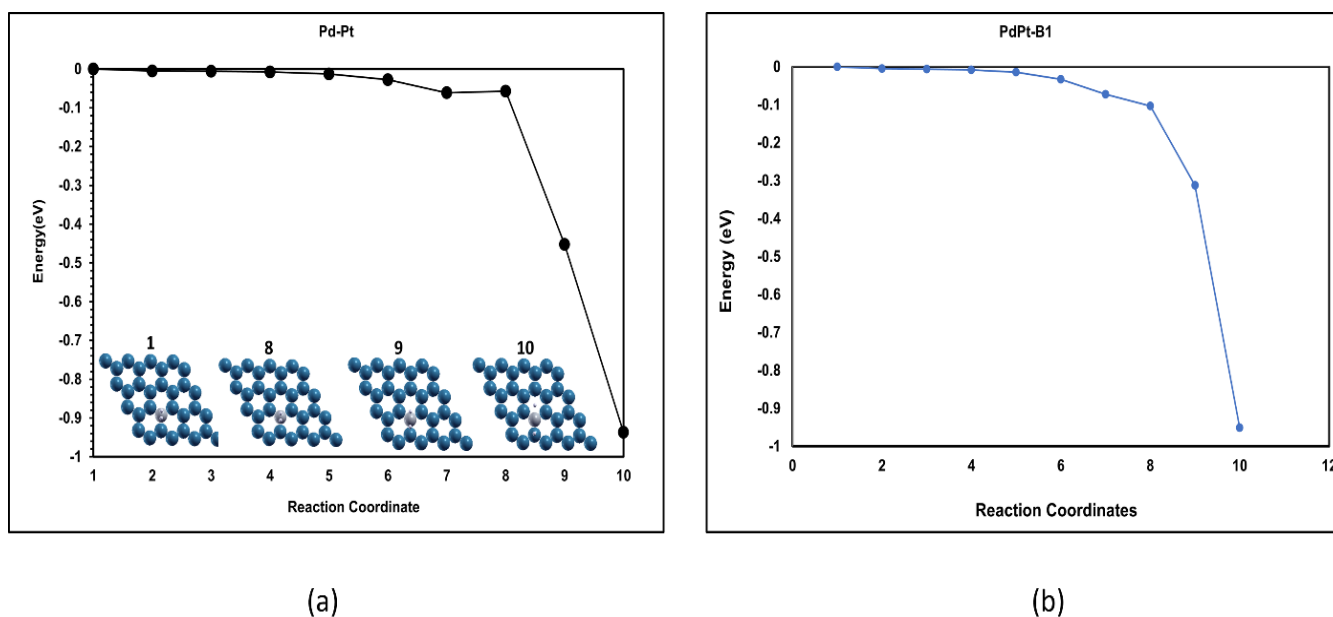


Figure 33. Dissociation barrier path of H<sub>2</sub> initially placed on T0 in (a) and on B1 in (b)

## 5.5 Electronic Charge Density Difference Analysis of H<sub>2</sub>-PdPt Interaction

Nonetheless, the Pt atom's valence electron configuration may be the cause of the low barrier to H<sub>2</sub> dissociation at the T0 (Pt-atom) location. Pt is in the valence electron configuration  $6s^15d^9$ . In contrast to Pd atoms with valence electron configurations of  $5s^04d^{10}$ , the Pt atom possesses two kinds of partially filled orbitals (i.e., s and p). The dissociative adsorption of H<sub>2</sub> on a metal surface may be described by these orbitals and the surface s- and d-electrons. The H<sub>2</sub> molecule orbitals start to overlap with the surface

s-electrons as they get closer to a metal surface. This is confirmed by the electronic charge density difference plot of  $H_2$  interaction shown in Figure 34. The H s-electron is therefore rejected (by the Pauli exclusion principle) for a substrate atom whose valence electron states are completely occupied, leading to a high energy barrier. The following is how the surface d-electrons participate. As  $H_2$  gets closer to the surface, charge is given back to the  $H_2$  anti-bonding state from the surface d-states and from the  $H_2$  s-orbital to the surface d-states. It may be expressed as follows:  $H_2$  dissociation on the surface is enhanced by the interaction between the surface d-electrons and molecules orbitals of  $H_2$ . The H s-electron repulsion is consequently mild for Pt where there is empty surface s- and d-states, but  $H_2$  dissociation is enhanced, leading to a very low energy barrier [59,69]. Therefore, our result shows that  $H_2$  should easily dissociate on Pd-Pt surface due to the low dissociation barrier on T0(Pt top site) as shown in **Figure 33(a)** and barrier free on the bridge site (B1) in **Figure 33(b)**.

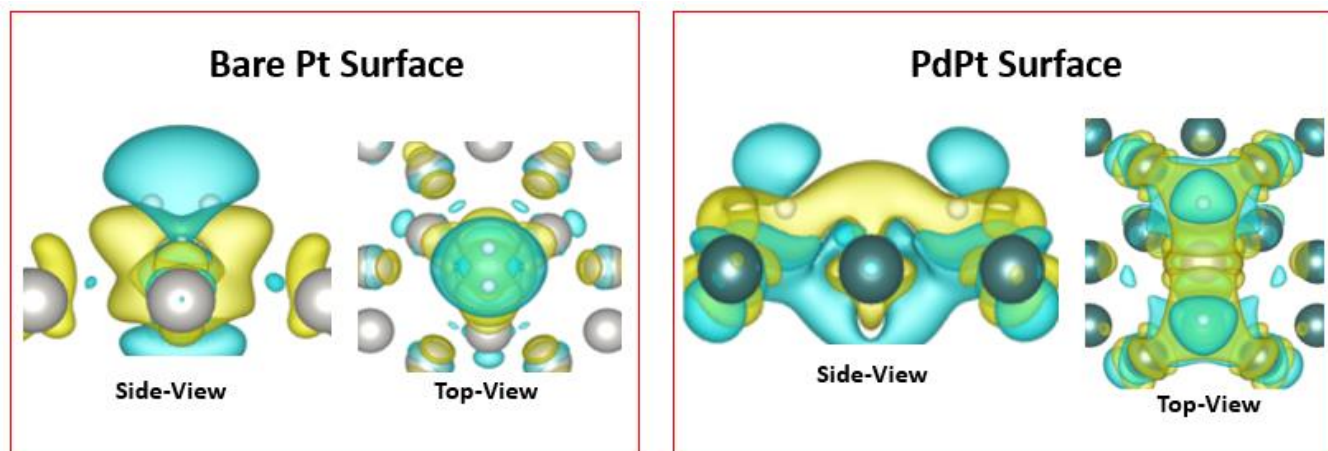
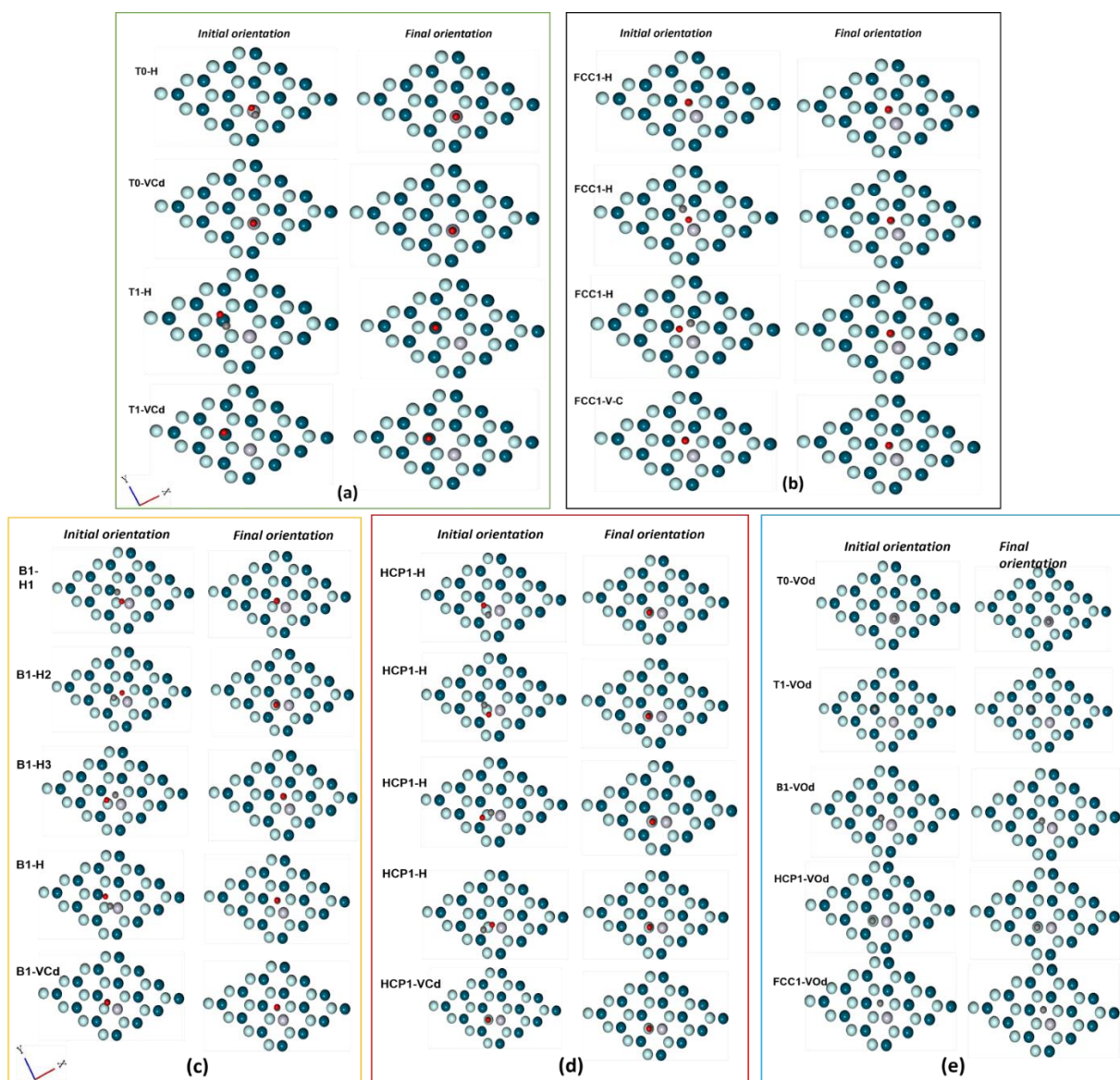


Figure 34. Electronic charge density difference of  $H_2$  interaction with bare Pt and Pd-Pt alloy surfaces.

## 5.6 Adsorption of CO and $H_2S$ on Pd-Pt surfaces

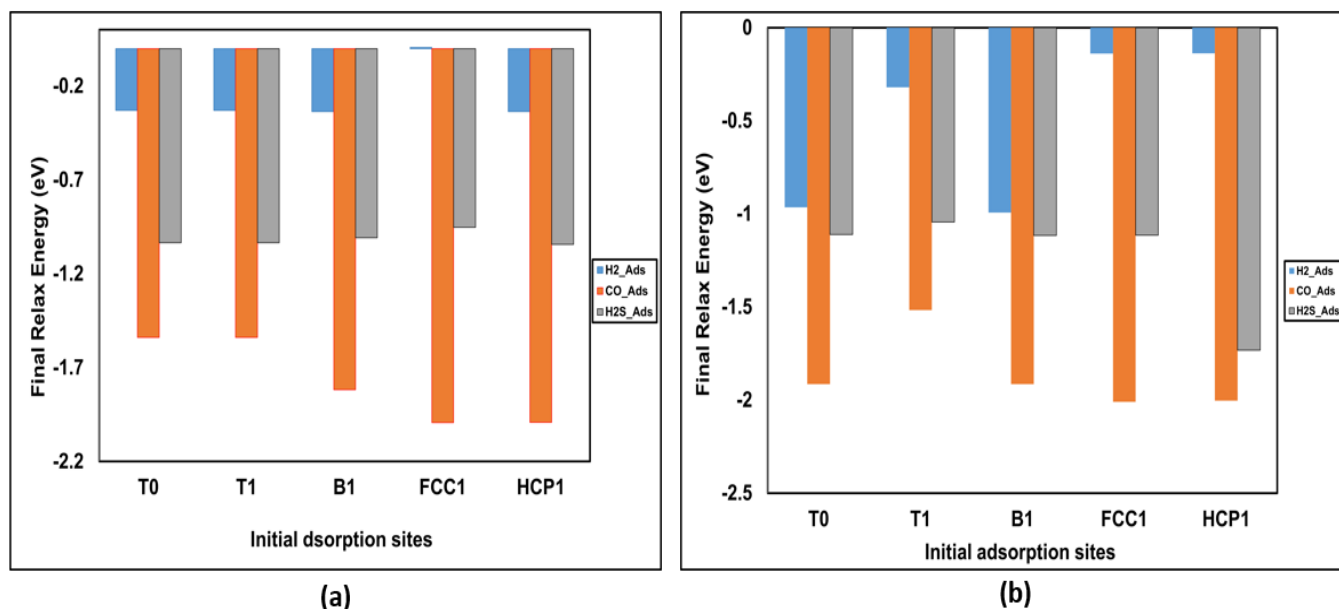
Surface poisoning of Pd base membrane is one of the great challenges hindering the wider application of Pd-based membrane. Poisoning gases can influence the binding energy of  $H_2$  molecules to the Pd-membrane or inhibit the accessible adsorption sites, which can influence the adsorption of  $H_2$

molecules. Finding the most likely location and orientation for these poisoned gases to bond to the Pd-Pt surface is essential to examining the effects of these gases. On the Pd-Pt(111) surface, **Figure 25** depicts the initial and relaxed geometry of CO gas at various locations with different orientations in the diluted region. A 3x3 slab was used for the computation; however, for clarity's sake, only a portion of the slab is included in the figure.



**Figure 35.** The initial and relaxed orientation of CO on the available site (T0, T1, B1, FCC1, and HCP1) in the dilute region on the Pd-Pt(111) surface.

The adsorption energy of CO and on the Pd-Pt surface(111) is shown in Figure 36. It was observed that when CO is adsorbed at a vertical orientation with the oxygen atom positioned near the Pd-Pt surface (cases in the last block of **Figure 35(e)**), the binding energy of CO on the Pd-Pt surface decreases. This vertical orientation results in a binding energy of just -0.14 eV for the four adsorption sites of the top, bridge, fcc, and hcp hollow, and the CO goes far beyond the surface from its original height of 1.8 Å to 4.17 Å. An indication that CO has a lower chance of being adsorbed at these locations with such orientations on the surface. Furthermore, all initial geometry of CO at the horizontal orientation is relaxed to a vertical orientation with carbon atoms facing down close to the Pd surface as seen in **Figure 35** block (a), (b), (c), and (d) a similar behavior that was observed on a bare Pd (100)[27]. This means CO always prefers such geometry irrespective of the facet and possibly the composition of the surface since the presence of Pt on the Pd-Pt surface does not affect such behavior. Another observation is that Pd and O do not spontaneously want to interact for a reason which could result from the nature of their valence electronic configurations. The most negative adsorption energy of CO is about -2.0eV which was achieved at the FCC, and HCP hollow sites with vertical CO orientation while C-atoms close to the Pd surface (situations in block (b), (c), and (d) ). The CO relaxed at 1.4 Å above the Pd surface. The bond length of C-O slightly elongates after the physisorption process from around 1.140 Å (at the gas phase) to about 1.189Å. Furthermore, depending on the initial distance between the CO molecule and the Pd surface, it has been noted that occasionally, the CO molecule relaxes at a location other than the one it was initially given. Figure 36 presents more information about the energy of these instances. Moreover, the T1 sites also exhibited large adsorption energies of -1.52 eV.

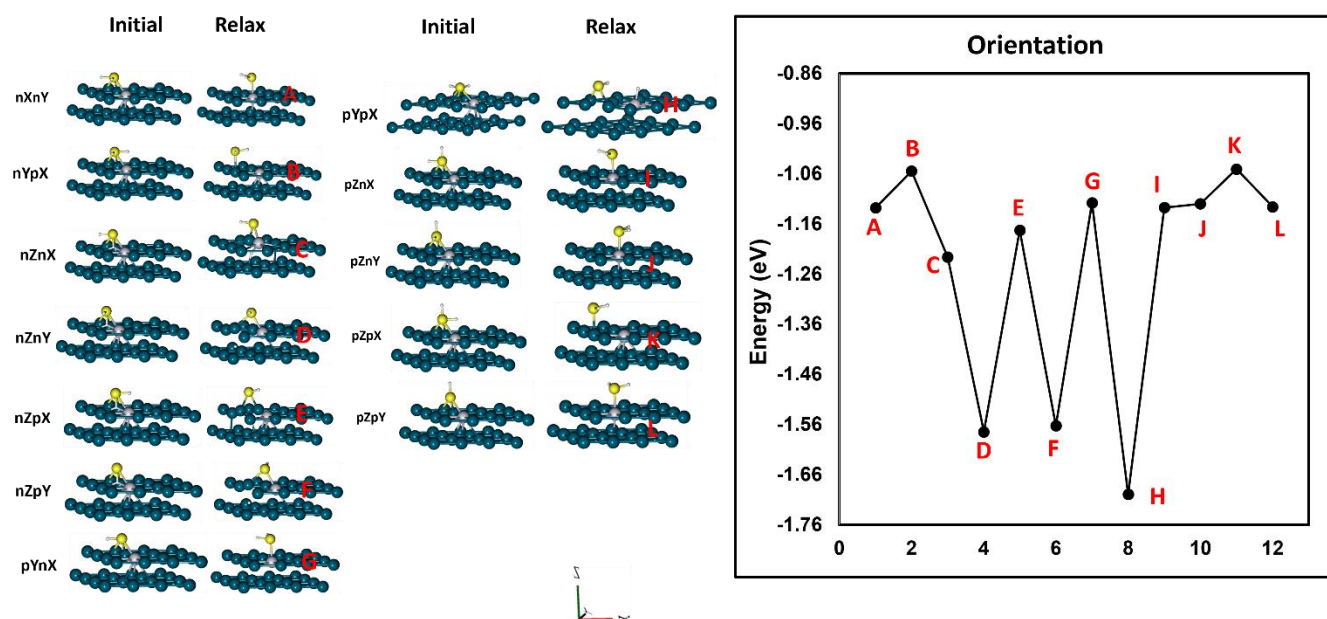


**Figure 36. Adsorption energy of H<sub>2</sub>, CO, and H<sub>2</sub>S on (a) the available sites of bare Pd(111) and (b) Pd-Pt(111) surfaces.**

In comparison, the minimum adsorption energy of CO on Pd-Pt(111) surface (-2.0 eV) is slightly higher than the adsorption energy of CO on bare Pd(111) of -1.99 still obtained on hollow hcp and hollow fcc sites. Hence, the presence of Pt does not significantly affect the adsorption of CO on the surface and generally, Pd(111) could be more susceptible to CO poisoning compared to the bare Pd(100) which adsorbed CO with the energy around 0.117 eV as reported by Abuelyamen et. al [27]. In Figure 36, the adsorption energy of CO on bare Pd and Pd-Pt is presented among others.

Similarly, the adsorption energy of H<sub>2</sub>S on Pd-Pt was investigated, starting with the determination of the minimum energy orientation then followed by the most favorable adsorption site. H<sub>2</sub>S was oriented such that the two H-atoms attached to the sulfur kept varying in coordinates. We denoted ‘n’ as negative, and ‘p’ as positive which are attached to the XYZ axis to logically define the possible orientation to analyze as shown in Figure 12. When H<sub>2</sub>S was initially oriented with H-atoms as pXpY meaning one H-atom in the positive X direction and the other H-atom in the positive Y-direction, it relaxed after dissociating into HS and H with the most minimum energy (Label ‘H’ in **Figure 37**). The HS binds to Pd-

atom and the H binds to Pt as shown in **Figure 37** (pXpY). Moreover, for all other possible orientations, H<sub>2</sub>S relaxes mostly to pXpY and in few cases to nXnY, or pXnY or nXpY geometries, hence H<sub>2</sub>S adsorption and dissociation can easily be achieved while in pXpY orientation. Then, we consider this orientation to further determine the most favorable adsorption site for H<sub>2</sub>S adsorption. **Figure 38**. Shows the initial and relaxing geometry of H<sub>2</sub>S on the top, bridge, and the hollow sites. Regarding the site, H<sub>2</sub>S is adsorbed with minimum energy of -1.03eV and -1.73eV on HCP for both bare Pd and Pd-Pt respectively (Figure 36 (a) and (b)). The adsorption of H<sub>2</sub>S is non-active from the gas phase and is exothermic [29]. The adsorption energy of H<sub>2</sub>S, SH, and S are correlated with lattice constant. Accordingly, the Fermi level, d-state density at the Fermi level, and d-band center relative to the Fermi level are the determinants of H<sub>2</sub>S binding energy [31].



**Figure 37. H<sub>2</sub>S orientations with their respective relaxed energies.**

Though the Pd-Pd surface could be vulnerable to H<sub>2</sub>S poison, it can play a major role in processes that require the dissociation of H<sub>2</sub>S such as petroleum refining, waste-water treatment, sulfur recovery among others. Dominic et. al claim that H<sub>2</sub>S dissociation is exothermic with a low barrier and that its

decomposition on Pd(1 1 1) surface is facile [29]. , it dissociates to produce an additional H-atom to the total number of dissociated atoms on the surface and the hydrogen content  $n$  (hydrogen per metal atoms ratio) and the coefficient of diffusion  $D_H$  are isothermally related [70]. This implies that Pd-Pt surface could potentially produce hydrogen from H<sub>2</sub>S as a feed.

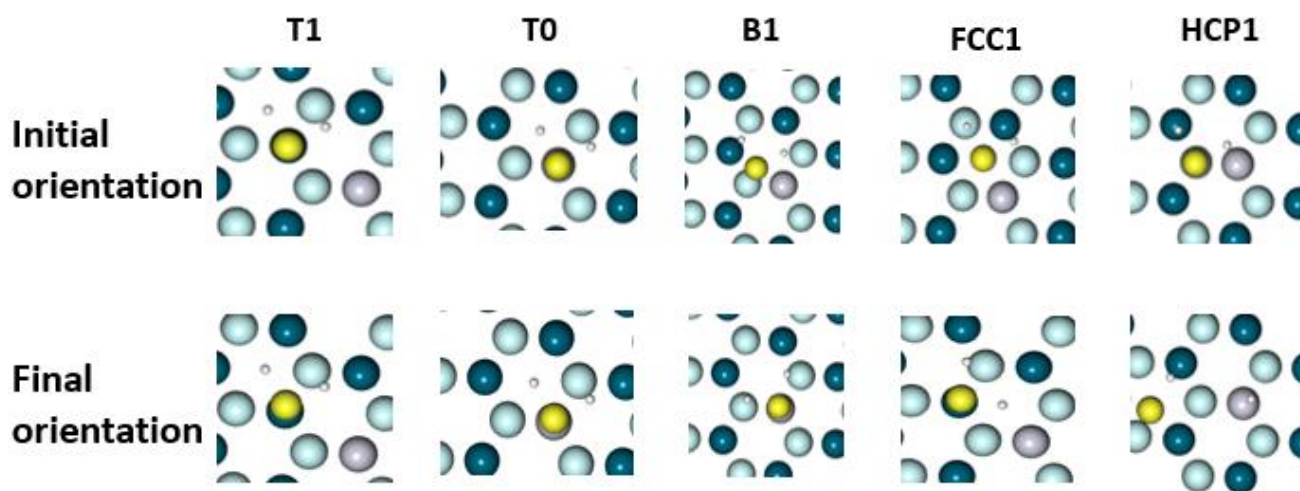
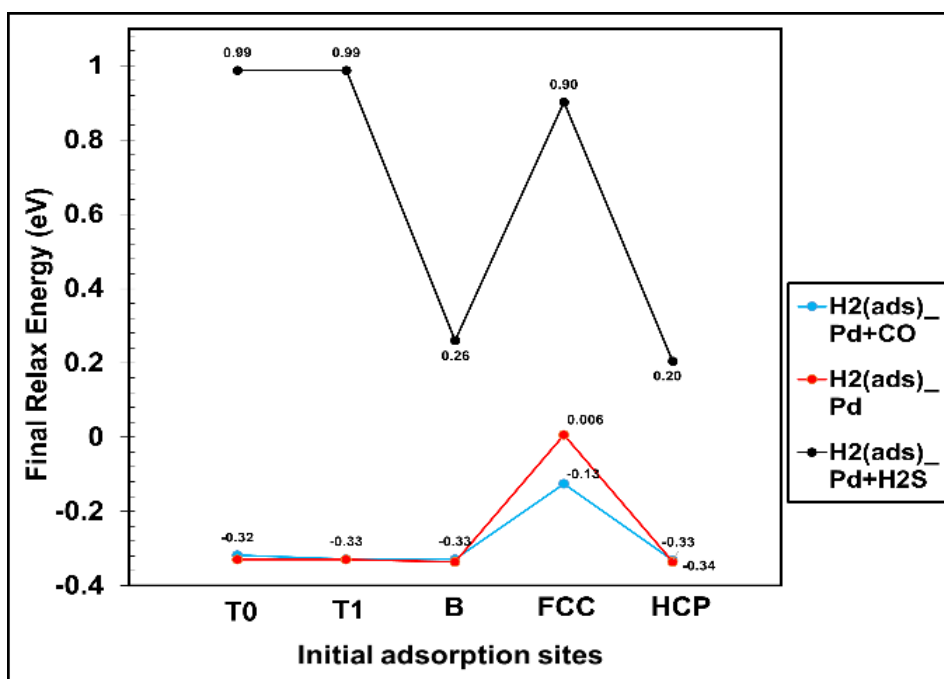


Figure 38. The Initial and relaxed geometry of possible sites for H<sub>2</sub>S adsorption on Pd-Pt Surface

## 5.7 Effect of CO and H<sub>2</sub>S on H<sub>2</sub> Adsorption on Pd-Pt Surface

CO and H<sub>2</sub>S could greatly affect hydrogen processes such as permeance on a bare Pd membrane surface [71]. The CO and H<sub>2</sub>S either compete with H<sub>2</sub> for adsorption sites, thereby blocking the chances for H<sub>2</sub> to get absorbed on the surface, or completely poisoning the surface and compromising its primary function. How soon H<sub>2</sub>S poisoning develops is unknown due to the large variations in H<sub>2</sub> and H<sub>2</sub>S concentrations and site availability [30] However, studying these effects is of paramount importance especially when attempting to improve the properties of a Pd membrane. The CO and H<sub>2</sub>S effects on H<sub>2</sub> adsorption were investigated on the PdPt surface to observe the improvement that doping Pt on the Pd membrane surface can make. On a bare Pd membrane surface, CO was observed to inhibit hydrogen permeation through the membrane and lead to deviations from Sievert's law [28,72]. Depending on how

the metal is used, such as in fuel cells, the presence of CO may passivate the surface and reduce the performance of the device [73]. However, it was observed here that H<sub>2</sub> adsorption energy is almost the same both alone and in the presence of CO. H<sub>2</sub> adsorbed equally with and without CO with energy -0.32eV, -0.33eV, and -0.34eV when initially at T0, T1, B, and HCP respectively. The only case where H<sub>2</sub> adsorption varies, with and without CO is when initially at the FCC hollow site where the energy is 0.006eV and -0.13eV without CO and with CO respectively. Fonseca et. al, also calculated the adsorption of H<sub>2</sub> on a hollow FCC site of a Pd surface in the presence of a pre-adsorbed CO and obtained an energy 0.11eV lower than on bare surface [73,74].



**Figure 39.** H<sub>2</sub> adsorption on bare Pd surface, in the presence of CO and H<sub>2</sub>S

On the other hand, H<sub>2</sub>S strongly affects H<sub>2</sub> adsorption. The H<sub>2</sub> adsorption energy becomes greater. It adsorbed weakly by 0.99eV when it was initially at T0 and T1, moreover, when the H<sub>2</sub> was originally located at FCC, B, and HCP, it relaxed and adsorbed with the energy of 0.90eV, 0.26eV, and 0.20eV respectively. **Figure 39** presents the adsorption of H<sub>2</sub> on a bare Pd without any poison gas and with two

poison gases each.

However, when platinum is doped onto the bare Pd surface, the adsorption of  $H_2$  on PdPt surfaces is highly enhanced. The adsorption energy is minimized to as low as -0.96eV with  $H_2$  at its initial site T0, -0.32eV at T1, -0.99eV at FCC hollow, and -0.14 when it is at HCP initially. Moreover, in the presence of pre-covered CO, the  $H_2$  adsorption is affected when it is initially located at bridge site(B) where the adsorption energy increased from -0.99eV to -0.32eV and minimized from -0.14eV to -0.32eV at HCP hollow site. Apart from the case where  $H_2$  was located initially at the bridge and at the HCP hollow,  $H_2$  adsorption remains the same with respect to other sites(T0, T1 and FCC) just as those on bare Pd (see Figure 15). Furthermore, in the presence of  $H_2S$ , again the  $H_2$  adsorption is good. It is adsorbed from its initial positions T0, T1, B, FCC, and HCP to its relaxed geometry with energy -0.90eV(T0, B), -0.32eV(T1), -0.30eV(FCC) and -0.88eV(HCP). The adsorption for the case of T0, B and HCP site are dissociative. Rupprechter et. al [75] studied the dissociative hydrogen adsorption on CO-recovered Pd(111) for CO coverages between 0.75 and 0.33 ML and concluded that H adsorption is very unlikely. The H-H bond break takes place somewhat distant from the surface before the adsorption.

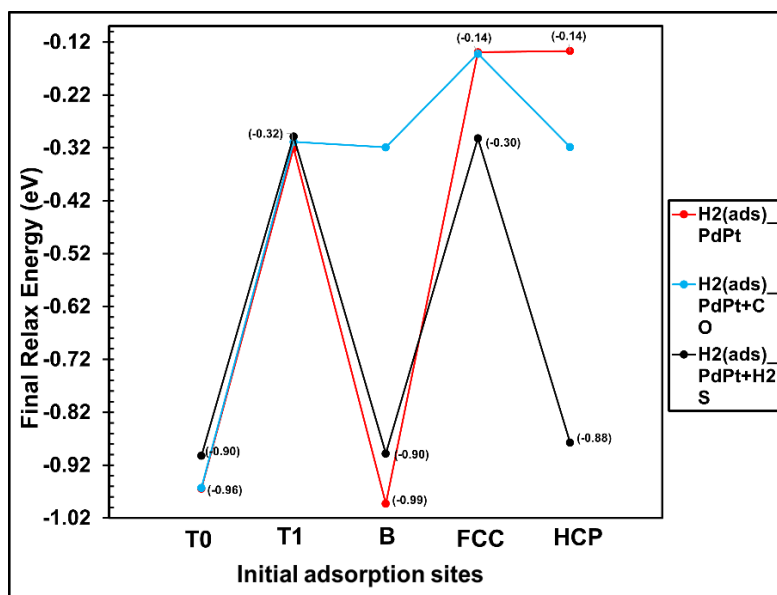


Figure 40. Figure 14.  $H_2$  adsorption on PdPt surface, in the presence of CO and  $H_2S$

## 5.8 Comparative analysis of improvement between bare Pd and PdPt surfaces

It is observed that the PdPt(111) surface exhibits significant adsorption of  $H_2$  even in the presence of CO and  $H_2S$  compared to Pd. To examine the consequences stemming from CO adsorption, we computed the energy required to adsorb a hydrogen atom onto a surface that already had a CO molecule pre-adsorbed. The energy of adsorption of  $H_2$  on both Pd and PdPt surfaces in the presence of the pre-covered CO are virtually the same with a difference only in the case where the  $H_2$  initial site is T0(Figure 42a). This similarity can be associated with the nature of the CO adsorption on the two surfaces. The CO adsorbed on the PdPt surface with nearly equal energy to the energy it adsorbed on the Pd surface(Figure 18a). This means the PdPt surface resists further effect of CO in addition to enhancing  $H_2$  adsorption(Figure 16).

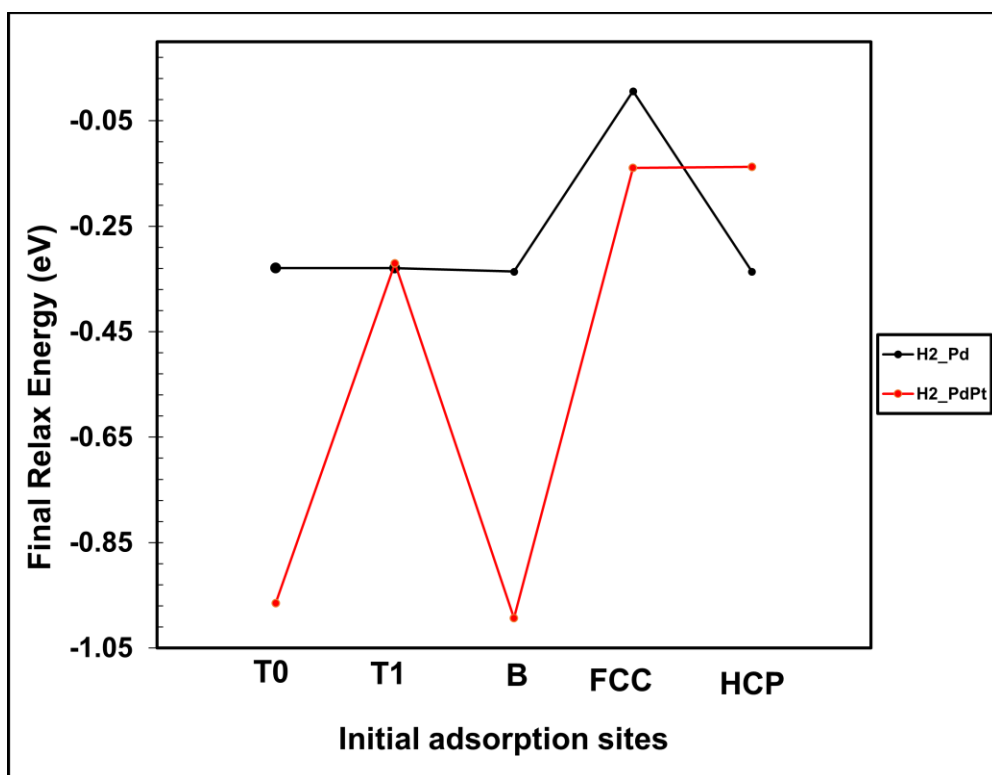


Figure 41.  $H_2$  adsorption on Pd and PdPt surfaces

In contrast,  $H_2$  adsorption is greatly enhanced on the PdPt surface in the presence of  $H_2S$ . It is weakly adsorbed on bare Pd with more positive values; 0.99eV, 0.26eV, 0.9eV, and 0.20eV when the initial location of  $H_2$  is T0-T1, B, FCC, and HCP. Compared to  $H_2$  adsorption in the absence of  $H_2S$  on bare Pd(see Figure 16), it will be noticed that the presence of  $H_2S$  woefully increases the energy required for the adsorption of  $H_2$  on the surface. The change in the adsorption energy toward more positive values can be attributed to the modification of the metal d band caused by its interaction with the  $H_2S$  states. Although  $H_2S$  adsorbed more on PdPt relative to the bare Pd surface(**Figure 43b**) however, on the PdPt surface, the adsorption of  $H_2$  records minimum energy when  $H_2$  originates from T0, T1, B, FCC, and HCP and relaxed with energy -0.9eV and -0.3eV(**Figure 42b**). This is a great improvement and the  $H_2$  might dissociated before adsorbing for the case with the most negative energy(-0.9eV).

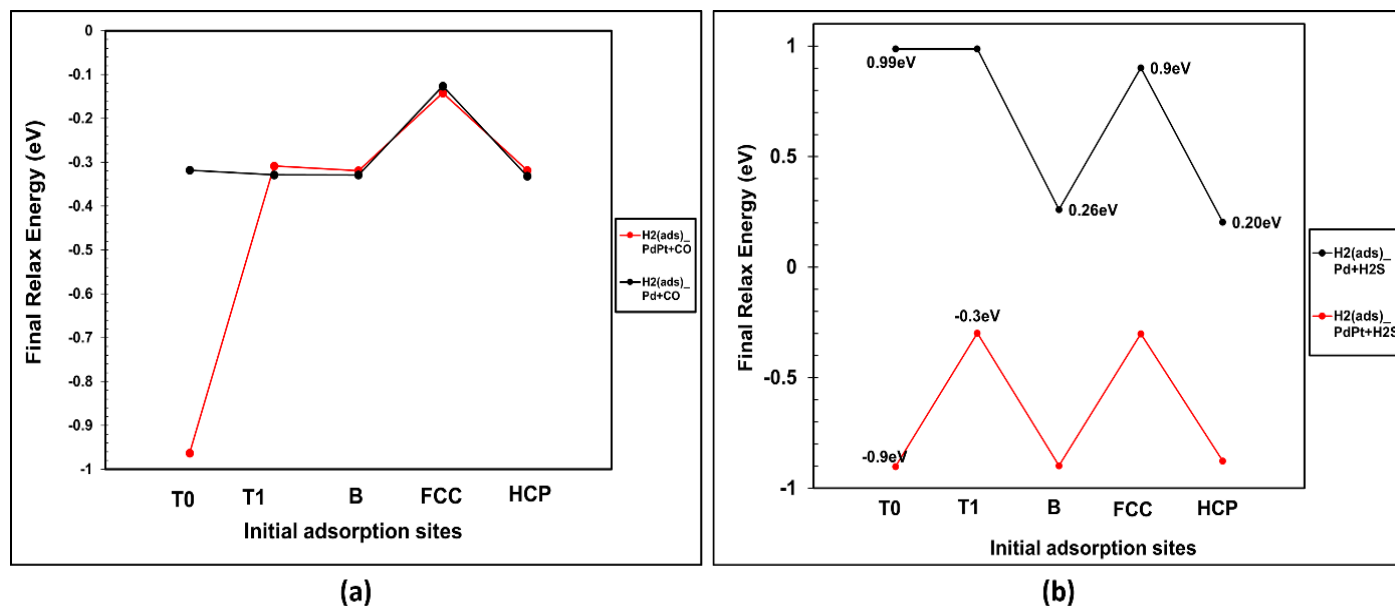


Figure 42. Comparison between the  $H_2$  adsorption energy on Pd and PdPt in the presence of (a) CO and (b)  $H_2S$

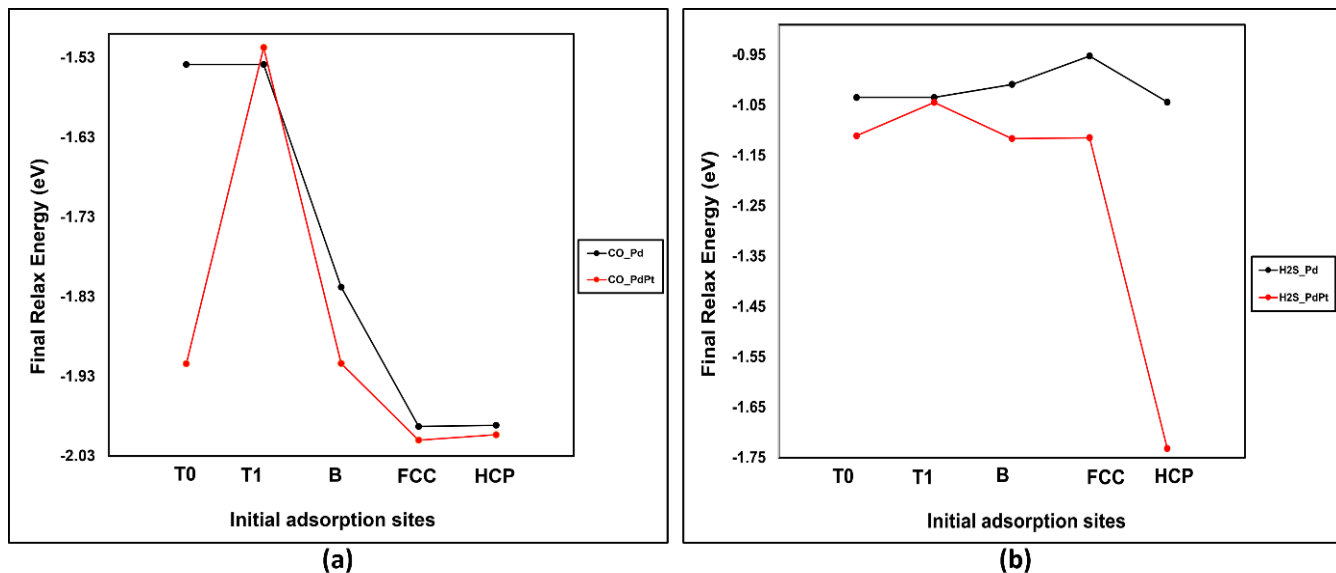


Figure 43. Comparison between (a) CO and (b) H<sub>2</sub>S adsorption energy on Pd and PdPt

## 5.9 Delta Analysis of H<sub>2</sub> adsorption in the presence of poisoning gases

Table 6 presents the summary of our findings, pointing out the differences between the energetic processes on bare Pd and the PdPt alloy surface. The magnitude of the differences will give a clear image of how the doping impacts the membrane surface processes. Concerning bare Pd which is always the reference, the first and second columns are energies of H<sub>2</sub> adsorption with and without CO, and their delta(difference) is computed on the third column. Furthermore, the fourth and fifth columns hold energies at which H<sub>2</sub> adsorbed with and without pre-covered H<sub>2</sub>S and the last column contains their difference(delta). Similarly, all the above energies corresponding to those on PdPt were computed as well and displayed under the Pd-Pt section in the table. Taking account into the variations of these energies we can justify that:

- (a) H<sub>2</sub> molecular adsorption is greatly favored to dissociation on PdPt.
- (b) The effect of CO on H<sub>2</sub> adsorption is almost similar on the two surfaces(bare Pd and PdPt).
- (c) The effect of H<sub>2</sub>S on hydrogen adsorption is minimal on PdPt.
- (d) The CO delta is comparable while the H<sub>2</sub>S delta shows the PdPt has less H<sub>2</sub> adsorption effect compared

to bare Pd.

**Table 6. Difference between H<sub>2</sub> adsorption energy with and without CO and H<sub>2</sub>S on Pd-Pt in comparison to that on bare Pd surface.**

| Sites      | Bare Pd                                 |                                             |                                                 |                                                           |                                                   | Pd-Pt                                   |                                             |                                                 |                                                           |                                                   |
|------------|-----------------------------------------|---------------------------------------------|-------------------------------------------------|-----------------------------------------------------------|---------------------------------------------------|-----------------------------------------|---------------------------------------------|-------------------------------------------------|-----------------------------------------------------------|---------------------------------------------------|
|            | H <sub>2</sub> E <sub>ads</sub><br>(eV) | H <sub>2</sub> E <sub>ads</sub> +CO<br>(eV) | $\delta_{(H_2ads+CO)}$<br>-(H <sub>2</sub> ads) | H <sub>2</sub> E <sub>ads</sub> +H <sub>2</sub> S<br>(eV) | $\delta_{(H_2ads+H_2S)}$<br>-(H <sub>2</sub> ads) | H <sub>2</sub> E <sub>ads</sub><br>(eV) | H <sub>2</sub> E <sub>ads</sub> +CO<br>(eV) | $\delta_{(H_2ads+CO)}$<br>-(H <sub>2</sub> ads) | H <sub>2</sub> E <sub>ads</sub> +H <sub>2</sub> S<br>(eV) | $\delta_{(H_2ads+H_2S)}$<br>-(H <sub>2</sub> ads) |
| <b>T0</b>  | -                                       | -                                           | -                                               | -                                                         | -                                                 | <b>-0.96</b>                            | -0.963                                      | 0.001                                           | <b>-0.902</b>                                             | <b>0.062</b>                                      |
| <b>T1</b>  | <b>-0.33</b>                            | <b>-0.329</b>                               | <b>0.001</b>                                    | <b>0.987</b>                                              | <b>1.317</b>                                      | <b>-0.32</b>                            | <b>-0.309</b>                               | <b>0.012</b>                                    | <b>-0.298</b>                                             | <b>0.022</b>                                      |
| <b>B</b>   | <b>-0.34</b>                            | <b>-0.329</b>                               | <b>0.007</b>                                    | <b>0.260</b>                                              | <b>0.596</b>                                      | <b>-0.99</b>                            | <b>-0.319</b>                               | <b>0.674</b>                                    | <b>-0.898</b>                                             | <b>0.095</b>                                      |
| <b>FCC</b> | <b>-0.01</b>                            | <b>-0.126</b>                               | <b>0.132</b>                                    | <b>0.902</b>                                              | <b>0.895</b>                                      | <b>-0.13</b>                            | <b>-0.142</b>                               | <b>0.003</b>                                    | <b>-0.302</b>                                             | <b>0.163</b>                                      |
| <b>HCP</b> | <b>-0.33</b>                            | <b>-0.332</b>                               | <b>0.004</b>                                    | <b>0.204</b>                                              | <b>0.539</b>                                      | <b>-0.13</b>                            | <b>-0.318</b>                               | <b>0.181</b>                                    | <b>-0.877</b>                                             | <b>0.740</b>                                      |



# CHAPTER 6

## CONCLUSION AND RECOMMENDATION

### 6.1 Conclusion

We investigated the performance of the Pd and Pd doped with other platinum-group elements on H<sub>2</sub> surface processes for H<sub>2</sub> application. The Pd-doped surfaces adsorbed more H<sub>2</sub> molecules by minimizing the energy required for H<sub>2</sub> to bind to the surface. These surfaces further dissociate those adsorbed molecules into their atoms. The dissociated atoms relaxed mostly in the hollow sites on the surfaces. H<sub>2</sub> adsorption and dissociation are the first two processes on metals and are desirable. Therefore, for most H<sub>2</sub> applications, especially H<sub>2</sub> purification and separation through Pd membrane and H<sub>2</sub> fuel cell with Pd electrodes, doping Pd surface will enhance the catalytic properties of the Pd used and hence improve the yield. Specifically, for H<sub>2</sub> separation and purification applications, doping the surface of bare palladium with few atoms of platinum will greatly resist the CO effect on the palladium-based membrane surface and burst the H<sub>2</sub> adsorption to the dissociative adsorption even in the presence of CO and H<sub>2</sub>S which are known to be the most poisonous gases to the hydrogen surface processes on Pd-based membranes.

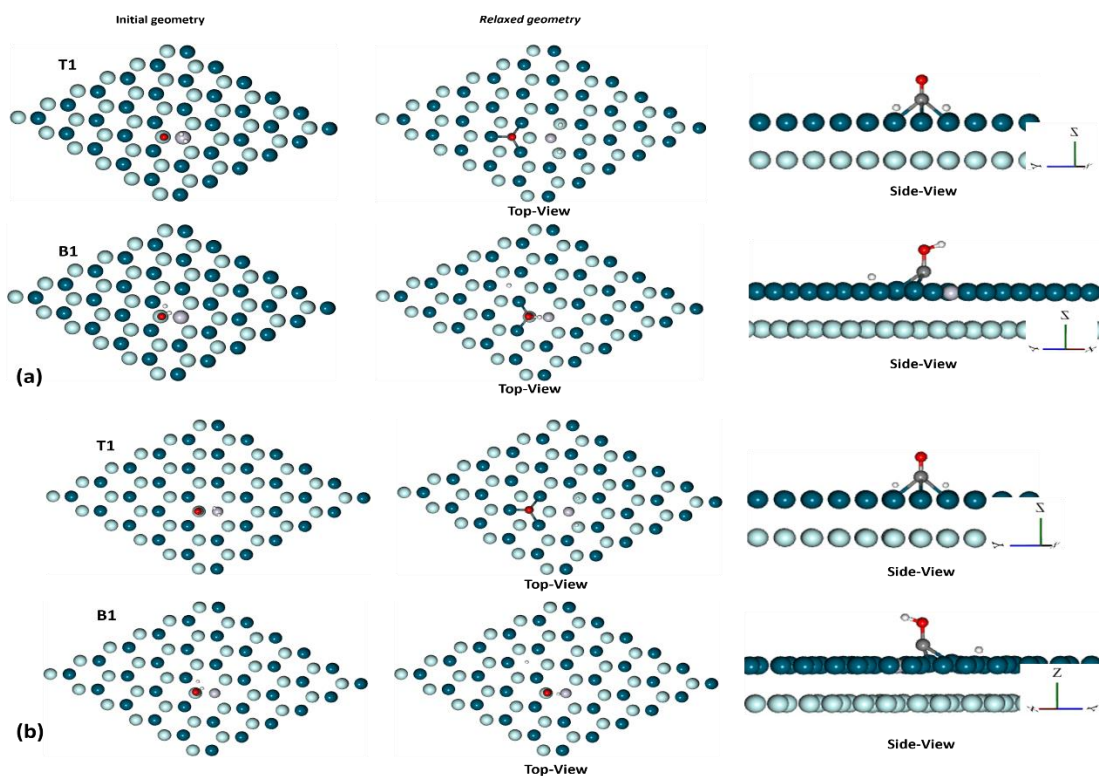
### 6.2 Future Recommendations

The research objectives of this study were accomplished with much effort. Still, there's always space for development. As a result, the following recommendations for expanding the work are provided:

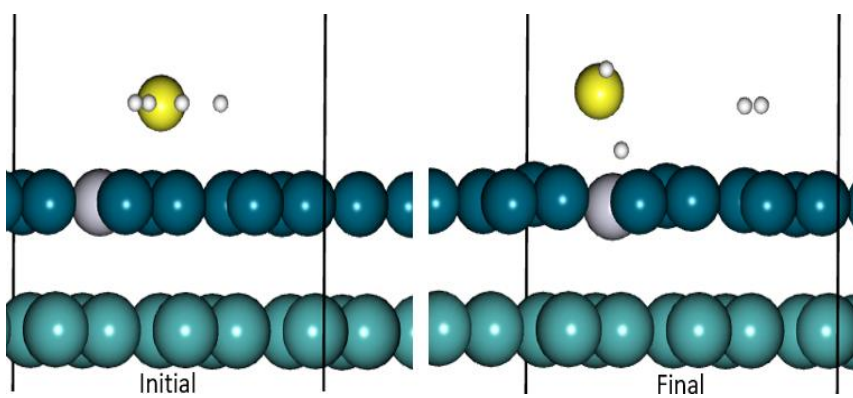
- Exploring the hydrogen permeation through the doped Pd-alloy membrane.
- Investigate the permeation of hydrogen on **binary** Pd-alloy with other metallic materials.

- Investigate **ternary** doped Pd-alloy on hydrogen adsorption, dissociation, and permeation instead of using binary alloys of Pd-membrane.
- More poisoning gases can be investigated such as CO<sub>2</sub> and CH<sub>4</sub>.

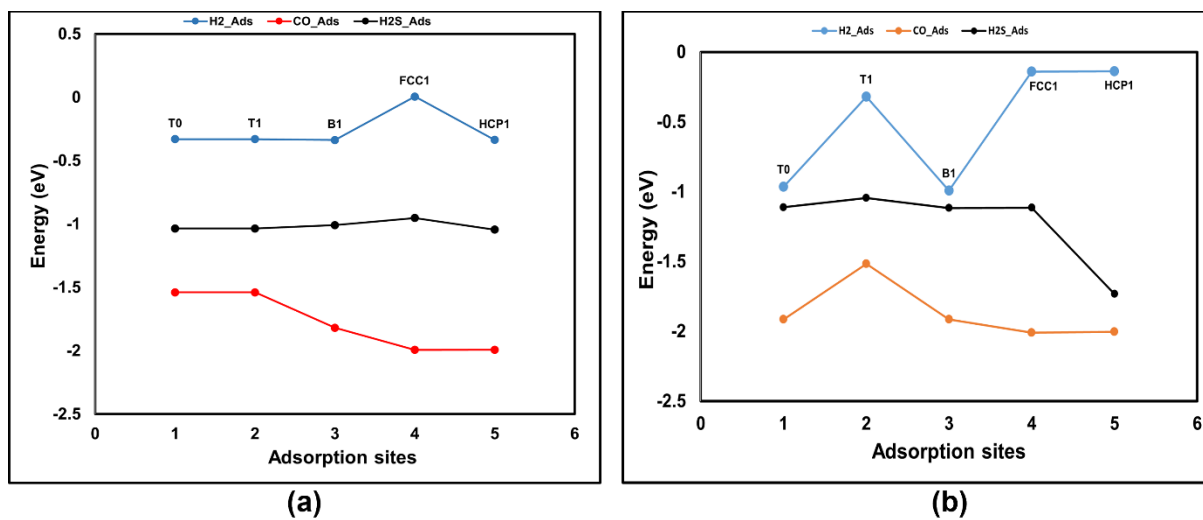
# APPENDIX



SI.Figure 44. CO poisoning on H<sub>2</sub> adsorption and dissociation



SI.Figure 45. Initial and relaxed state of H<sub>2</sub>S dissociation on Pd-Pt surface



SI.Figure 46. Plots of adsorption energy of H2, H2S and CO on the (a) bare Pd and (b) Pd-Pt surface



# REFERENCES

1. Singh V. FUNDAMENTALS AND USE OF HYDROGEN AS A FUEL Optimal operation of run-off river small hydro power plants View project. .
2. HYDROGEN STRATEGY Enabling A Low-Carbon Economy. .
3. Chapter I : HYDROGEN FUNDAMENTALS. .
4. ncert. Unit-9. .
5. Parra D, Valverde L, Pino FJ, Patel MK. A review on the role, cost and value of hydrogen energy systems for deep decarbonisation. *Renewable and Sustainable Energy Reviews* 101 2019 279–294.
6. Zhang K, Way JD. Palladium-copper membranes for hydrogen separation. *Sep Purif Technol* 2017; 186: 39–44.
7. Hydrogen: Separating hype from reality. .
8. Al-Mufachi NA, Rees N V., Steinberger-Wilkens R. Hydrogen selective membranes: A review of palladium-based dense metal membranes. *Renewable and Sustainable Energy Reviews* 47 2015 540–551.
9. Aditiya HB, Aziz M. Prospect of hydrogen energy in Asia-Pacific: A perspective review on techno-socio-economy nexus. *International Journal of Hydrogen Energy* 46 2021 35027–35056.
10. Bossel U, Eliasson B. Energy Hydrogen Economy. .
11. pidjoe. The Future of Hydrogen. .
12. Jokar SM, Farokhnia A, Tavakolian M *et al.* The recent areas of applicability of palladium based membrane technologies for hydrogen production from methane and natural gas: A review. *International Journal of Hydrogen Energy* 48 2023 6451–6476.
13. Menezes MW, Simmons DR, Winberg S, Baranwal R, Hoffman P, Genatowski SL. U.S. Department of Energy Hydrogen Program Plan. .
14. Arratibel Plazaola A, Pacheco Tanaka DA, Van Sint Annaland M, Gallucci F. Recent Advances in Pd-Based Membranes for Membrane Reactors. *Molecules* (Basel, Switzerland) 22 2017.
15. Conde JJ, Maroño M, Sánchez-Hervás JM. Pd-Based Membranes for Hydrogen Separation: Review of Alloying Elements and Their Influence on Membrane Properties. *Separation and Purification Reviews* 46 2017 152–177.
16. NATIONAL BUREAU OF STANDARDS-963-A. .
17. Ku AY, Kocs EA, Afzal S *et al.* Opportunities for the materials research community to support the development of the H2 economy. *MRS Energy and Sustainability* 10 2023 158–173.
18. Grashoff GJ, Pilkington CE, Corti CW. The Purification of Hydrogen A REVIEW OF THE TECHNOLOGY EMPHASISING THE CURRENT STATUS OF PALLADIUM MEMBRANE DIFFUSION. .
19. Pyle WR. Hydrogen Purification Hydrogen space heating View project One-step solar water splitting View project. 1998.
20. Yuan M, Lee K, Van Campen DG, Liguori S, Toney MF, Wilcox J. Hydrogen Purification in Palladium-Based Membranes: An Operando X-ray Diffraction Study. *Ind Eng Chem Res* 2019; 58: 926–934.
21. Boon J, Pieterse JAZ, van Berkel FPF, van Delft YC, van Sint Annaland M. Hydrogen permeation through palladium membranes and inhibition by carbon monoxide, carbon dioxide, and steam. *J Memb Sci* 2015; 496: 344–358.
22. Sonwane CG, Wilcox J, Ma YH. Achieving optimum hydrogen permeability in PdAg and PdAu alloys. *Journal of Chemical Physics* 2006; 125.
23. Nicholson KM, Chandrasekhar N, Sholl DS. Powered by DFT: Screening methods that accelerate materials development for hydrogen in metals applications. *Acc Chem Res* 2014; 47: 3275–3283.
24. Gómez E del V., Amaya-Roncancio S, Avalor LB, Linares DH, Gimenez MC. DFT study of adsorption and diffusion of atomic hydrogen on metal surfaces. *Appl Surf Sci* 2017; 420: 1–8.
25. Hao Z, Wang Q, Chen P, Xie P, Wei Z, Zhao S. Establishment of descriptor for screening high-performance catalysts for hydrogen peroxide production through surface stress modulation induced by metal atom doping. *Appl Surf Sci* 2024; 646.
26. Hong S, Rahman TS. Adsorption and diffusion of hydrogen on Pd(211) and Pd(111): Results from first-principles electronic structure calculations. *Phys Rev B Condens Matter Mater Phys* 2007; 75.
27. Abuelyamen A, Ben-Mansour R, Habib MA *et al.* Poisonous effect of carbon bearing species on adsorption of hydrogen

- on Pd-membrane surfaces. *Int J Hydrogen Energy* 2023;
28. Chen J, Hu L, Tang T. Ab Initio Microkinetic Modelings of Molecular Reactions on Pd(100), Pd(110), and Pd(111) Surfaces: A CO<sub>2</sub>/CO Reduction Case Study. *Journal of Physical Chemistry C* 2022; 126: 7468–7481.
  29. Alfonso DR, Cugini A V., Sorescu DC. Adsorption and decomposition of H<sub>2</sub>S on Pd(1 1 1) surface: A first-principles study. *Catalysis Today*, 2005, 315–322.
  30. Rivera DJ, Muhich CL. Preventing H<sub>2</sub>S poisoning of dense Pd membranes for H<sub>2</sub> purification using an electric-field: An Ab initio study. *Surf Sci* 2023; 733.
  31. Hyman MP, Loveless BT, Medlin JW. A density functional theory study of H<sub>2</sub>S decomposition on the (1 1 1) surfaces of model Pd-alloys. *Surf Sci* 2007; 601: 5382–5393.
  32. Liu LC, Gong HR, Zhou SF, Gong X. Adsorption, diffusion, and permeation of hydrogen at PdCu surfaces. *J Memb Sci* 2019; 588.
  33. Easa J, Yan C, Schneider WF, O'Brien CP. CO and C<sub>3</sub>H<sub>6</sub> poisoning of hydrogen permeation across Pd<sub>77</sub>Ag<sub>23</sub> alloy membranes: A comparative study with pure palladium. *Chemical Engineering Journal* 2022; 430.
  34. Song D, Liu X, Shen X. Hydrogen diffusion on and into the hydrogen-covered Pd(1 0 0) surfaces from first-principles. *Chem Phys Lett* 2022; 794.
  35. Liang T, Kang H, Zhong W, Bian H, Zhao J. Impact of surface adsorbed gases on hydrogen diffusion into Pd(1 0 0) subsurface from first principles. *Appl Surf Sci* 2019; 473: 476–485.
  36. Hooshmand Z, Le D, Rahman TS. CO adsorption on Pd(111) at 0.5ML: A first principles study. *Surf Sci* 2017; 655: 7–11.
  37. Shahbaz M, Al-Ansari T, Aslam M *et al.* A state of the art review on biomass processing and conversion technologies to produce hydrogen and its recovery via membrane separation. *International Journal of Hydrogen Energy* 45 2020 15166–15195.
  38. Gabitto JF, Tsouris C. Sulfur Poisoning of Metal Membranes for Hydrogen Separation. 2009.
  39. Peters T, Caravella A. Pd-based membranes: Overview and perspectives. *Membranes* 9 2019.
  40. Younas M, Shafique S, Hafeez A, Javed F, Rehman F. An Overview of Hydrogen Production: Current Status, Potential, and Challenges. *Fuel* 316 2022.
  41. Ernst S, Deutsche Wissenschaftliche Gesellschaft für Erdöl E und Kohle. Preprints of the DGMK-Conference 'The future role of hydrogen in petrochemistry and energy supply'. German Society for Petroleum and Coal Science and Technology, 2010.
  42. Kalamaras CM, Efstathiou AM. Hydrogen Production Technologies: Current State and Future Developments. *Conference Papers in Energy* 2013; 2013: 1–9.
  43. Anderson JR, Boudart M, eds. *Catalysis*. Berlin, Heidelberg: Springer Berlin Heidelberg, 1984.
  44. Definition, mineralogy and deposits Definition and characteristics. 2009.
  45. Chen Y, Wang Y, Xu H, Xiong G. Efficient production of hydrogen from natural gas steam reforming in palladium membrane reactor. *Appl Catal B* 2008; 81: 283–294.
  46. Das JK, Das N, Bandyopadhyay S. Materials for energy and sustainability The Merck Index 15 th Edition Highly oriented improved SAPO 34 membrane on low cost support for hydrogen gas separation †. 2013, 4913–5180.
  47. Hinchliffe AB, Porter KE. A comparison of membrane separation and distillation. *Chemical Engineering Research and Design* 2000; 78: 255–268.
  48. Sjardin M, Damen KJ, Faaij APC. Techno-economic prospects of small-scale membrane reactors in a future hydrogen-fuelled transportation sector. *Energy* 2006; 31: 2523–2555.
  49. *Membrane Reactors for Hydrogen Production Processes*. Springer London, 2011.
  50. FIRST-PRINCIPLES STUDY OF PALLADIUM-BASED METAL ALLOYS AS HYDROGEN PURIFICATION MEMBRANES. 2009.
  51. Uemiyu S. State-of-the-art of supported metal membranes for gas separation. *Separation and Purification Methods* 1999; 28: 51–85.
  52. Løvvik OM, Peters TA, Bredesen R. First-principles calculations on sulfur interacting with ternary Pd-Ag-transition metal alloy membrane alloys. *J Memb Sci* 2014; 453: 525–531.
  53. Sholl DS, Steckel JA. *DENSITY FUNCTIONAL THEORY A Practical Introduction*. .
  54. Semidey-Flecha L, Ling C, Sholl DS. Detailed first-principles models of hydrogen permeation through PdCu-based

ternary alloys. *J Memb Sci* 2010; 362: 384–392.

55. Sholl DS, Steckel JA. DFT Calculations for Simple Solids. In: *Density Functional Theory*. John Wiley & Sons, Inc., 2009: 35–48.
56. Nicholson KM, Chandrasekhar N, Sholl DS. Powered by DFT: Screening methods that accelerate materials development for hydrogen in metals applications. *Acc Chem Res* 2014; 47: 3275–3283.
57. Kumar N, Chattaraj D, Ghosh P, Majumder C. Microscopic Insights into Hydrogen Permeation Through a Model PdCu Membrane from First-Principles Investigations. *Journal of Physical Chemistry C* 2018; 122: 12920–12933.
58. Sholl DS, Steckel JA. Calculating Rates of Chemical Processes Using Transition State Theory. In: *Density Functional Theory*. John Wiley & Sons, Inc., 2009: 131–161.
59. Arboleda NB, Kasai H, Diño WA, Nakanishi H. Potential energy of H<sub>2</sub> dissociation and adsorption on Pt(111) surface: First-principles calculation. *Japanese Journal of Applied Physics, Part 1: Regular Papers and Short Notes and Review Papers* 2007; 46: 4233–4237.
60. Ling C, Sholl DS. Using first-principles calculations to predict surface resistances to H<sub>2</sub> transport through metal alloy membranes. *J Memb Sci* 2007; 303: 162–172.
61. Sholl DS, Steckel JA. DFT Calculations for Surfaces of Solids. In: *Density Functional Theory*. John Wiley & Sons, Inc., 2009: 83–112.
62. Kang SG, Coulter KE, Gade SK, Way JD, Sholl DS. Identifying metal alloys with high hydrogen permeability using high throughput theory and experimental testing. *Journal of Physical Chemistry Letters* 2011; 2: 3040–3044.
63. Sholl DS, Steckel JA. *Density functional theory : a practical introduction*. Wiley, 2009.
64. Sholl DS, Steckel JA. Accuracy and Methods beyond ‘Standard’ Calculations. In: *Density Functional Theory*. John Wiley & Sons, Inc., 2009: 209–233.
65. Sholl DS, Steckel JA. What is Density Functional Theory? In: *Density Functional Theory*. John Wiley & Sons, Inc., 2009: 1–33.
66. Chen WH, Chen ZY, Lim S, Park YK, Show PL. Hydrogen permeation in a palladium membrane tube: Impacts of outlet and vacuum degree. *Int J Hydrogen Energy* 2022; 47: 40787–40802.
67. Sharma R, Sharma Y. Hydrogen permeance studies in ordered ternary Cu-Pd alloys. *Int J Hydrogen Energy* 2015; 40: 14885–14899.
68. Chen WH, Chen ZY, Lim S, Park YK, Show PL. Hydrogen permeation in a palladium membrane tube: Impacts of outlet and vacuum degree. *Int J Hydrogen Energy* 2022; 47: 40787–40802.
69. Setyawan W, Senor DJ. Influence of hydrogen isotopes on vacancy formation and antisite defect diffusion in palladium and vanadium metals. *Comput Mater Sci* 2021; 197.
70. Gough DO, Gilliland RL. 16. Parkinson, I. H. 1971.
71. Abir H, Sheintuch M. Modeling H<sub>2</sub> transport through a Pd or Pd/Ag membrane, and its inhibition by co-adsorbates, from first principles. *J Memb Sci* 2014; 466: 58–69.
72. Alkali A, Abdullahi K. A Comparison of the Inhibiting Effect of CO and CO<sub>2</sub> to Hydrogen Permeation and n-Value in Pd and Pd/Ag Membranes Prepared on Alumina Support. *Journal of Power and Energy Engineering* 2019; 07: 1–14.
73. Fonseca S, Maia G, Pinto LMC. Hydrogen adsorption in the presence of coadsorbed CO on Pd(111). *Electrochem commun* 2018; 93: 100–103.
74. Murmura MA, Sheintuch M. Permeance inhibition of Pd-based membranes by competitive adsorption of CO: Membrane size effects and first principles predictions. *Chemical Engineering Journal* 2018; 347: 301–312.
75. Rupprechter G, Morkel M, Freund HJ, Hirschl R. Sum frequency generation and density functional studies of CO-H interaction and hydrogen bulk dissolution on Pd(1 1 1). *Surf Sci* 2004; 554: 43–59.



# VITAE

|                                                                                                                                                                                                                                                                                                    |   |                                                  |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---|--------------------------------------------------|
| Name                                                                                                                                                                                                                                                                                               | : | Lawan Muhammad Adam                              |
| Nationality                                                                                                                                                                                                                                                                                        | : | Nigerian                                         |
| Date of Birth                                                                                                                                                                                                                                                                                      | : | 11/08/1992                                       |
| Email                                                                                                                                                                                                                                                                                              | : | lawanummati@gmail.com                            |
| Address                                                                                                                                                                                                                                                                                            | : | No. 56 Yan-Karfe Graceland Hanwa, Zaria-Nigeria. |
| Academic<br>Background                                                                                                                                                                                                                                                                             | : |                                                  |
|                                                                                                                                                                                                                                                                                                    |   |                                                  |
| ❖ Bachelor of Science in Physics, Federal University Dutse, Nigeria (November 2019)                                                                                                                                                                                                                |   |                                                  |
| ❖ Publication:                                                                                                                                                                                                                                                                                     |   |                                                  |
| <ul style="list-style-type: none"> <li>Tasiu Zangina, Mahmud Idris, <b>Lawan Muhammad Adam Ummati</b>, Alhassan Muazu, Ibrahim Saadu, Ibrahim Murtala Musa, “Atomic absorption spectroscopy analysis of heavy metals in water”, (2019), ISSN (online): 2616-1370</li> </ul>                        |   |                                                  |
| <ul style="list-style-type: none"> <li>Tasiu Zangina, <b>Lawan Muhammad Adam Ummati</b>, Mahmud Idris, Alhassan Muazu, Aminu Aliyu Safana, Ibrahim Saadu, “Material Analysis of Gross Alpha and Beta activity in Drinking Water and Untreated Sewage”, (2019), ISSN (Online): 2635-3490</li> </ul> |   |                                                  |
| <ul style="list-style-type: none"> <li><b>Lawan Muhammad Adam</b>, Abduljabar Sayoud, “Barrier-free Dissociation of Hydrogen on Perfect (111) Palladium-Platinum Group Doped Surfaces for Hydrogen Applications”. Submitted</li> </ul>                                                             |   |                                                  |
| <ul style="list-style-type: none"> <li><b>Lawan Muhammad Adam</b>, Abduljabar Sayoud, “Micro-kinetics of Hydrogen Separation on Pd-Pt Alloy Surface (DFT-Investigation)”</li> </ul>                                                                                                                |   |                                                  |

