

**HYDROGEN SEPARATION THROUGH A SOLID
Pd-BASED MEMBRANE (DFT STUDY)**

BY

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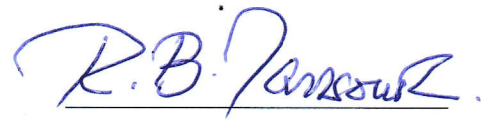
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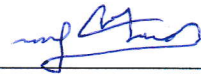
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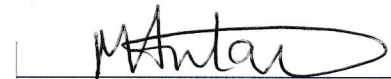


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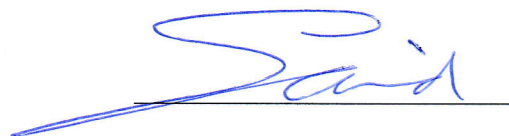


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Dedication

*This work is dedicated to the people who extended their help in the midst of problems
while doing this work |*

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LIST OF ABBREVIATIONS

DFT	:	Density Functional Theory
NEB	:	Nudge Elastic Band
D	:	Diffusion coefficient ($m^2.s^{-1}$)
E	:	Energy (J)
J	:	Diffusion flux ($mol.m^{-2}.s^{-1}$)
K, K₀	:	Permeance and its pre-exponential factor. ($mol.m^{-2}.s^{-1}.Pa^{-n}$)
M_{w,i}	:	Molecular weight of species i
$\dot{Q}$	:	Volume flow rate (L/min)
S	:	Solubility constant ($mol.m^{-3}.Pa^{-1}$)
S_m, S_i, S_E	:	Source term in mass, species and energy respectively.
T	:	Temperature (K)
R	:	Universal gas constant ($8.314 J.mol^{-1}.K^{-1}$)
R_i	:	The net rate of production of species i by chemical reaction
X_i	:	Local mole fraction of species i .
Y_i	:	Local mass fraction of species i .
c	:	Concentration ($mol.m^{-3}$)

h	:	Enthalpy (J/kg)
k_e	:	Effective thermal conductivity ($W.m^{-1}.K^{-1}$)
p	:	Pressure (Pa)
v	:	Velocity ($m.s^{-1}$)
x	:	Membrane thickness (m)
ρ	:	Density ($kg.m^{-3}$)
Φ	:	Permeability ($mol.m^{-1}.s^{-1}.Pa^{-n}$)
τ	:	The stress
μ	:	Viscosity ($kg.m^{-1}.s^{-1}$)
f	:	Feed
p	:	Permeate
sw	:	Sweep

|

ABSTRACT

Full Name : [Ahmed Salih Hamza Abuelyamen]

Thesis Title : [Hydrogen Separation through a Solid Pd-based Membrane (DFT Study)]

Major Field : [Mechanical Engineering]

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Hydrogen separation through a Palladium-based membrane is one of the most promising technology to produce pure H_2 . This work investigates numerically the hydrogen permeation processes (adsorption, dissociation, and diffusion) through a Pd-based membrane. A detailed reactions of hydrogen transition through Pd-based membrane is developed using density functional theory (DFT). The interaction between the hydrogen and the Pd-based membrane was investigated at atomic level (quantum level). This level of quantum investigation reveal information about how the membrane characteristic would influence the hydrogen permeation along with predicting parameters related to hydrogen flux through the membrane. Accordingly, the characteristics of Pd-based membrane such as binding energy and lattice parameter along with the binding energy of various gases (H_2 , CO_2 , CO , and CH_4) were estimated using DFT calculation and validated against data from the literature. After that, the adsorption process of hydrogen gas on bare Pd and dilute alloy of PdAu is evaluated at various sites on the membrane surface and various gas orientations. Also, the influence of poisoning gas and hydrogen coverage were examined. The highest adsorption energy for H_2 is estimated to be -0.343 eV and -0.347 eV on bare Pd and PdAu surfaces, respectively. These values were achieved at bare surface that have neither

poisoning gas nor pre-dissociated hydrogen atoms. Furthermore, the dissociation of H_2 to two hydrogen atoms on the Pd-based surface was also evaluated. It turns out the activation energy for this process is about -0.233 eV, while the reverse process of H_2 association on the other surface of the membrane requires -0.748 eV. In addition, the hydrogen diffusion process through pure Pd and PdAu bulk is studied. Alloying Pd membrane with Au atom reduces the diffusion energy barrier from 0.166 eV to 0.150 eV. Moreover, obtained results out of the DFT model could be integrated later to a computational fluid dynamic model to explore the applications of fuel reforming reactor and hydrogen purification in the continuum level. This can be achieved by using Arrhenius equation which depends on the activation energy. To reflect the potential usefulness of the proposed DFT work in the application of hydrogen purifications, a CFD model is developed based on experimental data from the literature. The impact of operational conditions along with the utilization of sweeping gas and applying vacuum pressure on the performance of hydrogen permeation are examined.

ملخص الرسالة

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عنوان الرسالة: فصل غاز الهيدروجين عن طريق غشاء مصنوع من مادة البلاديوم (دراسة عن طريق نظرية الدالة الوظيفية للكثافة)

التخصص: هندسة ميكانيكية

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تعد تقنية فصل غاز الهيدروجين من الغازات الاخرى بواسطة غشاء البلاديوم من اكثر التقنيات الواعدة لانتاج الهيدروجين. في هذا البحث تمت دراسة عملية انتقال غاز الهيدروجين من خلال غشاء البلاديوم بطريقة حساب عددية للعمليات الثلاثة: الامتزاز، والتفكيك، والتغلغل داخل الغشاء. تمت الدراسة من خلال استخدام نظرية الدالة الوظيفية للكثافة، حيث تمت دراسة التفاعل بين غاز الهيدروجين وغشاء البلاديوم على مستوى الذرة (المستوى الكمي). يكشف هذا النوع من التحقيق على المستوى الكمي كيف يمكن لخصائص غشاء البلاديوم ان تؤثر على عملية انتقال غاز الهيدروجين داخل الشغاء بالاضافة الى التنبؤ بمعدل تدفق غاز الهيدروجين داخل الغشاء مصنوع من مادة البلاديوم. بناءً على هذه الامكانيات التي يمكن التحصل عليها بواسطة نظرية الدالة الوظيفية للكثافة فقد تم حساب خصائص غشاء البلاديوم والمتمثلة في قوة الربط بين ذرات الغشاء و المسافة بين وحدة الذرات. كذلك تم حساب طول الترابط بين ذرات غاز ثاني اوكسيد الكربون، واول اوكسيد الكربون، وغاز الميثان وتمت مقارنتها مع المعلومات المتوفرة في المؤلفات العلمية المنشورة. بعد ذلك تم تقييم عملية الامتزاز لغاز الهيدروجين في عدة توجهات للغاز وعدة مناطق على سطح غشاء مصنوع فقط من البلاديوم واخر مصنوع من سبيكة البلاديوم والذهب. ايضاً تمت دراسة تأثير امتزاز عدد من الغازات على كيمية الطاقة المطلوبة لامتزاز غاز الهيدروجين. اقصى طاقة امتزاز تم تقديرها هي 0.343- الكترون فولت عند استخدام غشاء مصنوع من البلاديوم فقط، وتصل هذه القيمة الى 0.347- الكترون فولت عند استخدام سبيكة غشاء من البلاديوم والذهب. قيم طاقة الامتزاز السابقة تم التحصل عليها في ظل سطح غشائي نظيف لا يحتوي على اي من الغازات الاخرى او ذرات هيدروجين تم تفكيكها مسبقا على السطح الغشائي. علاوة على ذلك، تم تقييم التفاعل اللازم لتفكيك غاز الهيدروجين الى ذرتين على سطح غشاء البلاديوم. اتضح ان الطاقة المطلوبة لتنشيط هذا التفاعل

مقدارها 0.233- إلكترون فولت، بينما العملية العكسية لتجميع ذرتي هيدروجين لتكوين غاز الهيدروجين على سطح غشاء البلاديوم تتطلب طاقة تنشيطية مقدارها 0.748- إلكترون فولت. بالإضافة الى ذلك فقد تمت دراسة عملية تغلغل ذرات الهيدروجين خلال غشاء البلاديوم وغشاء سبيكة البلاديوم مع الذهب. النتائج المتحصل عليها تشير الى ان سبك غشاء البلاديوم بذرات الذهب يؤدي الى خفض حاجز الطاقة المطلوب لعملية التغلغل من 0.166- الى 0.150- إلكترون فولت مقارنةً بغشاء مصنوع من البلاديوم فقط. كذلك يمكن دمج النتائج المتحصل عليها من نموذج نظرية الدالة الوظيفية للكثافة مع نموذج تحسيب ومحاكاة حركة الموائع لدراسة فصل غاز الهيدروجين في مفاعلات اعادة تشكيل الوقود. لتحقيق هذا الدمج بين النموذجين الكمي والاستمراري يمكن استخدام معادلة "أرهينيوس" والتي تعتمد على الطاقة التنشيطية المتحصل عليها من نموذج نظرية الدالة الوظيفية للكثافة. لتبيين عملية الدمج بين النموذجين تم تطوير نموذج تحسيب ومحاكاة حركة الموائع بناءً على طاقات تنشيطية متحصل عليها من التجارب العلمية المنشورة، حيث تم اختبار عدد من العوامل التشغيلية على معدل انتقال غاز الهيدروجين خلال غشاء البلاديوم وكذلك تم اختبار عدة طرق لسحب الهيدروجين من غشاء البلاديوم.

CHAPTER 1

INTRODUCTION

Recently, efforts have been focused on reducing the reliance on fossil fuel due to its global issues. Using hydrogen gas is one of the solutions that have a higher potential to solve this issue. For instance, an efficiency of 40-55% can be achieved by combining electromotor along with hydrogen-powered fuel cells. This efficiency is higher than the efficiency of internal combustion engines (13-30%) [1].

1.1 Methods of Hydrogen Production

Hydrogen gas is produced through different methods. One of the easiest and simplest technique is by using alkaline water electrolysis. Nonetheless, major disadvantages are required to be overcome such as energy consumption, safety, durability and reliability [2]. Another method of hydrogen production is through steam reforming of methane. In this method, the hydrogen is extracted from different gaseous components. Various techniques such as cryogenic separation, pressure swing adsorption (PSA) and membranes could be utilized to separate hydrogen from the hot gas mixture. In the cryogenic distillation technique, the separation is performed based on the temperature of the boiling point. Since H_2 has the lowest boiling point ($-252.9\text{ }^{\circ}\text{C}$) it remains in a gaseous state while all other impurity gases condense to form a liquid phase. This technique is limited to large industrial scales and it separates hydrogen with a purity of 99% [3]. High

hydrogen purification can be obtained by using PSA (99 to 99.999%). In the PSA separation method, the gas mixture passes through an adsorber material which allows hydrogen to permeate through the adsorbent material while it adsorbs other impurity gases. This process is driven by the partial pressure of the impurity gases between the feeding gas and the exhaust. The impurity gases are then removed by swing the system pressure from the feeding pressure to the exhaust pressure value. The third technique of hydrogen separation is by using a hydrogen-selective membrane. This technique is driven also by pressure gradient where a high pressure feeding gas mixture is applied on one side of the membrane whilst the other side is maintained at low pressure. Only hydrogen can permit through the membrane. The membrane separation technique can work at a large range of operating temperature and pressure which may reach up to 900 °C [3]–[5].

1.2 Mechanism of Hydrogen Permeation through the Membrane

The hydrogen permeation mechanism through the membrane takes place in the multi-stage process under pressure difference driving force [6], [7]. The flow moves in the direction from the high to the low pressure. In the first step (i) the hydrogen molecules diffuse to the membrane surface, (ii) reversible dissociative adsorption on the palladium surface, (iii) the atomic hydrogen dissolute into the bulk material and then it diffuses through a bulk material. While the hydrogen atoms diffuse through the lattice of bulk material, the electrons interact with the metal lattice [8] until it reach the other side of the membrane where (iv) the hydrogen atoms associate again on the palladium surface. After that, (v) the molecular hydrogen desorbs from the surface and (vi) diffuses away from the membrane surface.

1.3 Motivation and Significance of the Study

The hydrogen permeation through Pd-based membrane is known to be an effective method to produce purify hydrogen gas at high yield. However, the hydrogen purification through this method depends on several factors, for instance; the species type in the gas mixture and their concentrations, Pd-alloy percentages of the membrane, operating temperature, system shape, etc. Investigating all these factors experimentally is extremely expensive due to enormously high number of experiments require to be conducted along with the difficulty of some experimental-setups when it comes to study various shapes of separation system. The computational fluid dynamic method can play critical role in facilitate this difficulties when it comes to optimize the hydrogen separation system shape or to do parametric study to understand the impact of each parameter. Nevertheless, to model the hydrogen permeation through Pd-base using computational fluid dynamics, some data related to the membrane characteristics should be extracted from experiments. The DFT calculation is capable in predicting membrane characteristics, so it can reduce the dependency of CFD model on the experiments to get the membrane features. Accordingly, the current work would be focusing on the DFT work to predict the membrane characteristics that might help the CFD model or other continuum-level model to simulate the hydrogen permeation through Pd-base membrane. Also, the DFT model can help in understanding the process of hydrogen permeation through the membrane, and hence, altering the parameters which influence this process for higher hydrogen flux.

1.4 Research Objectives

The overall objective of this work is to develop a DFT model of hydrogen permeation through a pure Pd and Pd₉₅Au₅ for the purpose of hydrogen separation and purification.

Accordingly, it can be divided to specific objectives as following:

- Develop a CFD model based on data from the literature to investigate the impact of operating parameters on hydrogen purification process and reflect the usefulness of DFT model on extracting some of parameters required for the CFD model.
- Carry out a series of calculation of density functional theory (DFT) on pure Pd-surface (100) to identify the hydrogen adsorption energy and energy barriers during the dissociative-adsorption and diffusion processes, and also identify their dependence on hydrogen coverage.
- Study the impact of poisoning gases on the adsorption energy of hydrogen molecule on Pd-membrane.
- Investigate the influence of Pd-alloying (Pd₉₅%Au₅%) on the hydrogen adsorption and dissociation process at surface (100), in addition to its impact on hydrogen diffusion through bulk material.

CHAPTER 2

LITERATURE REVIEW

2.1 Pd-membrane Types

There are various types of the hydrogen-selective membrane (dense polymer, dense ceramic, dense metallic, porous carbon, etc. [9]–[12]). Among them, the Pd-based dense metal membrane has a relatively high hydrogen permeability and it does not have a tendency to form a stable oxide layer under ambient conditions like other dense membranes such as vanadium (V), niobium (Nb) and tantalum (Ta). High yield of hydrogen can be obtained at low operational cost by merging hydrogen generation reactor and hydrogen-selective membrane at the same unit [13]. If a palladium membrane is applied in the membrane reactor, highly pure hydrogen will be achieved. Nonetheless, some limitations might be encountered for pure palladium membranes. Pure palladium is expensive because it is a precious metal with a limited supply. Also, the pure Pd is vulnerable to the surface poisoning by gases like H_2S , CO_2 and CO which are present in the atmosphere [14], [15]. These impurities reduce the available site numbers on the surface of the catalytic, and hence it affects the dissociative and adsorption processes of the hydrogen on the membrane surface. Furthermore, hydrogen embrittlement occurs due to the phase transformation of the palladium from α to β phase at temperature below 300 C. The α phase has small lattice (3.89 Å) compared to the β phase (4.02 Å) [16]. So, during several cycles of operation, the β phase grows and it induces strain in the system which causes membrane embrittlement. This kind of phase transformation can be limited by alloying palladium with other metals

[17]. Alloying Pd with other elements such as copper, yttrium or silver results in remarkable enhancements in mechanical durability, hydrogen permeability and in some cases resistance to contamination by Sulphur-containing compounds [18]–[20].

2.2 Experimental Works on H₂ Permeation through Pd-based Membrane

Many studies have been performed regarding hydrogen separation and purification by means of Pd-based membranes. Zhao et al. examined the influence of a contaminated mixture of H₂/N₂ with H₂S (7-35ppm) on the separation of hydrogen using Pd-Cu membrane. Their results indicate that at the higher temperature the sulfur inhabitation of the membrane becomes weaker while higher H₂ recovery makes it stronger due to the high concentration of contaminant H₂S [21]. Furthermore, they increase the hydrogen permeation rates by adding Ag and reducing the Cu amount in the membrane [22]. The activation energy for H₂ permeation showed a reverse relation with the Pd-Cu-Ag lattice constant. Also, they indicated the importance of reducing the support mass transfer resistance in the situation where sweep gas is used as it could contribute to 40% of hydrogen transfer-resistant at high pressure [23]. Nayeboossadri et al. [24] investigated the hydrogen separation from a natural gas mixture using Pd, PdCu₅₃ and PdAg₂₄ membranes. Among these membranes, only PdAg₂₄ is capable to separate H₂ at concentration drops to 15% while the others work only up to hydrogen concentration of 25% at 400 °C and 5 bar differential pressure. The membrane permeability decreases with the time due to the partial oxidization of the membrane surface and the potential defects as confirmed by SEM and elementary analysis in the study of Iulianelli et al. [7]. The hydrogen separation via Pd-alloy membrane along with the high pressure feed gas or vacuum pump at the permeance

side was introduced in many types of research [25]–[27]. Chen et al. [27] showed that applying vacuum pressure can improve the H₂ permeation rate through the Pd membrane by 30% if pure hydrogen gas is used, while the percentage improvement reaches up to 140% for a gas mixture of 90%H₂ and 10%CO. This indicates that vacuum is an effective countermeasure to reduce the concentration polarization which diminishes also with temperature [28].

2.3 CFD works of H₂ permeation through membranes

The utilization of membrane reactor in fuel reforming has been receiving increased attention in the industry for hydrogen production because it enhances the fuel conversion. Many numerical studies have conducted analyzing this kind of hydrogen production [29]–[35]. Ghasemzadeh et al [36] compared the performance of Pd-Ag membrane reactor for two methanol-reforming methods: autothermal reforming and steam reforming. Their CFD results showed that about 11% improvement could be achieved by using methanol autothermal reforming. Benguerba et al. [37] used computational fluid dynamics to simulate the hydrogen separation from a gas mixture of H₂/N₂ through a membrane of nickel/ α -alumina. The study was conducted for a temperature greater than 400 C with different pressure values. Also, they compared the performance of two different porous membranes, Ni-Al₂O₃ and Pd-Ag membranes, at different operation temperatures and pressures [38]. It was found that rising the operating pressure deteriorates the hydrogen selectivity of Ni-Al₂O₃ membrane and makes it permeable to other gas, thus, it is required to operate it at lower pressure. Ghasemzadeh et al [39] showed that, for higher pressure and lower reaction temperature, Pd-Ag membrane reactor has better ethanol conversion than traditional reactor where about 98% of hydrogen conversion and 37% of hydrogen

recovery is achieved at 2 atm and 350 C. Another study also emphasized that high methane conversion can be achieved by continuously removing hydrogen from the reactive steam by using hydrogen selective material [40]. Furthermore, they indicated that the reactor performance is kinetically limited by the hydrogen separation when the temperature is above 500 C, while it is limited by the reforming reaction when the temperature is below this value. Coroneo et al [41], [42] used CFD to study the operating conditions as well as geometrical configurations, by adding baffles, on the performance of Pd-Ag membrane reactor.

2.4 H₂ Permeation Characteristic through Density Functional Theory

The group of David Sholl is one of the leaders in the DFT studies related to hydrogen permeation through Pd-membrane. Their earliest studies start by investigating the bulk diffusion of H-atom in pure Pd and CuPd52at.% [43]. They are interested in the diffusion pathways and the activation energy for hydrogen travelling between different binding sites. They concluded that the activation energy for O-O pathway is around 0.39 eV. However, this value might be overestimated as they fixed the atom's position of Pd-membrane at the location which gives minimum energy at octahedral site while relaxing the H-atom, then computed energy of interstitial H atom at straight line points between O-O sites. Fixing the Pd-position might increase the energy barrier when the H-atoms reach the bridge site, so it is expected at that position the at least the Pd-atoms close to the H-atom move slightly to minimize the system energy. They modified the previous method further step of fixing the H-atom and relaxing Pd atoms at each step of the pathway [44]. The O-T straight-line pathway has an activation energy of 0.16 eV at hydrogen concentration of 3.7 at.% while the reverse pathway has only 0.06 eV. They extended their work further to include Pd(111)

surface [45]. Where they examined the adsorption of S atom at Pd and Pd-alloy with coverage of 0.25 (super-cell of 2x2x2). The hollow site of fcc gives the most negative binding energy (4.85 eV). This value increases slightly to 4.95 eV when the Sulphur coverage reduced from 0.25 to 0.11 indicating that Sulphur is highly binds to the surface at low coverage. Also, alloying Pd reduces the Sulphur binding energy compared to pure Pd. In addition, they characterize diffusion of carbon on Pd and Pd-alloy bulk membrane [46]. They highlight that the stable site for C is the octahedral site and the minimum diffusion pathway on pure Pd is O-T-O with an activation energy of 1.33 eV. They proposed a screening method for H permeation on 78 Pd-binary intermetallics using DFT and KMC. The DFT is used to determine the diffusion activation barrier which utilized as a filter to narrow down membrane with favorable permeability range. Thus, material with $E_{act} > 0.6$ eV results in very low diffusivity values that would render the material as unsuitable for membrane applications. They reported that minimum activation barrier for pure Pd is 0.21 eV. The same group also investigated the adsorption of various species on the Pd surface of (111). For instance, they examine the structure of monocarboxylic acid anion (formate species) on Pd(111) with a system of 3x3 super-cell [47]. They concluded that the formate get adsorbed at O-C-O plane perpendicular to Pd-surface with C-O bond of 1.26 Å and O-C-O angle of 130°, C-H distance 1.1, Pd-O distance of 2.13 Å. Another investigation of the same group reveal that, at low coverage, the value of surface binding for various amino acids (glycine, alanine, norvaline, valine, proline and serine) on Pd(111) is constant regardless of the adsorbates, except for cysteine [48]. More investigations of the same group on Pd-alloys related to hydrogen permeations can be found on [49], [50], [59], [51]–[58].

The hydrogen permeation through Pd membrane attracts also other researchers in the field of DFT simulation. Hadas and Moshe [60] utilized the DFT and NEB to study the H diffusion on Pd and Pd₃Ag starting from surface (111). The activation energies for the pathway on pure Pd are ranged from (0.22-0.63 eV), while for Pd₃Ag the proposed two pathways varies according to the Ag-alloying atoms on the membrane. The resulting activation energy for the first pathway ranged between (0.0-0.72 eV), while the second one has values between (0.15-0.97). Filhol et al [61] performed a DFT calculation for Ethylene co-adsorption with H-atoms on Pd surface (110) at B- and T-sites (with 3 horizontal-orientations at T-site). There were three different unit cells have been used: (4×2), (2×2), and c(2×2) with one ethylene molecule inside and different numbers of H atoms. Thus they studied a coverage range 0.125-0.5 monolayer (ML). Axel G. studied the adsorption of hydrogen molecule on a clean surface from other gases, but it was pre-covered with H-atoms [62]. They used molecular dynamic aiming to find the dynamical factors that determining the adsorption probability on the pre-covered surface of Pd(100). They concluded that, at the same coverage value, the arrangement of H-atoms on the surface has an impact on the dissociative adsorption process. Where the sticking probability can be increased and promotes the H₂ dissociation through even distribution of hydrogen atoms on the surface.

Wikle et al [63] investigated the impact of sulfur pre-covered of pure Pd(100) on the adsorption of H₂ on hollow and bridge sites. The system has a size of 2x2 super-cell with three layers thickness. When they located the S-atoms on H-site, with $\theta_s=0.25$ while changing θ_H between 0.25 and 0.75, the adsorption energy reduced to a range of 0.33-0.51 eV/H compared to the value at clean Pd surface which reach to 0.61 eV/H at the hollow

site. Also, they concluded that only at high coverage of sulfur the hydrogen get blocked where the Eads reach 0.02 at $\theta_s=0.5$ and $\theta_H=0.5$. Suggested that presence of S may affect the dissociation pathways, and hence the energy barriers, but they did not showed any DFT calculation regarding this topic.

Further study on Pd membrane poisoning impact was conducted by Fonseca et al on Pd(111) [64] with a 2x2 super-cell and three layers thickness under a coverage value of 0.25. They are interested only on the electronic effects of CO gas on adsorption of H-atoms without taking into consideration the H₂ dissociative process. They relied the decrease of H adsorption energy due to the presence of CO (from -0.66 to -0.55 eV on hollow fcc site with coverage of 0.25) to the modification of the palladium d-band when it interacts with CO. Also, they reported some adsorption energy values of H-atom and CO on bare Pd at various sites (top, bridge, hollow fcc, and hollow hcp).

The dissociation of H₂S on 2x2 super-cell of five layers of Pd(100) was investigated by Jiang et al [65] at a coverage value of 0.25. Among the three adsorption sites of top, bridge or hollow-sites, the most stable value for H₂S was obtained at the top site (-0.83 eV/H) while for HS, S, and H the most stable values (-3.55, -5.56, and -2.79 eV) which occurs at the hollow sites. They put the H₂S plane parallel to the substrate surface without investigating various orientation which may have more stable adsorption energy. According to the site and orientation that they examined, the energy barriers of the first and second dissociation steps (i.e H₂S → HS + H, and HS → H + S) are 0.37 and 0.34 eV, respectively.

Further study on hydrogen sulfide was carried out by Liu et al [66] on 2x2 super cell of Pd(111) of 4 layers slab. Similar to the surface 100, the H₂S is also most favorable to be adsorbed at top site ($E_{ads} = -0.79$ eV), while S and H prefer the hollow-fcc site ($E_{ads} = -5.17$ and -2.92 eV, respectively). In contrast to the case of Pd(100), HS locates at the bridge side ($E_{ads} = -3.0$ eV) of Pd(111) instead of the hollow site as in the case of Pd(100) ($E_{ads} = -3.55$ eV). Comparing the work adsorption energy of H₂S, HS, S and H on Pd(100) and Pd(111), the former has more negative adsorption energy for all the species except the H-atom. However, this comparison may not be accurate as the two studies have different coverage value. Furthermore, there is no sign in their investigation that they have examined various orientation of H₂S adsorption on top-site, where the plane of H₂S is not parallel to the surface substrate as in the case of Pd(100).

Namba et al [67] clarify the impact of alloying only the top layer of Pd surface of (110) on the penetration barrier energy of H atom to the sub-layers of the membrane. Their system consists of 2x3x6 super-cell. Where they showed by adding 0.5 ML of Au on the top layer of Pd(110), the penetration energy barriers reduce to a value of 0.39 eV as the H-atom diffuses from the octahedral site on the top-surface (O1) to the second octahedral site on the sub-layer (O2). This happened because the Au destabilizes the H atom at the O1 where it has less binding energy compared to bare Pd-surface. Also, the AuPd surface leads to higher binding energy of H at O2 compared to bare Pd surface. This indicates that the Au-alloying has an impact up to the third sub-layer, while the binding energy at O3 showed similar value for both bare Pd and AuPd surface.

Another study on subsurface diffusion barriers was conducted by Namba et al. [68] on Pd(100) nanocubes coated with copper(II) 1,3,5-benzenetricarboxylate (HKUST-1), which

is a type of metal–organic framework. Doing so reduces the hydrogen interface diffusion barrier because of destabilization of H adsorption at the surface caused by the change of electronic structure of the Pd surface. The activation barrier between O-site on the surface to T-site on the subsurface just beneath HKUST-1 was reduced from 0.41 eV on bare Pd to two transient states with activation barriers of 0.20 and 0.23 eVs. Another H-diffusion pathway near the HKUST-1 showed a barrier of 0.28 eV indicating that HKUST-1 can improve the subsurface diffusion of hydrogen, however, the large size of HKUST-1 may block many adsorption sites of H₂, so more investigations are required.

Hong et al [69] compared the adsorption and diffusion of H atom on Pd(211) and Pd(111) at coverage of 0.25 ML. They reported that the hydrogen barrier for subsurface diffusion on Pd(211) is 0.33 eV which is slightly less than at Pd(111) by about 0.08 eV. Thus, an improvement of hydrogen subsurface adsorption may be expected for Pd(211) as compared to that on Pd (111). The most preferred adsorption site on Pd(211) is the threefold hollow site ($E_{\text{ads}} = -0.52$ eV) which is more energetic than $E_{\text{ads}} = -0.59$ eV on Pd(111) at hollow fcc site. They indicated that lowering E_{ads} may also be accompanied by lowering the diffusion barrier which may reflect an increase in reactivity of the stepped surface.

Hooshmand et al [70] studied the adsorption of CO on Pd(111) surface for a system with super-cell of (4x2) (i.e. coverage = 0.5 ML). They tried to locate all possible combinations of adsorption sites for CO on Pd(111). However, their study was only limited the CO adsorption at an axis oriented vertically to the Pd surface. They concluded that the CO molecules prefer to adsorb either only on the hollow (FCC or HCP) sites or only at sites which are located in-between the bridge and the FCC sites. The Bridge-Bridge, Bridge-TOP, FCC-Bridge and HCP-Bridge structures are found to relax to FCC-HCP. While the

FCC-FCC combination relaxed into a new configuration they called it FCC-Bridge-Hybrid which has small transition barrier to FCC-HCP (0.0013 eV) while the reverse transition has large barrier (0.12 eV) indicating that FCC-HCP is the most configuration for 0.5 ML of CO on Pd(111).

Shen et al [71] investigated the H-atom diffusion on both the surface and subsurface for different metal catalysts including Pd(100) and Pd(111). Four layers slab are selected for the study with 2x2 super cell. As expected, surface hydrogen transition between two hollow sites on the surface (pathways of H-B-H or H-T-H) is most likely occurs through bridge site (100:H-B-H, or 111:FCC-B-HCP) as it has less barrier compared to the case of hydrogen passing through the top site (100:H-T-H, or 111: HCP-T-HCP). Regarding the H subsurface diffusion, they concluded that Pd has the lowest diffusion barrier (0.806 and 0.780 for 100 and 111 surfaces, respectively) while the Pt has the highest barriers energy (1.740 and 1.285 eV for 100 and 111 surfaces, respectively).

Liu et al. [72] studied the adsorption, dissociation and diffusion of hydrogen molecule on Pd₅₀Cu₅₀ membrane. They conclude that the adsorption of molecular hydrogen is less stable at the surface of FCC (111) than at BCC (110) surface. However, the adsorption energy is much smaller in the case of FCC (111). Also, they found that the diffusivity of the hydrogen on PdCu-bulk is much greater than the value on PdCu-surface due to smaller activation energy on the bulk. This conclusion is tested to the surface of FCC (111) and BCC (110). Another study is conducted to investigate the adsorption of hydrogen on a various facet of PdCu-membrane with different environmental values [73]. It is found that the coverage of the hydrogen is affected by the temperature and the pressure of the hydrogen. Furthermore, when the hydrogen coverage is taken into account the facet has various favourable

adsorption sites, while when the coverage of the hydrogen is ignored the bridge site becomes the most favoured adsorption site for (111) surface and the hollow sites show the most favoured adsorption sites for surfaces of (110), (100) and (112). The study of Kumar et al [16] showed that the H₂ permeation through the BCC structure of PdCu membrane is limited by the diffusion of H atoms to the first subsurface on the feeding side as well as the reassociations of the atoms again at the permeate side. More specifically, for thinner membranes (< 0.5 μm), the limitation comes from the formation of hydrogen on the permeate side while for thicker membranes the hydrogen permeation rate-limiting is due to either the bulk diffusion of the hydrogen or the formation of H₂. This transformation of hydrogen permeation from surface-process rate-limiting to bulk diffusion is affected by both thicknesses of the membrane and the temperature.

More membrane alloys, other than PdCu-membrane, are investigated also for their hydrogen permeation. Ling et al performed a many DFT calculation of hydrogen permeation on PdCuAg ternary alloys to generate contour maps for the hydrogen solubility, diffusivity and permeability as a function of Ag and Cu compositions. The results reveal that as the Ag concentration increased, the hydrogen solubility increased also while the diffusivity decreased. However, the net permeability of the hydrogen improved the thing that indicates the solubility plays a major role in this PdCuAg ternary alloy than the diffusivity [55]. Likewise, the effect of adding Ag to PdCu membrane on the adsorption and dissociation of hydrogen molecules is investigated by Liu et al [74]. It turns out that Ag increases the adsorption and the energy barriers of hydrogen diffusion on the PdCu surface, although it lowers the activation energy of recombinative desorption of H atoms on FCC (111) and BCC (110) surfaces of PdCu.

CHAPTER 3

BACKGROUND AND RESEARCH METHODOLOGY

3.1 Background Theory of DFT

In the density functional theory (DFT), a system that involve interaction of several-bodies is described through its particle density rather than wave-functions of these bodies. The theorem of Hohenberg-Kohn (HK) [75] is considered as basis for DFT. Where the system properties are taken to be functionals of ground state density only. By the help of Born-Oppenheimer (BO) approximation [76] and Kohn-Sham (KS) [77], the DFT calculation becomes available by means of so-called exchange-correlation (XC) potential. For a system involve nuclei and electrons, the time-independent Schrodinger equation and Hamiltonian equation can be written as:

$$H_{tot}\psi(\{\mathbf{R}_I\},\{\mathbf{r}_i\}) = E\psi(\{\mathbf{R}_I\},\{\mathbf{r}_i\}) \quad (3.1)$$

$$H_{tot} = -\sum_I \frac{\hbar}{2M_I} \nabla_{\mathbf{R}_I}^2 - \sum_i \frac{\hbar}{2m_e} \nabla_{\mathbf{r}_i}^2 + \frac{1}{2} \sum_{\substack{I,J \\ I \neq J}} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{I,i} \frac{Z_I e^2}{|\mathbf{R}_I - \mathbf{r}_i|} \quad (3.2)$$

where $\psi(\{\mathbf{R}_I\},\{\mathbf{r}_i\})$ is the total wave-function of the system and E its total energy. The first two term of left hand side of the equation 3.2 represents 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. In fact, if Schrodinger equation is solved, then every information about the system would be known, nevertheless it is impossible to do so practically. Considering that nuclei have much

heavyweight 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 considered to be fixed when the electrons are moving. This leads to two separate Schrodinger equations:

$$H_e \phi(\{r_i\}; \{R_I\}) = V(\{R_I\}) \phi(\{r_i\}; \{R_I\}) \quad (3.3)$$

$$\left[-\sum_I \frac{\hbar}{2M_I} \nabla_{R_I}^2 + V(\{R_I\}) \right] \Theta(\{R_I\}) = E' \Theta(\{R_I\}) \quad (3.4)$$

$$H_e = -\sum_i \frac{\hbar}{2m_e} \nabla_{r_i}^2 + \frac{1}{2} \sum_{\substack{I,J \\ I \neq J}} \frac{Z_I Z_J e^2}{|R_I - R_J|} + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \frac{e^2}{|r_i - r_j|} - \sum_{I,i} \frac{Z_I e^2}{|R_I - r_i|} \quad (3.5)$$

The movement of the nuclei can be obtained by solving equation 3.4 after obtaining eigenvalues of the energy $V(\{R_I\})$ from equation 3.3. This approach is considered as starting point for the DFT, where the nuclei are considered to form an external potential field in which electrons are moving. Khon and Sham (KS) replaced the interacting system by an auxiliary non-interacting system whose particle number density is same as the interacting system. Accordingly, the auxiliary Hamiltonian reduced to equation 3.6. For a system of N non-interacting electrons, the Schrodinger equations of N one-electrons (**equation 3.7**) 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 3.8. Then the KS one-particle potential can be considered as sum of external potential, Hartree potential, and an exchange potential as expressed in 1st, 2nd, and 3rd terms of equation 3.9, respectively. Since the KS potential and the energy density are connected, these equations

must be solved in self-consistence manner. After that various quantities can be calculated such as electron density of states, total energy, band structure, forces, etc.

$$\hat{H}_{KS} = \left[-\frac{1}{2} \nabla^2 + V_{KS}(r) \right] \quad (3.6)$$

$$\hat{H}_{KS} \psi_i(r) = \varepsilon_i \psi_i(r) \quad (3.7)$$

$$n(r) = \sum_{i=1}^N |\psi_i(r)|^2 \quad (3.8)$$

$$V_{KS}(r) = V_{ext}(r) + \frac{\delta E_H[n(r)]}{\delta n(r)} + \frac{\delta E_{XC}[n(r)]}{\delta n(r)} \quad (3.9)$$

3.2 Calculation procedure of DFT

In this work, a numerical model is developed using DFT calculation to study the hydrogen separation through a solid Pd-membrane. The characteristic features of the hydrogen 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 Pd-based membrane would be studied. The steps required to complete the work can be summarized as following:

1. 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 got the volume that has minimum equilibrium energy (as showed in Figure 1) which will be used for the study of hydrogen interaction with the membrane, so the hydrogen will diffuse through this volume.

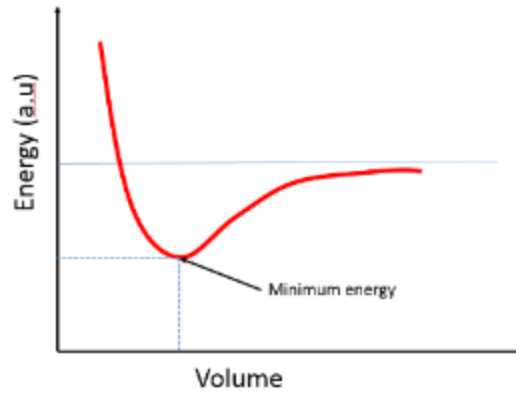


Figure 1. Energy-volume curve

2. Construct the actual surface of the membrane:

The FCC unit volume will be cut the low index surfaces (100) to study the adsorption and dissociation of hydrogen on this surfaces (Figure 2). The atoms on the surface will be relaxed so its location will change to minimize the energy. Accordingly, the surface energy can be obtained as:

$$E_{\text{surface}} = E_{\text{relaxed-surface}} - E_{\text{bulk}} \quad (3.1)$$

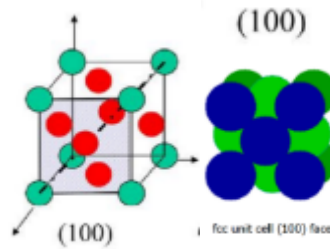


Figure 2. Crystal planes at low index surfaces

3. Determine the sites for gas adsorption and dissociation:

At the top layer of the membrane surface, the hydrogen molecule may site at different sites; at the top of Pd-atom, on the bridge between two Pd-atoms or at

the hollow (i.e. on the center between Pd-atoms). Figure 3 shows the three available sites of surface (100). The site type, at which the hydrogen will sit, affects the adsorption process because there are different energy for each site. So the site with the low state of energy will be the one that H₂ would prefer to be adsorbed at it.

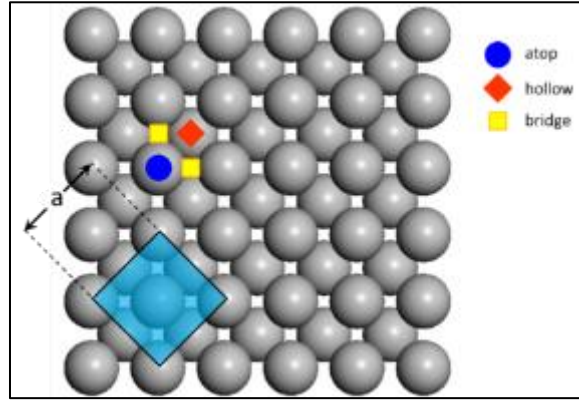


Figure 3. Sites available for FCC structure.

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

$$E_{ads} = E_{slab+nX} - E_{slab} - yE_{H_2} \quad (3.2)$$

where E_{system} is the total energy of the simulated cell which contain the membrane slab and gases, and $E_{system-X}$ is total energy of the system without the gas of interest which we want to get its adsorption energy, E_X is the energy of gas alone, and y is number of molecules. Thus, X can be H₂/CO₂/CO/CH₄ or H-atom. In the case of X represents H-atom, the value of y is equivalent to half of total number of H-atoms, and also in that case E_X is multiplied by y . To calculate E_{ads} of H₂ at co-adsorption with poisoning gases (CO₂/CO/CH₄) or at presence of various coverage of H-atoms that have dissociated from previous

steps, $E_{system-X}$ represents the energy of the all system including the slab and any molecule of H-atoms except H₂ molecule.

4. Specify the adsorption orientation

The hydrogen molecule may stick to membrane surface at different orientations, hence, the orientation that makes minimum energy of the state will be the preferred orientation. Accordingly, this step represents how the hydrogen molecule will sit on the available sites of Pd-surface (Figure 4).

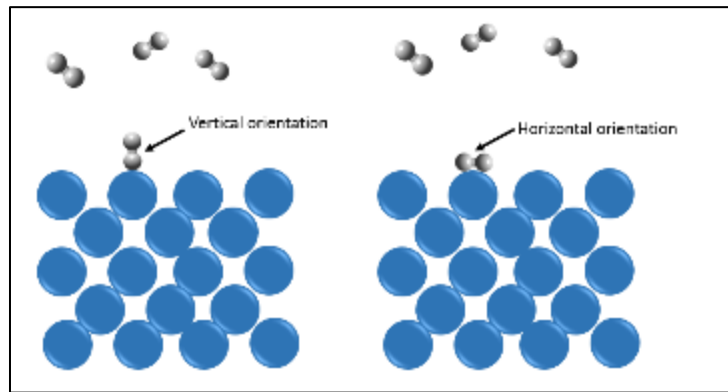


Figure 4. The orientation of gas molecule adsorption at the membrane surface.

5. Determine the lowest adsorption energy for the different combination of the steps 3 and 4 (orientation and sites) to define where the H₂ will sit on the membrane surface.

6. 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 have also favorable sites similar to the case of the H_2 molecule. This location is the final state of the dissociation process.

7. Finding the barrier of H_2 dissociation to hydrogen atoms:

After the hydrogen molecule get adsorbed at the surface, the hydrogen atoms may take different paths to reach a minimum state of the energy on the membrane surface (i.e. final state of dissociation which obtained from step 6). This could happen at 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 the nudged elastic band (NEB).

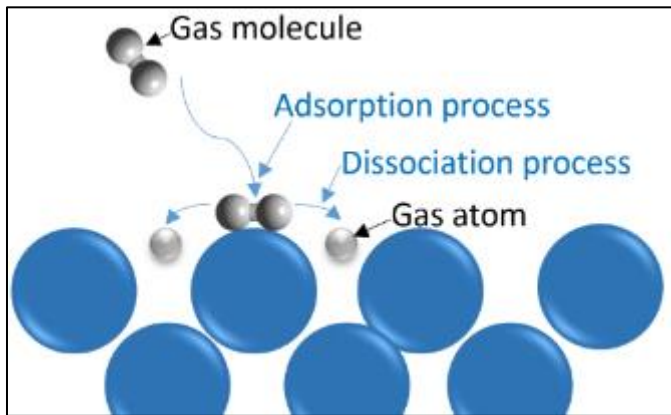


Figure 5. Dissociation of the gas molecule to gas atoms.

8. Obtaining the hydrogen diffusion path:

Once the dissociation process complete, the hydrogen 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 NEB method. This method is used to obtain saddle points and minimum energy pathways between two know states (reaction and product

states). It conducted through optimizing several of intermediate reaction coordinates to their lowest possible energy. It conducted via 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.

3.3 DFT Parameter Optimizations

At the beginning, a vc-relax model is used to estimate the lattice constant. The vc-relax model bring the system to its ground state by allowing both cell size and atomic position to change. 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 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 repARATION 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 2nd order Birch equation of stat 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 obtain by taken the energy difference when the Pd-atoms are gathered together in the bulk and the state where the atoms are far away from each other so they are no longer interact with each other. The later state (i.e. the Pd-atoms

are far away from each other) is considered as reference state for the energy-volume curve.

3.3.1 Optimization of *ecutwfc* and *K-points*

The calculation of vc-relax model reveal 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 is examined. The total energy with respect to each *ecutwfc* is showed in Figure 6. The total energy stabilizes around (-18017.96 eV) after *ecutwfc* value of 200. The *K-points* is investigated for a range 2 to 14 where it was shown that the total energy stabilizes after *K-points* equal 6 at -18017.96 eV (Figure 7). Accordingly, *ecutwfc* and *K-points* of 200 and 6 are used to optimize the lattice constants. Lattice constants ranged between ± 10 percent of the initial value (3.937 Angstrom) is 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 depict in Figure 8, and hence it is considered as the lattice constant for the Pd (FCC). Furthermore, the fitting data of equation of stat indicates that the material has a bulk modulus of 169.375 GPa/atom.

Figure 8 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's, 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 the next cell's atom, so different cell length are examined until enough distance between Pd atoms that prevent any interaction between the periodic atoms. The results are summarized in Figure 9. At a distance

greater than 7.5 Angstrom the energy of Pd-atom fixed at -4500.556 eV and do not change which indicates that the Pd atoms are no longer interact with each other's. This value is for 1 Pd atom, so it multiplied by 4 in order 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 8 are shifted by the energy of the Pd bulk when the atoms are far away from each other's (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 1 summarize the results for this part of calculation. The lowest total energy of the Pd_{FCC} bulk (with 4 periodic atoms) is 3.935 eV/atom and it also represents the binding energy.

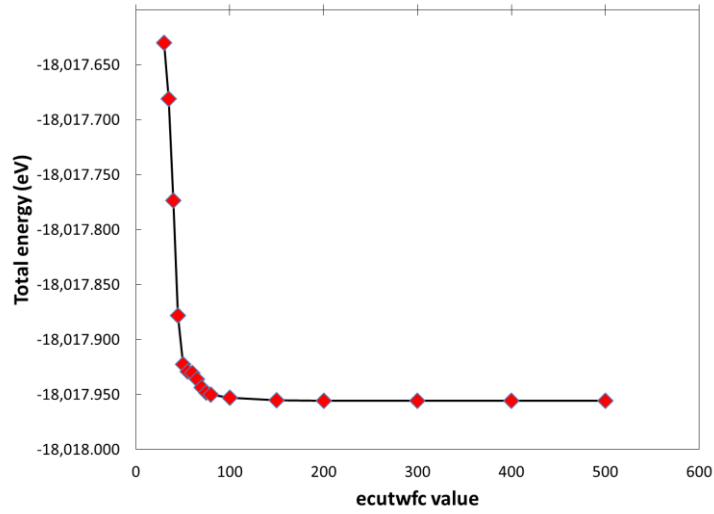


Figure 6. Convergence of total energy with respect to ecutwfc

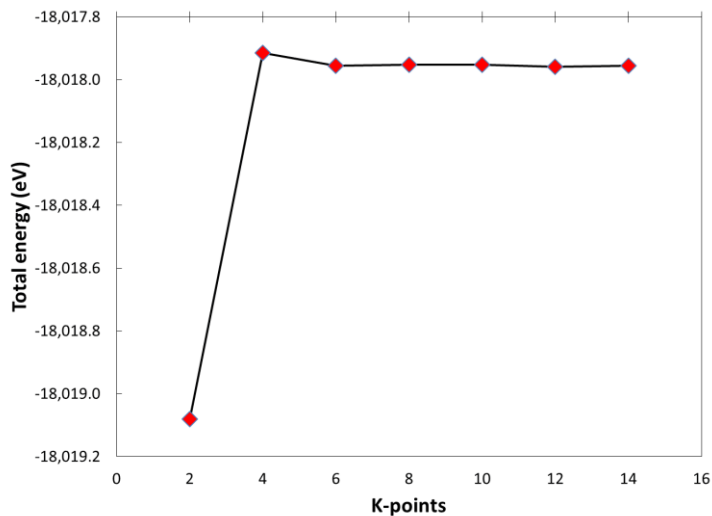


Figure 7. Convergence of total energy with respect to K-points.

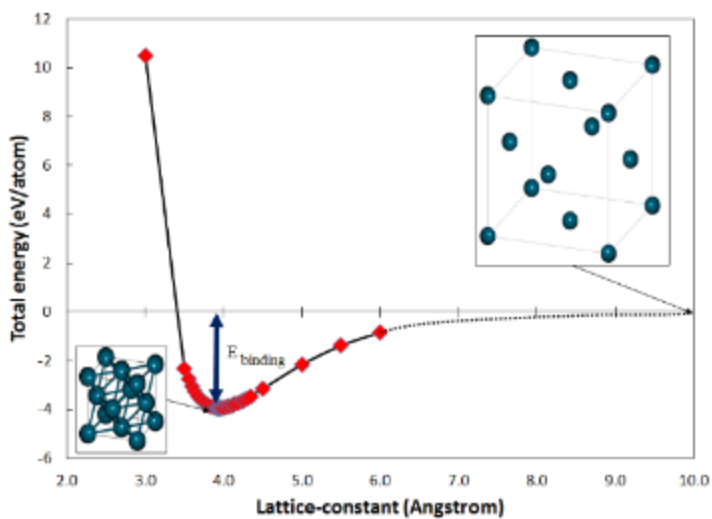


Figure 8. Change of total energy with the cell volume.

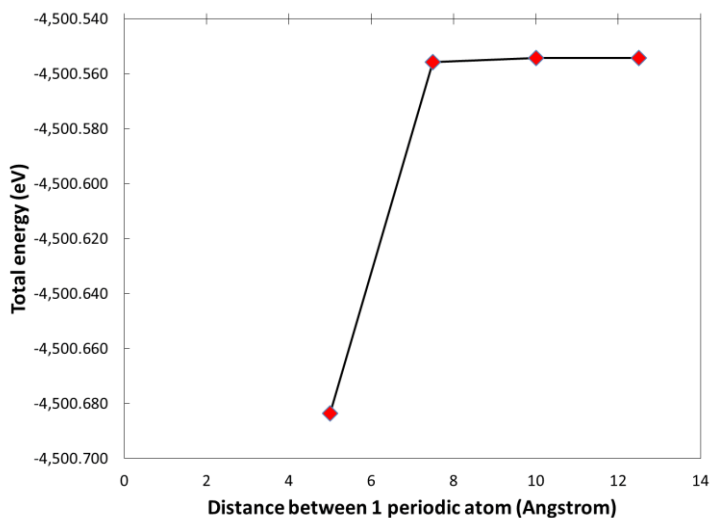


Figure 9. Interaction of 1 Pd atom due to periodic boundary condition at different distance apart each other's.

Table 1. Results summary of DFT calculation for Pd bulk

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

3.3.2 Selection of Pseudopotential file for Pd material

Different pseudo-potential files are downloaded from Quantum ESPRESSO website. For each pseudo-potential file, the *ecutwfc*, K-point, lattice-constant are optimized using SCF calculation. Additionally, the 2nd order Birch equation of state is used to obtain the equilibrium lattice constant and the bulk modulus. The binding energy is calculated by taking the difference in the energy between the state where the bulk is at the equilibrium lattice-constant (i.e. minimum energy) and that when the atoms are far away from each other.

The total energy becomes stable, for all cases, by using 6 and 200 for *Kpoint* and *ecutwfc* respectively. Figure 10 shows the Energy-Volume curve of bulk Pd material using different pseudopotential files. The lattice constant for each pseudo-potential file along with the bulk modulus and binding energy is listed in table 3. Since the binding energy and lattice

constant of Pd material are most critical properties for this study, the pseudopotential file will small error for these two parameters is selected (i.e. “Pd.pbe-n-kjpaw_psl.1.0.0.UPF”).

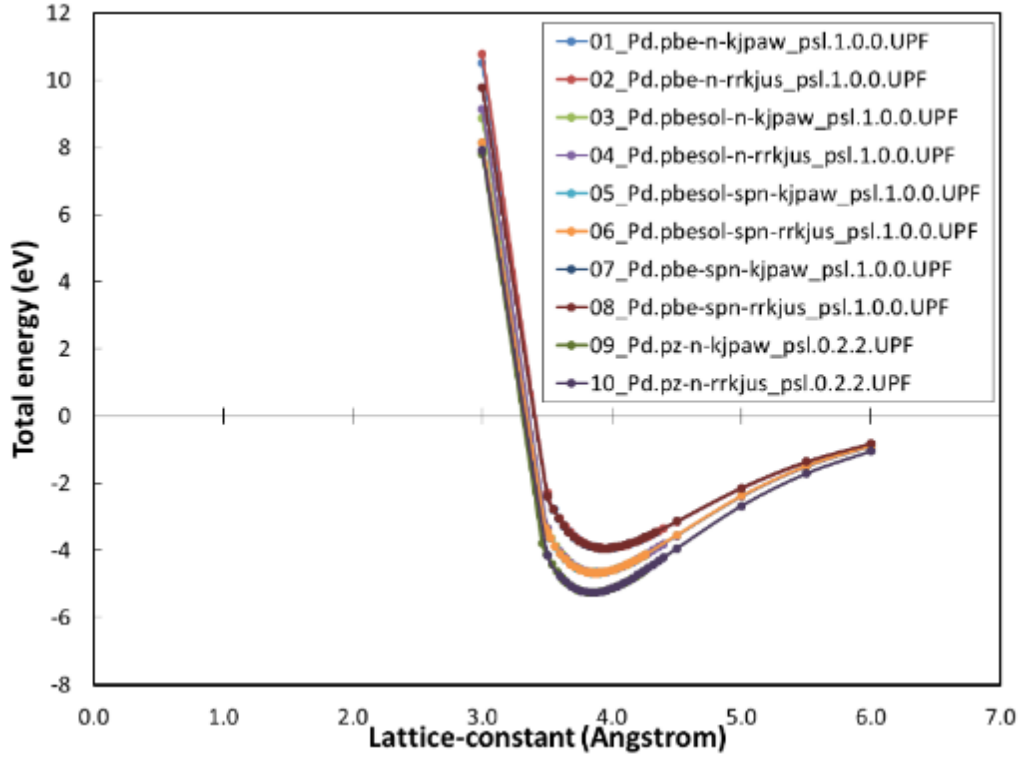


Figure 10. Total energy curve for different pseudopotential files.

Table 2. Comparison of lattice constant, bulk modulus, and binding energy of Pd material.

Pseudopotential	a ₀ (Å)	E _{bind} (eV/atom)	k ₀ (Gpa/atom)	Error (%)		
				a ₀	E _{bind}	k ₀
01_Pd.pbe-n-kjpaw_psl.1.0.0.UPF	3.948	3.935	169.375	1.89%	0.44%	-13.14%

02_Pd.pbe-n- rrkjus_psl.1.0.0.UPF	3.949	3.935	168.825	1.91%	0.43%	-13.42%
03_Pd.pbesol-n- kjpaw_psl.1.0.0.UPF	3.881	4.660	203.575	0.15%	18.93%	4.40%
04_Pd.pbesol-n- rrkjus_psl.1.0.0.UPF	3.882	4.659	204.525	0.18%	18.92%	4.88%
05_Pd.pbesol-spn- kjpaw_psl.1.0.0.UPF	3.872	4.670	203.550	-0.07%	19.20%	4.38%
06_Pd.pbesol-spn- rrkjus_psl.1.0.0.UPF	3.873	4.666	203.925	-0.05%	19.09%	4.58%
07_Pd.pbe-spn- kjpaw_psl.1.0.0.UPF	3.940	3.940	168.800	1.67%	0.55%	-13.44%
08_Pd.pbe-spn- rrkjus_psl.1.0.0.UPF	3.941	3.936	168.250	1.70%	0.46%	-13.72%
09_Pd.pz-n- kjpaw_psl.0.2.2.UPF	3.846	5.255	226.550	-0.76%	34.12%	16.18%
10_Pd.pz-n- rrkjus_psl.0.2.2.UPF	3.843	5.252	211.700	-0.82%	34.05%	8.56%
Experimental [78]	3.875	3.918	195.000			

3.4 Pd-surface Preparation

The aim of this part is to relax the atoms at Pd surface (100) and get the surface energy and final positions of the atoms. Once the bulk Pd (FCC) is prepared, it cut at the plane surfaces (100). Accordingly, atoms at the surface become only bonded from one side. Thus, those atoms at the surface of Pd-membrane move to reduce their energies. 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 relax model is used for the calculation as it allows the atoms to move, and also, it solve for the electron structure. 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 is applied so the results of both bulk and surface calculation are comparable. The unit cell representing surface 100 is tetragonal with dimensions of 3.948x3.948x45.923 Angstrom and it has 10 Pd atoms.

The resulting geometry out of the plane cut is represented in Figure 11. Five layers of atoms, in z-direction, is considered for the surface relaxation as shown in figure 19b. The two bottom layers are considered to be fixed in order to represent the bulk atoms, while the three top layers of atoms are set free to relax in a new positions. A large vacuum area is introduced above the top layer of atoms to insure that there is no any 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 12. Comparing 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_{FCC} has a binding energy of -3.935 eV/atom. This value

becomes less negative when bulk material is cut through the plane 100 (-3.631 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 100 has 10 atoms, so the total energy of that unit cell is divided by 10. Then, the binding energy (eV/atom) is obtained by taking the difference between the normalized cell total energy and the energy of normalized unit cell that have atoms apart enough from each other to prevent any interaction between them.

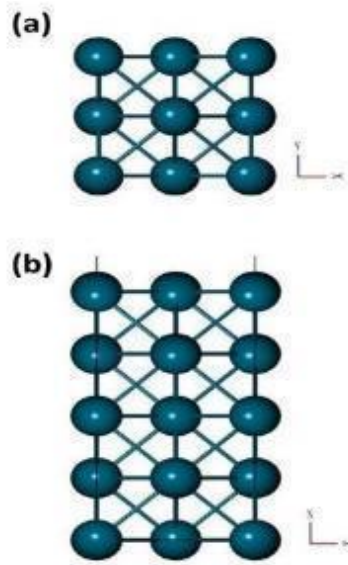


Figure 11. Atoms arrangement for surfaces (100). a) Top view and b) front view.

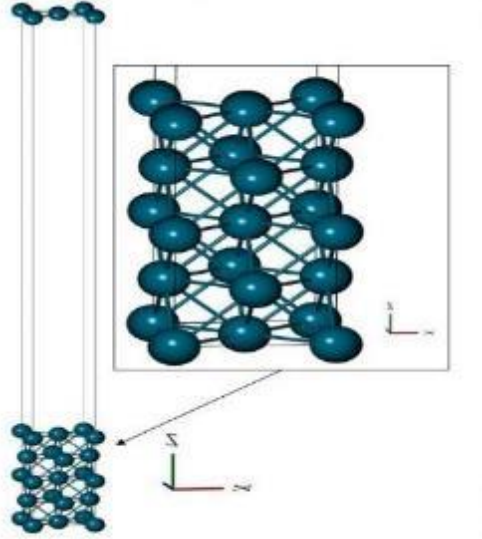


Figure 12. Unit cell used for surface relaxation.

3.5 CFD model

In this part, a study of hydrogen separation through Pd-based membrane is conducted for the system described in Figure 13 using CFD model based on experimental data extracted from published work. The system consists of two zones separated by a thin layer of Pd-membrane. The top zone called “feeding zone”. The gas mixture of different species (H_2 , N_2 , CO_2 and CO) enters this zone from the left (i.e. feed-inlet) and leaves it from the other side “feed-outlet”. As the gas species move over the top layer of the Pd-membrane, only hydrogen molecules could pass through the membrane to the bottom zone (which is referred to as permeation-zone). The permeation-zone is closed from one side and it is opened from the other side (permeation-outlet) where the permeated H_2 leaves the computational domain. When the sweeping gas method is applied, the left wall in the permeation zone is replaced to be the sweeping gas inlet.

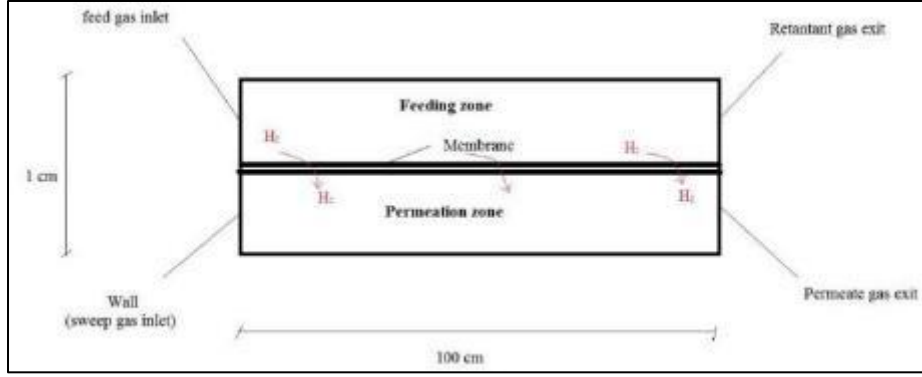


Figure 13. Schematic of the hydrogen separation system.

The flow condition is considered to be laminar steady flow since the Reynolds number is small. Hence, the conservations equations that control this type of flow are continuity, momentum and species transport equations which are applied at the feeding/permeation zones. These equations are represented as follows:

$$\text{Continuity: } \nabla \cdot (\rho \vec{v}) = S_m \quad (3.3)$$

$$\text{Momentum equation: } \nabla \cdot (\rho \vec{v} \vec{v}) = -\nabla p + \nabla \cdot \bar{\bar{\tau}} + \rho \vec{g} + \vec{F} \quad (3.4)$$

$$\text{Species transport equation: } \nabla \cdot (\rho \vec{v} Y_i) = -\nabla \cdot \vec{J}_i + R_i + S_i \quad (3.5)$$

$$\text{Energy equation: } \nabla \cdot (\vec{v} (\rho E + P)) = \nabla \cdot \left(k_{eff} \nabla T - \sum_j h_j \vec{J}_j + \bar{\bar{\tau}}_{eff} \cdot \vec{v} \right) + S_E \quad (3.6)$$

The permeability can be obtained from the experimental permeation data by plotting the total amount of gas that permeated through the membrane in ‘mole’ with the time in ‘s’ (i.e. Q vs t).

$$Q = JAt \square \frac{A\Phi}{\Delta x} (p_f^n - p_p^n) t = AK (p_f^n - p_p^n) t \quad (3.7)$$

$$\frac{\partial Q}{\partial t} = AK (p_f^n - p_p^n) \quad \text{where, } K = \frac{\Phi}{\Delta x}$$

According to the Arrhenius equation, the permeance can be represented as follows:

$$K = K_o \exp\left(\frac{-E_a}{RT}\right) \rightarrow \ln K = \ln K_o - \frac{E_a}{RT} \quad (3.8)$$

where K is the permeance, K_o is a pre-exponential factor that doesn't depend on the temperature (T), E_a is activation energy, and R is universal gas constant. This equation is correct when n does not depend on temperature [79].

Once the mesh size test was conducted successfully, the numerical model has examined against experimental data from the literature. Figure 14 compares the results of the current simulation with the experimental data of Arratibel [80]. Pd-based with 5 wt% Ag is used in the experimental setup. It has a layer thickness of 1 μm . It is clear from the figure that there is good matching between the CFD results and the experimental data. The activation energy used in this work is 5.54 kJ/mole which is slightly greater than the reported value (5.11 kJ/mole) in [80] and it is close to the reported values in [81] (5.47 - 7.81 kJ/mol) for Ag content of (5.7 – 9 wt%) with membrane thickness of (0.46 – 1.29 μm). In fact, the percentage of silver content and the membrane thickness affect the magnitude of activation energy as well as the membrane preparation method [82]. Table 3 shows the variation of the activation energy for different Pd-based membranes used for the purpose of hydrogen separation.

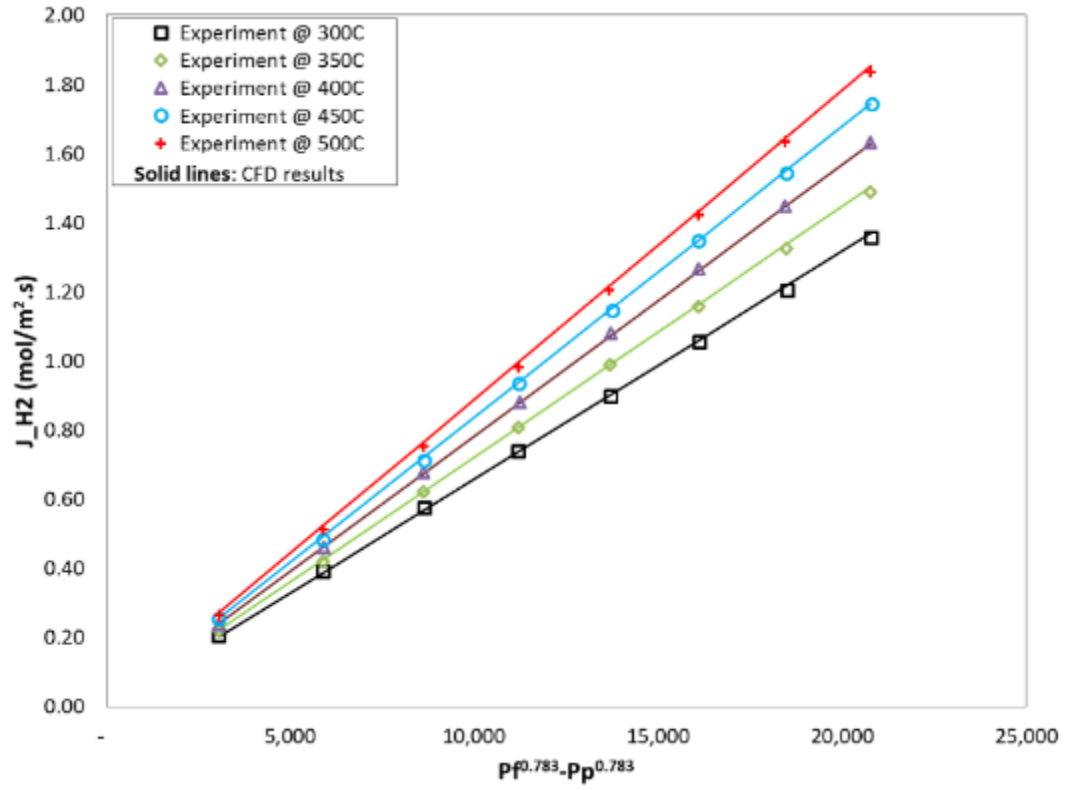


Figure 14. CFD model validation against experimental data of [80].

Table 3. Variation of activation energy due to different parameters

Selective layer-support	ΔP (kPa)	T (°C)	Thickness (μm)	$E_{activation}$ ($kJmol^{-1}$)	n	Ref.
Pd ₇₇ Ag ₂₃ -YSZ-Al ₂ O ₃ (HF)	100	450	0.4	8.76	1.09	[83]
Pd ₉₁ Ag ₉ -Al ₂ O ₃	100	400	0.46	5.47	0.81	[81]
Pd ₉₁ Ag ₉ -Al ₂ O ₃	100	400	0.78	6.6	0.67	[81]
Pd ₉₅ Ag ₅ -Al ₂ O ₃	100	400	1	5.11	0.783	[80]
Pd _{92.8} Ag _{7.2} -Al ₂ O ₃	100	400	1.17	7.81	0.62	[81]

Pd ₇₇ Ag ₂₃ -YSZ- Al ₂ O ₃ (HF)	100	450	1.2	13.64	1.09	[83]
Pd _{94.3} Ag _{5.7} /Al ₂ O ₃	100	400	1.29	7.67	0.64	[84]
Pd ₉₀ Ag ₁₀ /Al ₂ O ₃	400	400	2.1	5.77	0.5	[85]
Pd ₈₀ Ag ₂₀ /Al ₂ O ₃	400	400	2.2	2.93	0.5	[85]

CHAPTER 4

RESULTS OF CFD MODELING

A CFD model is developed to reveal how computational numerical modeling can be used to study the permeation of hydrogen gas. Different parameters are investigated such as sweeping method, pressurized and vacuum methods, a gas mixture of H₂/N₂, H₂/CO₂, or H₂/CO with different hydrogen percentage, feeding flow rate, and gas temperature. The impacts of all these parameters on the hydrogen flux on Pd-membrane are discussed in detail. The boundary conditions for each study are summarized in Table 4. The concept of the current CFD model can also be applied for other membrane types such as polymer membrane, ion transport membrane, mixed matrix membranes, or any other membrane type. However, one should carefully select the right model for the term J_i (diffusion flux of species i) in the species transport equation (Eq. 3.5) because each membrane type would have its own model of how the gas permeate through that membrane. So, the constant values in equation Eq. 3.7 and 3.8 should be modified if different membrane type is used. The DFT study can help in expecting these constants without needs for the experiment.

Table 4. Summary of boundary conditions used in each study section.

Effect of sweeping method	
Feed pressure	1.5×10^5 - 5×10^5 Pa
Permeate pressure	1×10^5 Pa
Temperature	300 °C
Feeding flow rate	14000 L/min

Sweeping flow rate	1000 L/min
Effect of flow rates	
Feeding pressure	1.5×10^5 & 5×10^5 Pa
Permeate pressure	1×10^5 Pa
Temperature	300 & 500 °C
Feeding flow rate	1 – 20000 L/min
Sweeping flow rate	1 – 1000 L/min
Pressurized method vs. vacuum method	
Feeding pressure	1×10^5 , 1.5×10^5 and 2×10^5 Pa
Permeate pressure	0×10^5 , 0.5×10^5 and 1×10^5 Pa
Temperature	300 °C
Feeding flow rate	14000 L/min
Sweeping flow rate	0 and 1000 L/min
Effect of different species flow	
Species	H ₂ /N ₂ , H ₂ /CO ₂ , and H ₂ /CO
H ₂ percentage	0-75 vol. %
Feeding pressure	5×10^5 Pa
Permeate pressure	1×10^5 Pa
Temperature	400 °C
Feeding flow rate	16400 L/min
Sweeping flow rate	0 and 1000 L/min
Effect of temperature and pressure	
Feed pressure	1.5×10^5 - 5×10^5 Pa
Permeate pressure	1×10^5 Pa

Temperature	300 – 500 °C
Feeding flow rate	14000 L/min
Sweeping flow rate	No sweep-gas

4.1 Effect of Sweeping Method

The geometry described in Figure 13. Schematic of the hydrogen separation system is considered to analyze the influence of sweeping gas on the hydrogen flux through the membrane. The hydrogen is fed to the upper zone from the left side, and it leaves from the right side. Nitrogen gas is swept at the bottom zone, and it enters the permeation-zone from the left side and leaves from the right side also (parallel flow). The sweeping gas enters and leaves at atmospheric pressure, while the feeding gas pressure is examined for gage pressure ranged from 1.5×10^5 Pa up to 5×10^5 Pa and at a temperature of 300°C. Figure 15 compares the hydrogen fluxes with and without sweeping gas at different feeding pressures. At low feeding pressure (1.5×10^5 Pa), the no-sweep case results in 202×10^{-3} mol.m⁻².s⁻¹. When the sweeping-gas is introduced, the hydrogen diffusion flux increases by 50×10^{-3} mol.m⁻².s⁻¹. This value is corresponding to an increase in hydrogen diffusion flux by nearly 25%. As the feed pressure increases from 1.5×10^5 Pa up to 5×10^5 Pa, the diffusion flux value increases also until it reaches $1,370 \times 10^{-3}$ mol.m⁻².s⁻¹ (no-sweeping case). Again, for all of these feeding pressure cases, the value of J_{H_2} increases by almost a constant value, which is around 44×10^{-3} to 50×10^{-3} mol.m⁻².s⁻¹ when the sweeping method is implemented. Hence, the percentage of the increase of J_{H_2} at higher pressure values such as 5×10^5 Pa becomes small. At 5×10^5 Pa feed pressure, the observed increases in J_{H_2} is only 3.4%. Thus, one can conclude that the sweeping method is highly effective at the low-

pressure difference between the feeding and permeation sides. Furthermore, it was noticed that the hydrogen diffusion flux profile along the membrane length remains almost constant at $1.37 \text{ mol.m}^{-2}.\text{s}^{-1}$ in the case of no sweep-gas (Figure 16). In contrast, in the case of sweep-gas, the J_{H_2} has high value at the entrance ($1.89 \text{ mol.m}^{-2}.\text{s}^{-1}$), but it decays sharply near the entrance before it gradually reduces to $1.46 \text{ mol.m}^{-2}.\text{s}^{-1}$ near the outlet (Figure 16). At the entrance of the permeation-zone, the driving force for J_{H_2} is tremendous since there is no hydrogen at that location (i.e., the partial pressure of hydrogen is zero). However, as H_2 permeates through the membrane, the partial pressure of H_2 in the permeation-zone rises results in less amount of J_{H_2} compared to hydrogen diffusion flux near the entrance.

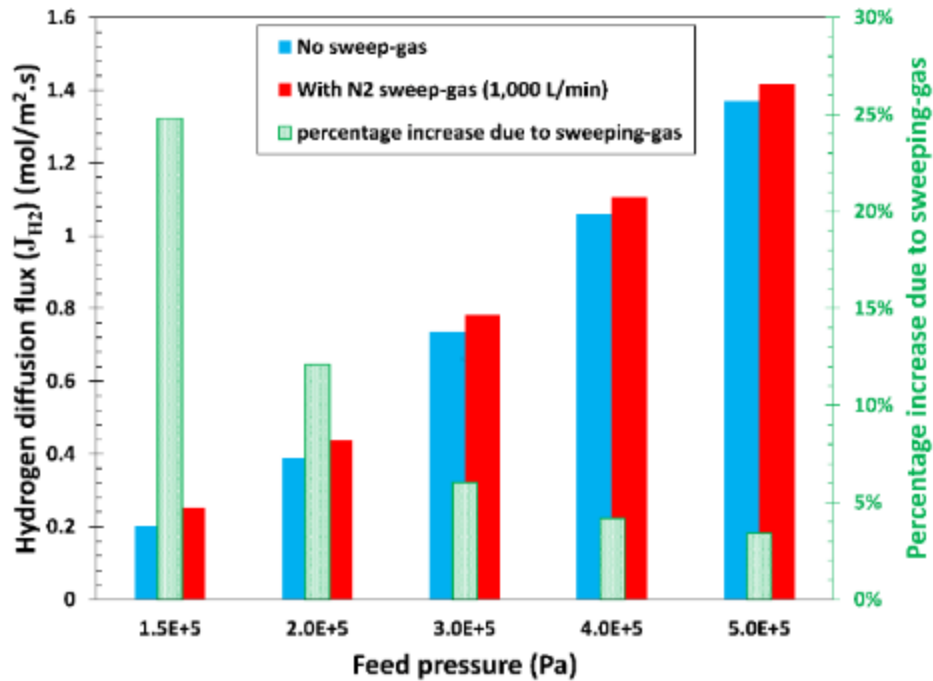


Figure 15. Impact of a sweep-gas method on hydrogen flux ($T=300^\circ\text{C}$, $P_p=1 \times 10^5 \text{ Pa}$, $\dot{Q}_f=14,000 \text{ L/min}$).

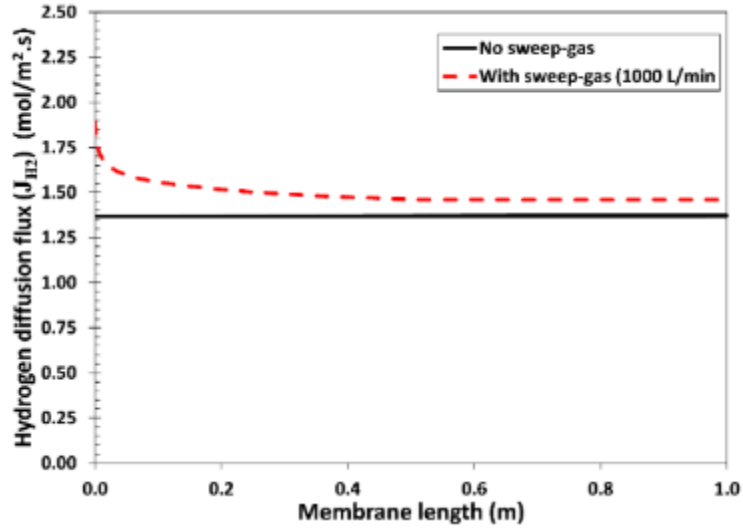


Figure 16. Comparison of hydrogen diffusion flux along the membrane length ($T=300^{\circ}\text{C}$, $P_p=1 \times 10^5 \text{ Pa}$, $P_f=5 \times 10^5 \text{ Pa}$, $Q_f=14,000 \text{ L/min}$).

4.2 Effect of Flow Rates

The above analysis of the sweeping method was performed under a high sweeping flow rate (1000 L/min). In this section of the study, the impact of sweeping nitrogen gas and hydrogen feeding gas flow rates on diffusion flux of the hydrogen are evaluated. The investigation cover flow rates starting from 1 L/min up to 1000 L/min for the sweeping nitrogen gas and 1 to 20,000 L/min for hydrogen feeding gas. The effect of nitrogen sweeping-gas flow rate is examined at 300°C for both cases $1.5 \times 10^5 \text{ Pa}$ and $5 \times 10^5 \text{ Pa}$ as feeding pressure while the permeation side is kept at atmospheric pressure ($1 \times 10^5 \text{ Pa}$). It turns out at low feed pressure, the hydrogen flux is highly influenced by the magnitude of the sweeping flow rate value. At nitrogen sweeping flow rate ranged between 1 and 100 L/min, the hydrogen diffusion flux rises by 13.4%-15.7% as it compares to the case of no-sweeping gas (Figure 17). While the percentages jump to the higher values of 21.3% and 24.8% at high nitrogen sweeping flow rates of 500 and 1000 L/min. On the other hand, as mention before, the sweeping gas method is less effective at high feeding pressure of 5×10^5

Pa, as indicated in Figure 15, which showed only 3.4% improvement in J_{H_2} due to applying sweeping gas. Consequently, as expected, changing the nitrogen sweeping flow rate results in a trivial impact on the hydrogen flux, where the improvement in J_{H_2} is less than 3.5% (Figure 17 at 5×10^5 Pa). The second part of the analysis is to examine the influence of the hydrogen feeding flow rate on J_{H_2} . The system was tested under low and high temperatures (300°C and 500°C), and the results are summarized in Figure 18. At each temperature value, two cases of pressure are examined, which are 1.5×10^5 and 5×10^5 Pa (absolute pressure). The results reveal that for the same values of pressure and temperature changing the feeding flow rate from 1 to 20000 L/min has no impact on the hydrogen diffusion flux, where the percentage difference between the J_{H_2} at 1 L/min and 20000 L/min as feeding flow rate does not exceed 1%.

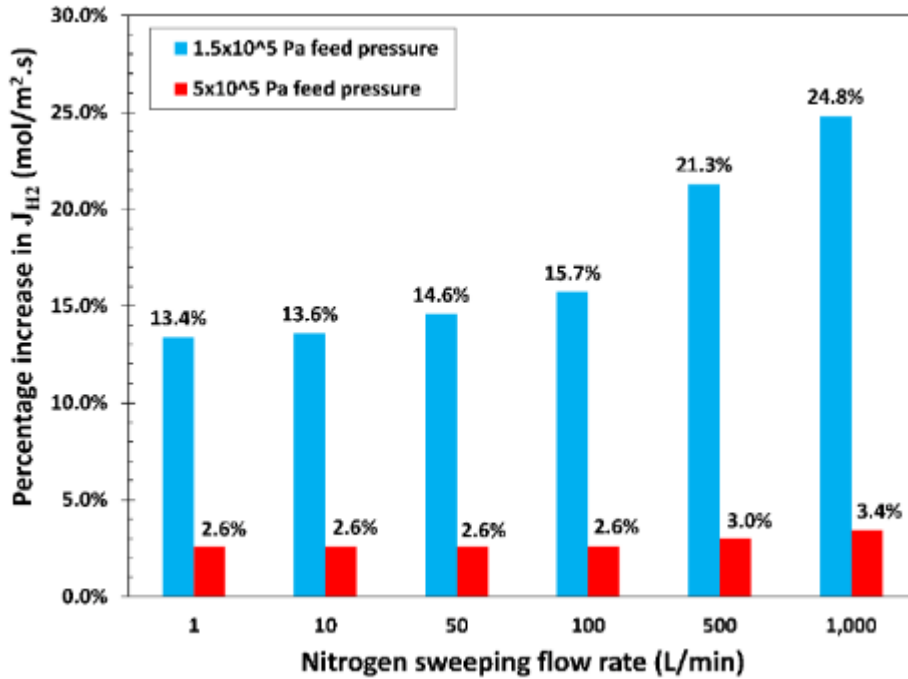


Figure 17. Percentage increase in J_{H_2} at various nitrogen sweeping flow rates ($T=300^\circ\text{C}$, $P_p=1 \times 10^5$ Pa, and $Q_{\text{feed}}=14000$ L/min).

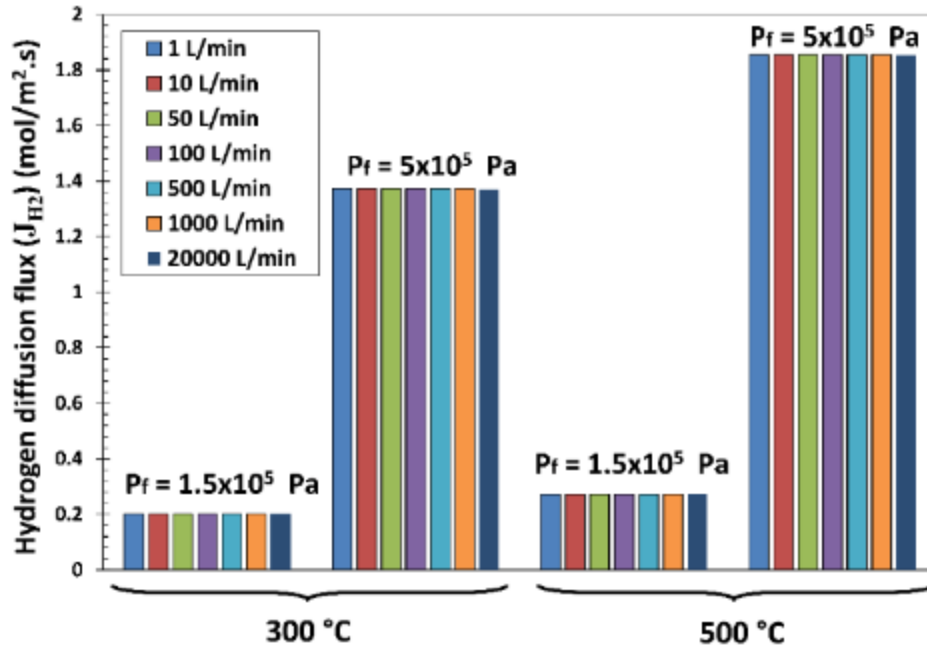


Figure 18. Impact of feeding flow rate on J_{H_2} with no-sweeping-gas ($P_p=1 \times 10^5$ Pa).

Furthermore, sweeping nitrogen gas is introduced to the permeation side at different flow rates (1 and 1000 L/min), and the results are represented in Figure 19. The results reveal that, at a similar value of sweeping gas flow rate, the J_{H_2} does not affect by the flow rate of the feeding hydrogen. For example, at a feeding pressure of 1.5×10^5 Pa with 1 L/min of N_2 sweeping gas, the hydrogen diffusion flux is around 0.229 mole/m².s for all tested values of hydrogen feeding flow rates. This value of J_{H_2} rises to 0.250 mole/m².s when N_2 sweeping flow rate changes to 1000 L/min instead of 1 L/min. The increase in J_{H_2} is mainly due to the increase in the N_2 sweeping flow rate because J_{H_2} remains constant at 0.250 mole/m².s for all feed flow rates ranged from 1 to 20,000 L/min at 1000 L/min of sweep-gas. Based on the results of Figure 19, one may wonder why changing the flow rate of sweep-gas is doing more good in rising J_{H_2} while the feed-gas flow rate showed no impact on J_{H_2} . To reveal this confusion, it is required to look back at the driving force for this

process, which is the hydrogen partial pressure on both sides of the membrane (p_f and p_p). The greater difference between p_f and p_p means the greater hydrogen diffusion flux. The hydrogen partial pressure can be expressed as (*partial pressure = mole fraction $\times$ (static pressure + dynamic pressure + operational pressure)*). Accordingly, changing the feed-gas flow rate has an influence only the dynamic pressure ($0.5\rho v^2$). The maximum dynamic pressure registered, due to increasing the feed-gas flow rate from 1 L/min to 20000 L/min, is 180 Pa (Figure 20). This value can be ignored compared to the feed-gas absolute pressure 1.5×10^5 Pa (*static pressure + dynamic pressure + operational pressure*). Thus, the feed-gas flow rate has a trivial impact on J_{H_2} since the dynamic pressure has is very small. On the other hand, the sweep-gas reduces the hydrogen molar-fraction in the permeation-zone, especially near the entrance, and it also drifts the permeated hydrogen towards the outlet. Subsequently, increasing the sweep-gas from 1 L/min to 1000 L/min leads to smaller hydrogen partial pressure in the permeate-side (p_p), especially near the entrance (Figure 21). Thus, it slightly increases the pressure differences ($p_f - p_p$).

This finding indicates that whether the hydrogen in the feeding side is moving slowly or moving rapidly, the diffusion flux would be the same. Therefore, the only parameters on the feeding-side that affect the hydrogen diffusion flux are the pressure and the temperature.

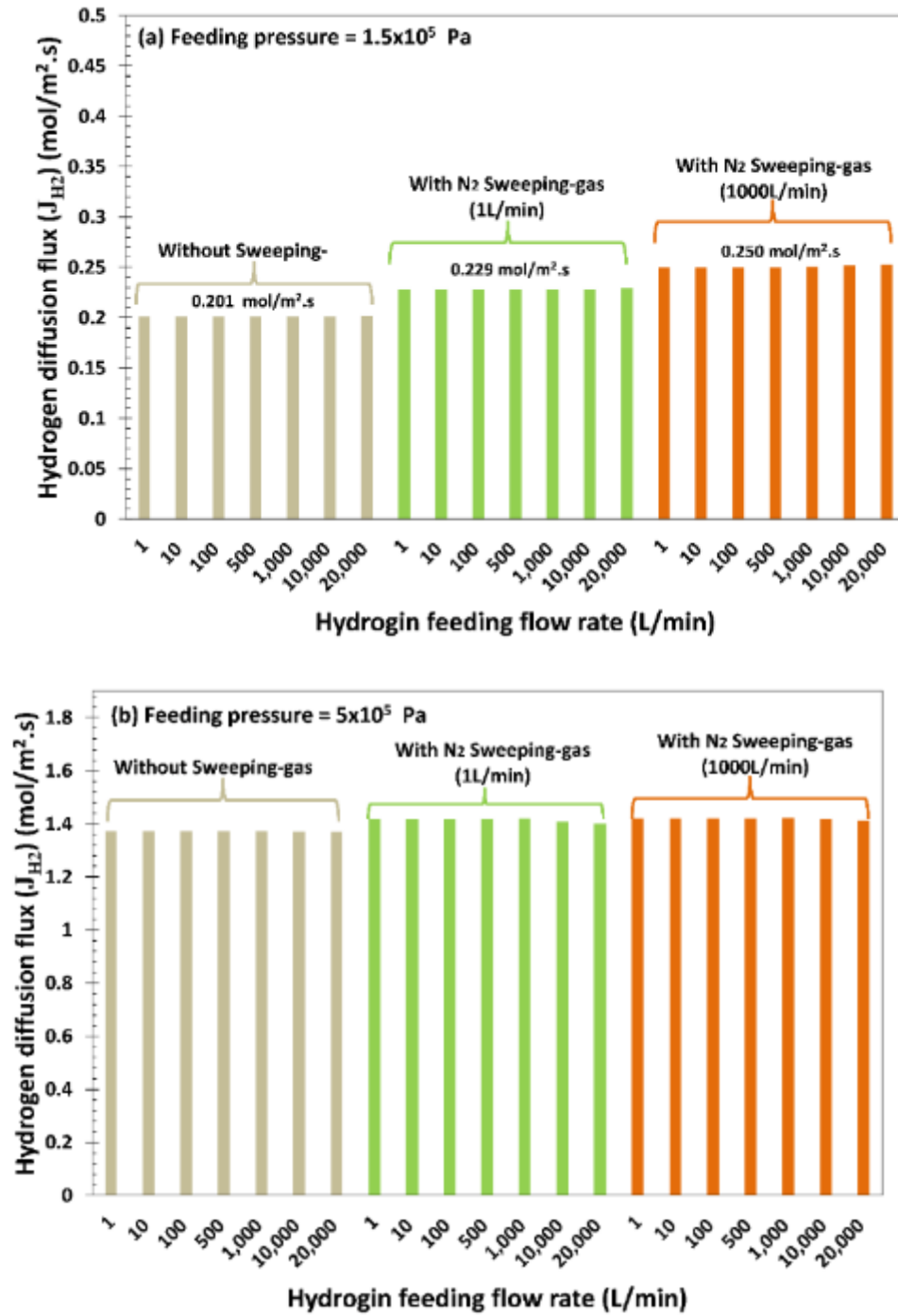


Figure 19. Impact of feeding flow rate on J_{H_2} at different boundary conditions ($T=300^\circ\text{C}$ & $P_p=1 \times 10^5$ Pa).

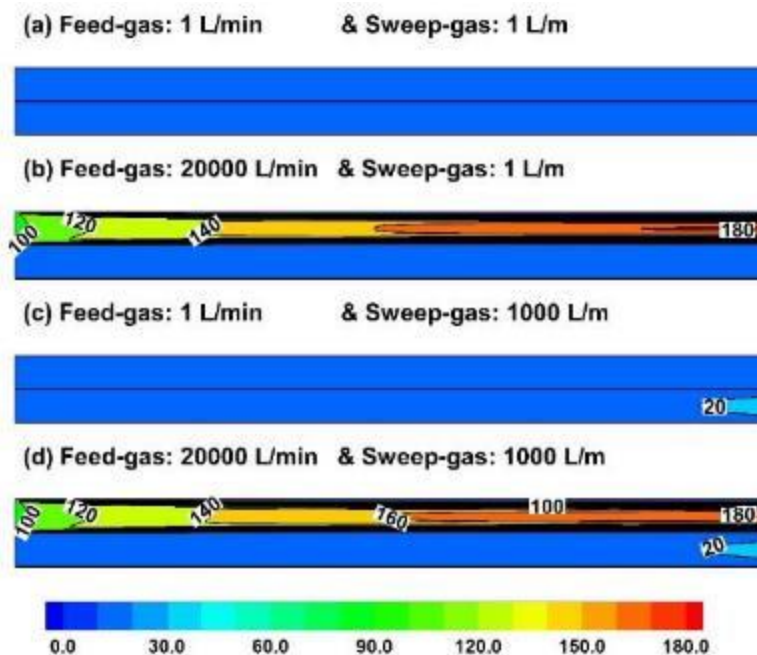


Figure 20. Comparison of dynamic-pressure in (Pa) at different feed-gas and sweep-gas ($T=300^{\circ}\text{C}$, $P_f=1.5 \times 10^5$ Pa, $P_p=1 \times 10^5$ Pa).

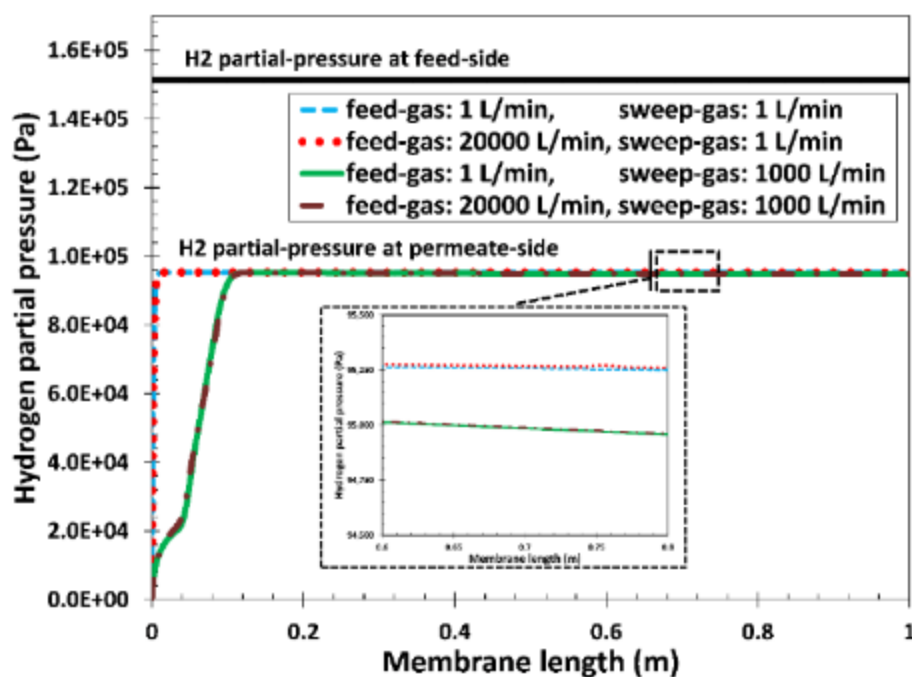


Figure 21. H₂ mole-fraction at different feed-gas and sweep-gas ($T=300^{\circ}\text{C}$, $P_f=1.5 \times 10^5$ Pa, $P_p=1 \times 10^5$ Pa).

4.3 Pressurized and Vacuum Methods

This section compares the impact of the two methods to create a pressure difference between the feeding-zone and the permeation-zone on the hydrogen diffusion flux. These methods are referred to as pressurized-method and vacuum-method. The pressurized-method is by running the hydrogen separation system at a pressurized feeding gas (higher than atmospheric pressure) while keeping the permeation side at atmospheric pressure (1×10^5 Pa). On the other hand, in the vacuum-method, the feeding gas enters the feeding-zone at atmospheric pressure while the permeation-zone is kept at vacuum ($p < 1 \times 10^5$ Pa). The two methods are tested at two values of pressure difference ($p_f - p_p$) of 0.5×10^5 and 1×10^5 Pa. In the pressurized-method, these values are applied as feeding pressure while keeping the permeate side at atmospheric pressure. In the vacuum-method, the pressure difference values are applied by changing the permeation-zone pressure value while keeping the pressure of the feeding zone atmospheric. Figure 22 summarizes the hydrogen diffusion fluxes at the two pressures difference (0.5×10^5 and 1×10^5 Pa). It is clear from the figure that lowering the pressure on the permeate side (i.e., applying vacuum method) is better than pressurizing the feeding gas by the same value of pressure difference, especially at higher pressure difference. For instance, by considering a pressure difference ($p_f - p_p$) of 1×10^5 Pa, if this difference in pressure is applied as vacuum pressure, the hydrogen diffusion flux would increase by 36% greater than if it is applied as a feeding pressure.

Moreover, running a sweeping gas at high vacuum pressure (1×10^5 Pa) would not add any benefits to the hydrogen diffusion flux. In contrast at small vacuum pressure (0.5×10^5 Pa), running the sweeping gas raises the hydrogen diffusion flux from 0.23 to 0.27 mole/m².s (17.4% increases). The reason behind that could be demonstrated by the help of

Figure 23 to 25, which represents the contours of H_2 partial pressure, N_2 mass fraction, and mixture density, respectively. In the case of low vacuum pressure with sweeping gas (Figure 23.b), the hydrogen partial pressure in the permeation-zone increases gradually from 0 to 0.18×10^5 Pa. Implementing N_2 sweeping gas to the vacuum-method at low vacuum pressure makes H_2 gas the less dominant gas at the permeation-zone, especially at the entrance, as shown in Figure 24.b. Thus, a small fraction of H_2 is located near the entrance of permeation-zone. As the H_2 gas permeates across the membrane length, the sweeping gas drifts it toward the outlet. So, the H_2 gas accumulates gradually, and its partial pressure rises until it reaches 0.18×10^5 Pa near the outlet. The maximum hydrogen partial pressure recorded in the permeation-zone for the case of low vacuum pressure with sweeping gas is 0.18×10^5 Pa. This partial pressure is very small compared to the same case of low vacuum pressure but without sweeping gas, where the maximum recorded value of hydrogen partial pressure is 0.5×10^5 Pa (Figure 23.a). Thus, implementing sweeping nitrogen gas to the vacuum-method at low vacuum pressure reduces the partial pressure of the hydrogen at the permeation-zone, and hence, expanding the gap difference of $(p_f - p_p)$, which acts as a driving force for J_{H_2} . This demonstrates the increases of J_{H_2} from 0.23 to 0.27 mole/m².s when the sweeping gas is applied to the vacuum-method at low vacuum pressure. On the other hand, at high vacuum pressure, the hydrogen partial pressure reaches to a very small value (63 Pa) without any sweeping gas (Figure 23.c). When the sweeping nitrogen gas is implemented to this high vacuum pressure, the sweeping gas enters the permeation-zone at a very small density (Figure 25.d) compared to the case of low vacuum pressure (Figure 25.b). Thus, nitrogen gas occupies the same volume of permeation-zone along with the hydrogen gas without making a considerable reduction in the partial pressure

of the hydrogen (Figure 23.c & d). Consequently, at high vacuum pressure, the partial pressure of the hydrogen at the permeation-zone remains at small value whether sweeping gas is applied or not, the thing that demonstrates why sweeping pressure is not effective at high vacuum pressure.

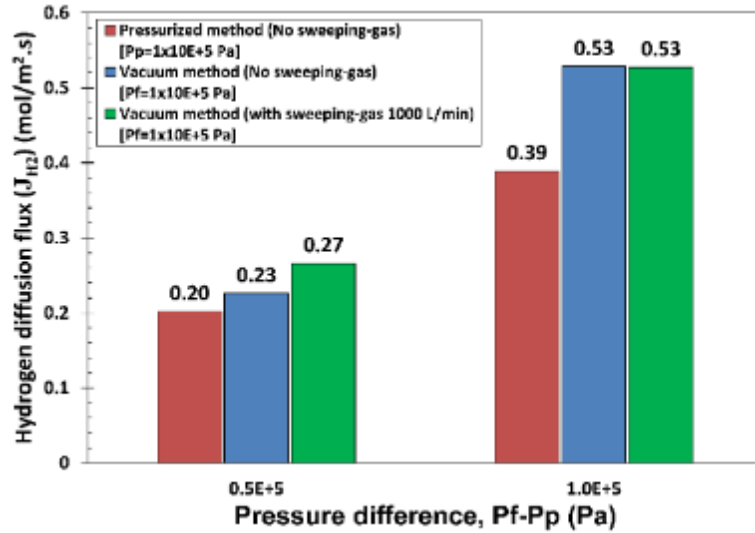


Figure 22. Comparison of pressurized and vacuum methods ($T=300^\circ\text{C}$ & $Q_{\text{feed}}=14000$ L/min).

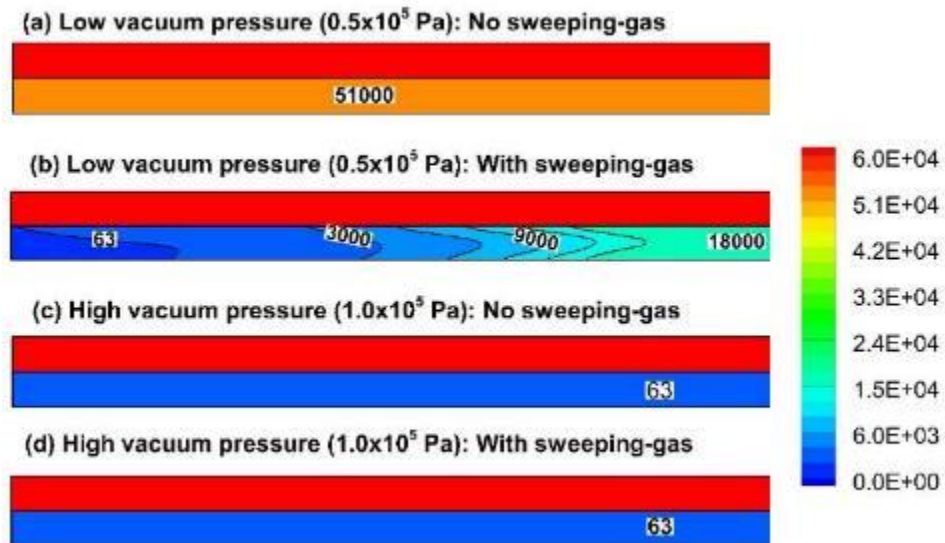


Figure 23. Hydrogen partial pressures for different vacuum pressures

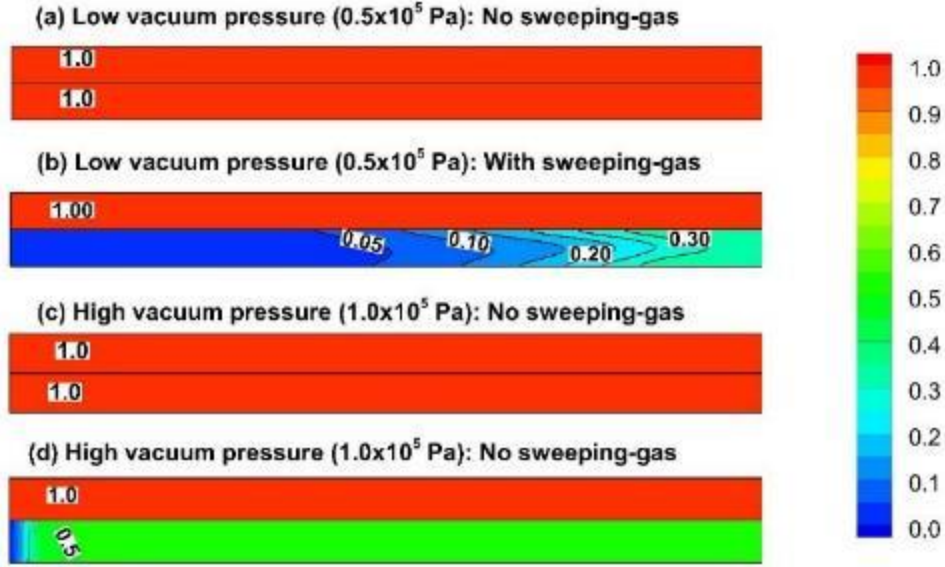


Figure 24. Hydrogen mass fractions at different vacuum pressures.

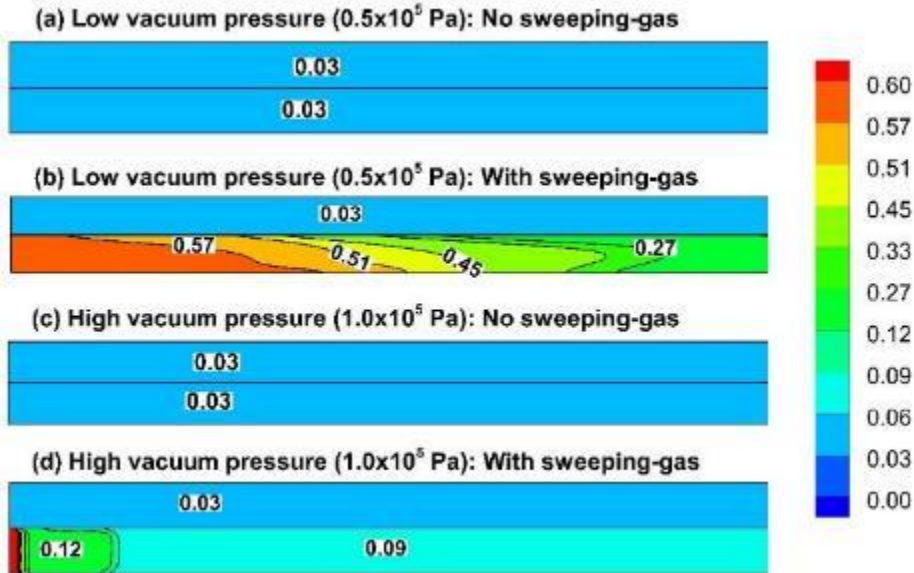


Figure 25. Mixture densities at different vacuum pressure.

4.4 Effect of Different Species Flow

In the previous sections, different parameters are investigated to quantify their effect on the hydrogen permeance flux. These studies were conducted for pure hydrogen; however, the membranes are practically used to separate H_2 gas from other gases. For example, the

process of water gas shift produces a gas mixture of carbon dioxide and hydrogen where a membrane separation technique can be applied to purify the hydrogen. Other examples are the hydrogen/methane separation in refinery off-gas and hydrogen/carbon monoxide adjustment in oxo-chemical synthesis plants [86]–[88]. All these processes produce gas mixture contains hydrogen. Accordingly, this part of the study considers the separation of hydrogen from a mixture contains H_2 gas. Different binary gas mixtures are investigated at different gas volume percentages. The study covers the following mixtures: H_2/N_2 , H_2/CO_2 , H_2/CO . The results of the CFD simulations of H_2/N_2 are compared with the experimental data of [80], and it shows proper agreement since the maximum registered error is about 13.5% (Figure 26).

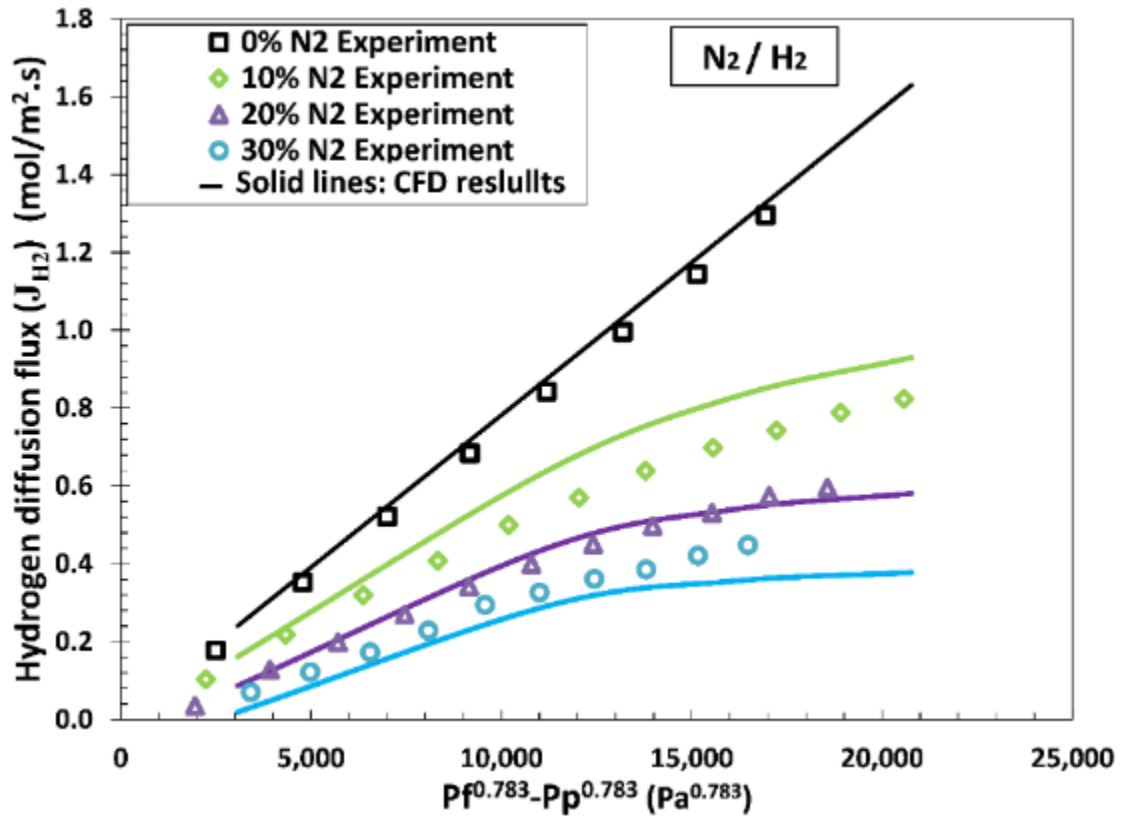


Figure 26. Comparison of predicted CFD results of hydrogen diffusion flux and experimental data [80] for the binary mixture (N_2/H_2) ($T=400^\circ C$ & $Q_{feed}=14000$ L/min).

Figure 27 summarizes the hydrogen diffusion flux for three binary gases hydrogen/nitrogen, hydrogen/carbon dioxide, and hydrogen/carbon monoxide. The mixture enters the feeding side at 5×10^5 Pa absolute pressure while the permeation side is kept atmospheric pressure (1×10^5 Pa, absolute pressure). As expected, for all gas mixtures, the permeated hydrogen value reduces with increases of the contamination gas percentage (i.e., N_2 , CO_2 and CO) due to the drop in the driving force $(p_f^n - p_p^n)_{\text{hydrogen}}$. The cases of feeding pure hydrogen gas represent maximum limits for the hydrogen-permeation flux.

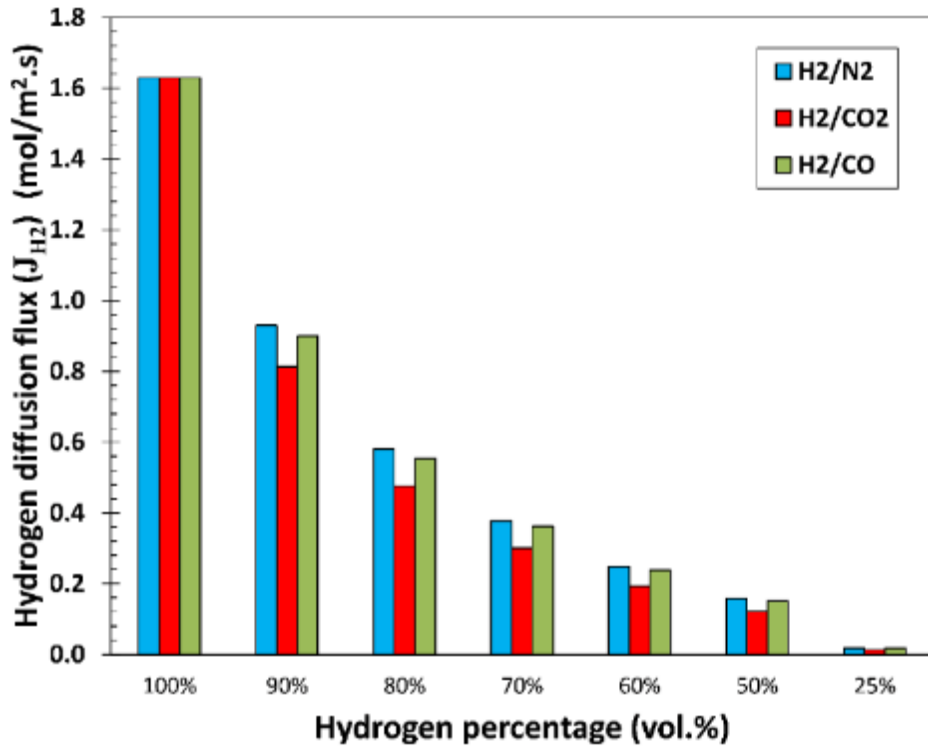


Figure 27. Hydrogen diffusion flux for various binary mixtures [$T=400^\circ\text{C}$, $p_f 5 \times 10^5$ Pa, and no sweep-gas].

Rising the contaminate gas percentage lowers the partial pressure of the hydrogen. Thus, keeping the permeated pressure (p_p) at the 1×10^5 Pa and reducing the partial pressure of the feeding-hydrogen (p_f), through increasing the percentage of contaminating gas, would lead to less permeance driving force. This demonstrates the reduction in J_{H_2} with an increasing percentage of the other gas in the mixture. Moreover, one can notice that at the same

volumetric percentage of contaminating gas, the hydrogen flux varies according to the gas type mixed with the hydrogen (i.e., N₂, CO₂, or CO). For instance, at 90% hydrogen with 10% of N₂, CO₂, or CO, the corresponding hydrogen-permeation fluxes are 0.93, 0.81 and 0.90 mole/m².s, respectively. In both binary mixture H₂/N₂ and H₂/CO, the hydrogen permeation flux is larger than the value in the case H₂/CO₂. This is also noticed in all other percentages of contaminating gases (Figure 27). A more detailed comparison of feeding gas mixture (with 90%H₂) is given in Figure 28. It shows the contours of mass fraction and partial pressure of hydrogen. Since N₂ and CO have a close molecular weight value ($M_{w,N_2}=28.0134$ and $M_{w,CO}= 28.01055$), the H₂ mass fraction distribution is almost similar in their binary mixture H₂/N₂ and H₂/CO. On the other hand, CO₂ has a higher molecular weight ($M_{w,CO_2}=44.00995$) than N₂ and CO, so it shows lower H₂ mass fraction distribution compared to the other cases. Accordingly, a hydrogen mixture of 10% CO₂ results in lower hydrogen partial pressure as it compares to the hydrogen mixture of 10% N₂ or 10% CO. This explains the small value of J_{H_2} in the mixture case of H₂/CO₂ compared to H₂/N₂ and H₂/CO mixtures.

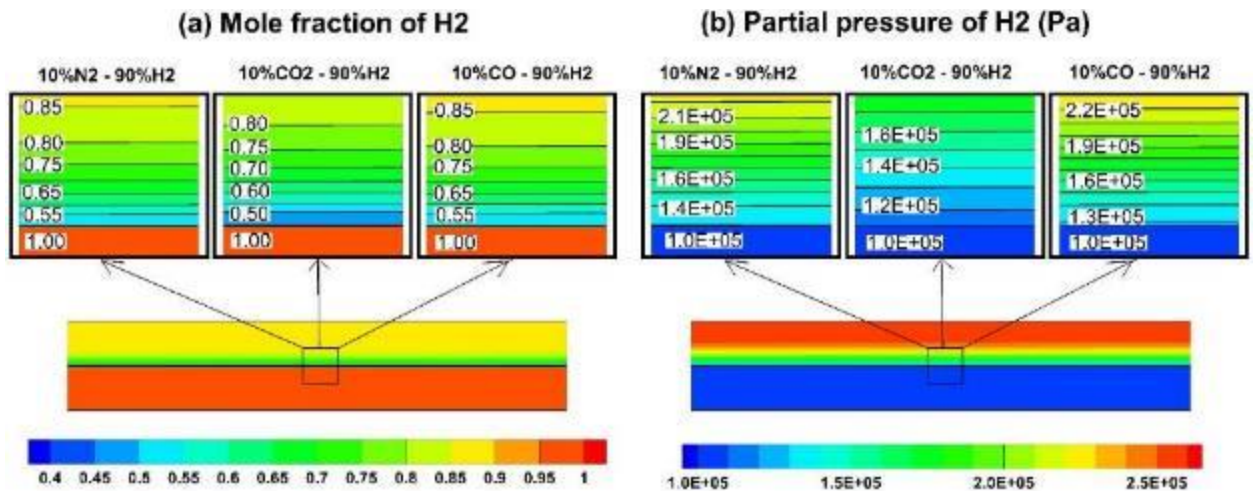


Figure 28. Contours comparison of the case 10% (N₂, CO₂ or CO) with 90% H₂ at [T=400°C, pf of 5x10⁵ Pa, pp of 1x10⁵ Pa, and no sweep-gas] (a) H₂ mole fraction (b) H₂ partial pressure.

Figure 29 represents the hydrogen diffusion flux across the membrane length for a pure hydrogen feeding gas as well as the mixture of 90% H₂ with 10% N₂, CO₂, or CO. There is no-sweep gas applied in the permeation-zone. In the case of feeding pure hydrogen, the hydrogen diffusion flux remains constant across the membrane length at 1.62 mole/ m².s. While in the case of a gas mixture, the maximum hydrogen diffusion flux occurs at the entrance of the feeding zone (1.43 mole/ m².s), then it decays quickly across the membrane length. All three binary mixtures recorded a similar value of J_{H2} at the entrance (1.43 mole/ m².s). Then, as the mixture advances through the feeding-zone toward the exit, the fraction of the hydrogen gradually reduces because as the hydrogen diffuses from the feeding-zone to the permeation-zone the hydrogen mole fraction in the feeding-zone reduces which reduces the hydrogen partial pressure in the mixture. The maximum hydrogen diffusion flux is recorded by using a binary mixture of N₂/H₂ then flowed by CO/H₂ and CO₂/H₂ with values of 0.93, 0.90 and 0.81 mole/ m².s, respectively.

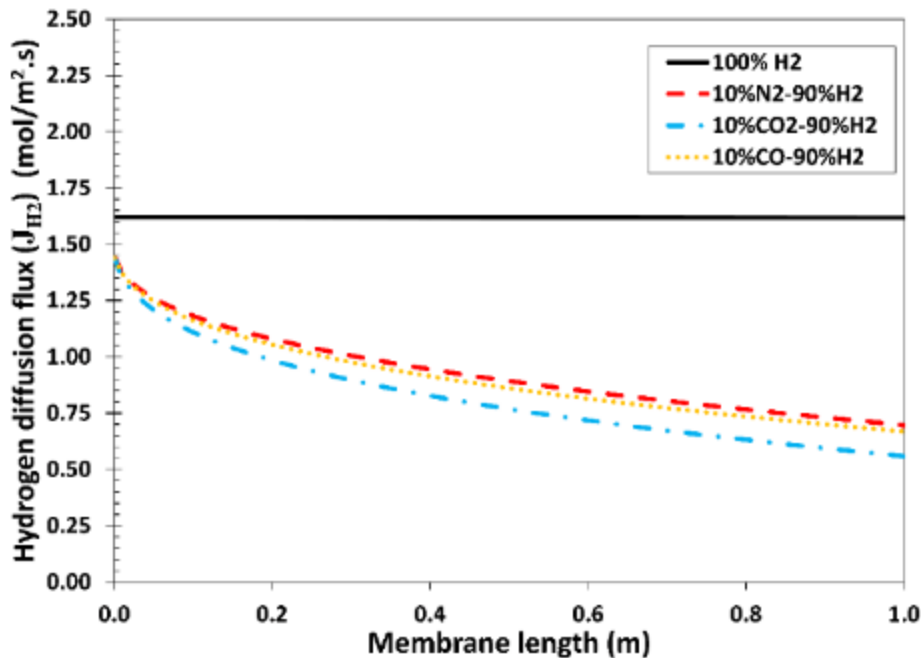


Figure 29. Hydrogen permeation profile across the membrane (400°C, pf of 5x10⁵ Pa, and no sweep-gas).

4.5 Effect of Temperature and Pressure

Figure 30 summarizes the influence of feeding temperature on the hydrogen permeation flux at temperature ranged 300°C to 500°C for different feeding pressure ranged from 1.5×10^5 Pa to 5×10^5 Pa. The amount of hydrogen flux increases proportionally with the feeding pressure. At lower feeding pressure (for example, 1.5×10^5 Pa), the hydrogen diffusion flux is very small; it changes from 0.2 to 0.27 mole/ m².s depending on the gas temperature. While, at a higher value of feeding pressure, more hydrogen molecules diffuse through the Pd-membrane, so the value of J_{H_2} reaches up to 1.85 mole/ m².s. At this high pressure (5×10^5 Pa), the impact of the temperature on the J_{H_2} can be noticed clearly, where it shows the value of 1.37 and 1.85 mole/m².s for the gas temperature of 300°C and 500°C, respectively. Rising the gas temperature from 300°C to 400°C or from 300°C to 500°C leads to an increase in the hydrogen diffusion flux by 19% and 35%. It is noticed that this increases the percentage is almost constant, and it is not affected by the feeding pressure. For instance, at 1.5×10^5 Pa feeding pressure and 300°C, the J_{H_2} is 0.20 mole/ m².s. Increasing the temperature up to 500°C results in a 35% increase in J_{H_2} ; thus, it reaches 0.27 mole/ m².s. On the other hand, at 5×10^5 Pa and 300°C, the hydrogen flux is 1.37 mole/ m².s which is much higher than the value at 1.5×10^5 Pa and 300°C. But, when the temperature rises from 300 to 500°C, the J_{H_2} also increases by 35% to reach 1.85 mole/ m².s. This notice is examined for all feeding pressures understudy, and it turns out to be valid. To summary up, increase the feeding temperature from 300°C to 350, 400, 450 and 500°C would improve the hydrogen permeation fluxes by 10%, 19%, 27.5%, and 35%, respectively, regardless of the feeding pressure value.

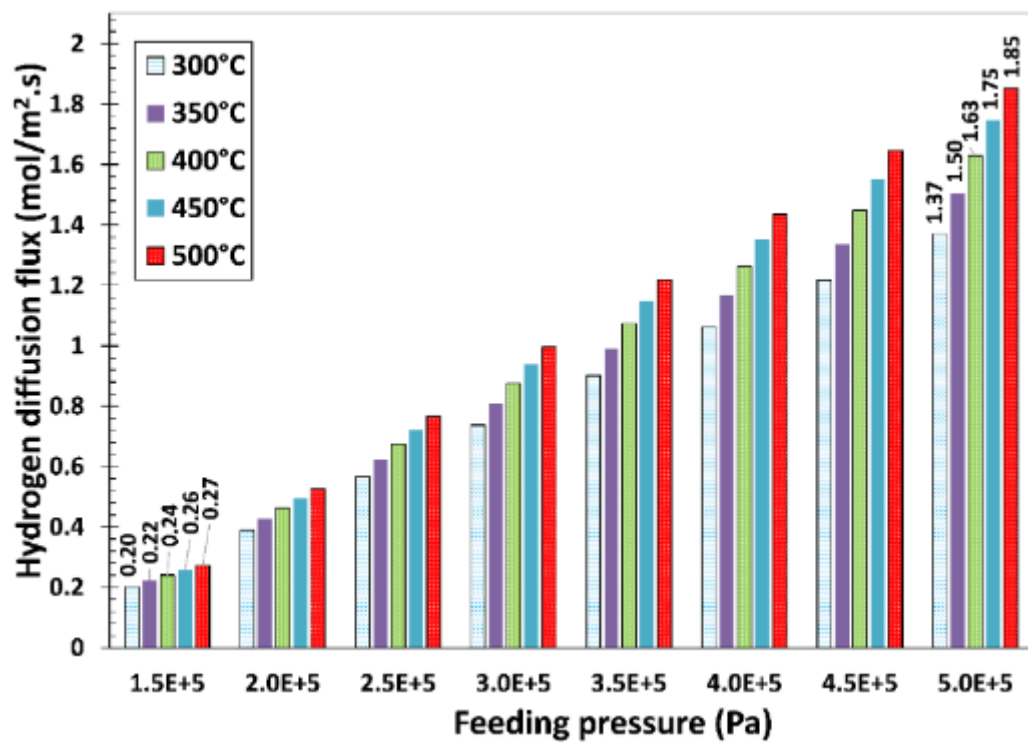


Figure 30. Influence of feeding temperature and pressure on hydrogen flux.

CHAPTER 5

HYDROGEN PERMEATION ON PURE Pd-MEMBRANE

This chapter focus on the permeation process through a pure Pd-membrane. These processes start by the physisorption of hydrogen molecule on the Pd-surface, then the dissociation of the H₂ molecule to two H-atoms. It followed by H-atom diffusion through the bulk membrane. The last two processes are the association of H-atoms to form H₂ molecule on the other side of the membrane, and desorption of H₂ from the Pd-surface. In order to validate the present calculation procedure, comparison of the present results were compared to available experimental data. As well, the present results of chemisorption were compared to available data in literature. Comparison of calculated variables are compared with experimental data as shown in **Table 5**. Furthermore, the present results of hydrogen chemisorption are perfectly fit with the data in literature [68], [89], [90] for the same surface (100) (see **Figure 31**). Good agreement is exhibited as shown in the figure.

Table 5. Comparison of current DFT results with data from literature.

Calculated Variables	Present value	Experimental/literature	Difference (%)
Bind energy of Pd-membrane (eV/atom)	3.935	3.918 [78]	0.44%
Lattice parameter of Pd-membrane (Å)	3.948	3.875 [78]	1.89%
Bond length of H ₂ (Å)	0.75	0.7414 [91]	1.16%
Bond length/angle of CH ₄ (Å/degree)	1.097Å/109.5°	1.096Å/109.4° [92]	0.10%
Bond length/angle of CO ₂ (Å/degree)	1.174Å/179.98°	1.160Å/179.995°[91], [93]	1.20%
Bond length of CO (Å)	1.140	1.1283 [91]	1.04%

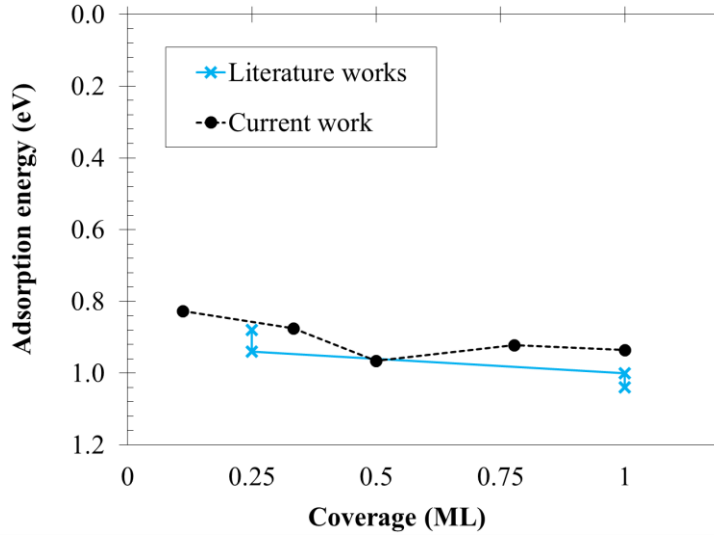


Figure 31. Comparing current results of chemisorption to literature data [68], [89], [90] (data are normalized to pair of H-atoms).

5.1 Physisorption of H₂ molecule on Pd-membrane

The first step of hydrogen permeation through a Pd-membrane starts by the physisorption of the hydrogen molecule on the membrane surface. Thus, the aim of this part is to calculate the adsorption energy ($E_{\text{ads, H}_2}$), along with the structural information of H₂ molecule on a bare Pd-surface (100). The H₂ adsorption is evaluated at three sites (top, bridge, and hollow), where each adsorption site is examined by different H₂ orientations as represented in Figure 32. Also, to ensure system of Pd/H reach to the global minimum energy, H₂ molecule at each case of site/orientation combination is located initially at various distances from the Pd-surface (starting from $d_{\text{Pd-H}_2} = 0.0$ Å up to 2.0 Å above Pd-surface, see SI.Fig1).

Table 6 summarizes the most negative adsorption energy for each site/orientation, while the detailed adsorption energy for various $d_{\text{Pd-H}_2}$ of each site/orientation case is shown on SI.Table1. The top site is the most attractive adsorption site for H₂ molecule compared to

bridge and hollow sites. On this site, top-site, $E_{\text{ads, H}_2}$ can reach up to -0.343 eV if H_2 molecule is oriented horizontally and making 45° with x-axis (case T.H045). Rotating the horizontal H_2 molecule to be parallel to x-axis (case T.H045) gives also high adsorption energy (-0.341 eV) indicating that horizontal/top-site is the most favorable orientation/site with less dependence on the rotation angle. Also, a closer value to maximum adsorption energy was obtained on the bridge site (-0.327 eV, case B.H045). In this case, B.H045, the H_2 molecule is initially located horizontally with $d_{\text{Pd-H}_2} = 0.0 \text{ \AA}$. However, the final relaxed H_2 molecule occurs at a distance of $0.9 \text{ \AA}$ above Pd-surface, and the axis connecting H-H atoms makes an angle of 64.5° with the Pd-surface instead of being horizontally (i.e. parallel to Pd-surface). Besides, the H_2 molecule comes close to the top site as depicted in Figure 33. When the adsorption energy of H_2 is evaluated on the bridge site with values of $d_{\text{Pd-H}_2}$ greater than zero, the resulted configurations have either low adsorption energy or the hydrogen atoms separated from each other and the physisorption was not detected. The latter case is identified by higher adsorption energy (chemisorption of two hydrogen atoms), and also, by the bond length of H_2 which becomes much greater than $0.75 \text{ \AA}$. In the physisorption of H_2 molecule there is a small change in the bond length. Most of strong physisorption cases have bond length between 0.85 and $0.9 \text{ \AA}$ as shown Table 6. On other hand, when weak physisorption is detected, the H-H bond length do not change much from $0.75 \text{ \AA}$. For instance, the case of B.H135 has a very weak adsorption energy of -0.079 eV and the recorded bond length of H_2 is about $0.754 \text{ \AA}$. Furthermore, the vertical orientation of H_2 has the least adsorption energy for all sites compared to the horizontal orientation. It recorded an adsorption energy of only -0.096 eV on the bridge and hollow-sites, and the value raises to about -0.116 eV on the top-site.

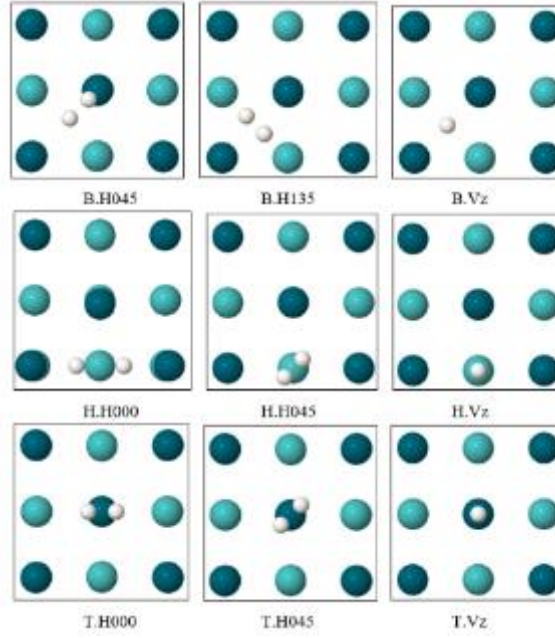


Figure 32. Top-view of H₂ physisorption on bare Pd-surface (100).

Table 6. H₂ physisorption on Pd-surface (100) at various sites/orientations.

Case	E_{ads} (eV)	$d_{\text{H-H}}$ (Å)
B.H045	-0.327	0.894
B.H135	-0.079	0.754
B.Vz	-0.096	0.758
H.H000	-0.229	1.433
H.H045	-0.071	0.754
H.Vz	-0.094	0.757
T.H000	-0.341	0.845
T.H045	-0.343	0.846
T.Vz	-0.116	0.767

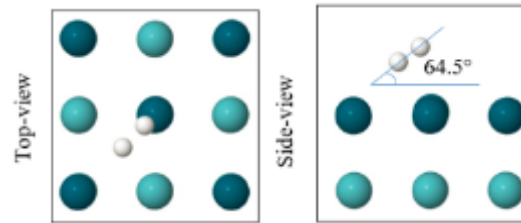


Figure 33. Relaxed location of H₂ adsorption on bridge site on Pd-surface (100).

5.2 Chemisorption Process at Various Hydrogen Coverage

When the hydrogen molecule get adsorbed on the Pd-surface, it dissociates to two hydrogen atoms and the chemical bond between H-H broke resulting in two separated H-atoms. The adsorption of these H-atoms is known as chemisorption process. The chemisorption energy of two H-atoms is much greater than the physisorption of one H₂ molecule on Pd surface. In this section, the impact of H-atoms coverage on the chemisorption is investigated to reveal to what extend the Pd-surface (100) can hold multi H-atoms, and how the adsorption energy would be affected. Accordingly, the Pd-surface is filled by H-atoms starting from low hydrogen coverage ($\Theta_{\text{H-atom}}$) of 0.11 ML up to 2.00 ML. It is assumed that the H-atoms fill the hollow site firstly (i.e. $\Theta_{\text{H-atom}} = 1.00$ ML), then, they start to fill the bridge sites. Also, for a coverage value of 0.11 to 1.00 ML, the hydrogen atoms are distributed with constrain of maintaining a semi-equal distance between them (Figure 34).

Figure 35 summarizes the chemisorption energy of hydrogen atoms at various coverage values, and compare it to chemisorption at other surfaces. The energy values were normalized by pair of H-atoms to be comparable to the physisorption energy of one H₂ molecule. The chemisorption of two separated H-atoms ($\Theta_{\text{H-atoms}} = 0.11$ ML) at Pd-surface (100) is about -0.827 eV/H₂ which is almost 2.5 times the physisorption of two H-atoms in gas phase (-0.343 eV/H₂). The chemisorption energy increase gradually with hydrogen coverage up to $\Theta_{\text{H-atoms}}=0.50$ ML, where it reaches a peak of -0.966 eV/H₂ (Figure 35). At this range of coverage ($0.11 \leq \Theta_{\text{H-atoms}} \leq 0.50$ ML), H-atoms are perfectly balanced in the hollow sites (Figure 34), and also, they get closer to the Pd-surface at higher chemisorption

energy (Figure 36) where the distance between Pd-surface and H-atoms reach about only 0.3 Å.

Adding more H-atoms ($\Theta_{\text{H-atoms}}$ 0.78 ML) disturbed the balance distribution of H-atoms on the surface which results in slightly reduction in the chemisorption energy from -0.966 to -0.922 eV/H₂ as the coverage value changed from 0.5 to 0.78 ML. In this case, some the H-atoms are not perfectly balanced at the hollow sites (Figure 34, $\Theta_{\text{H-atoms}}$ 0.78 ML). When all the hollow sites are filled with H-atoms ($\Theta_{\text{H-atoms}}$ 1.0 ML), the atom structure becomes perfectly balance from all directions, and hence, the chemisorption rises slightly to -0.935 eV/H₂. Covering the surface with $\Theta_{\text{H-atom}} > 1.0$ ML force some H-atoms to get adsorbed at bridge-site since all hollow-sites are filled. It was noticed that those H-atoms at bridge-sites have relatively higher distance from Pd-surface (around 1.2 – 1.4 Å) compared to those H-atoms adsorbed at the hollow-sites (< 0.3 Å) (see Figure 36 and SI.Fig.2). Consequently, sharp reduction in hydrogen chemisorption energy occurs due to less interaction of those far H-atoms from Pd-surface (Top-view and side-view showing the $d_{\text{Pd-Hatom}}$ is presented in SI.Fig.2). At $\Theta_{\text{H-atoms}} = 2.0$ ML, the chemisorption energy is very weak, -0.299 eV/H₂. Additionally, it was notice that the H-atoms at the hollow site of coverage greater than 1.0 ML become very close to the surface (0.15 Å) and in some cases those H-atoms move below the first layer of Pd-atoms (see Figure 36 and SI.Fig.2, at $\Theta_{\text{H-atoms}}$ 1.50 to 2.00 ML). Furthermore, the chemisorption of H-atoms is evaluated at $\Theta_{\text{H-atoms}} = 1.0$ ML on both hollow- and bride-sites (Figure 37). Locating the hydrogen atoms at bridge-site gives an adsorption energy of -0.696 eV/H₂ which is lower than the case of H-atoms at hollow-site (-0.935 eV/H₂). This emphasize that hollow-sites is much preferable than bridge-sites for hydrogen chemisorption. Moreover, the hydrogen coverage is increased to

3.0 ML which means all the hollow-sites and bridge-sites are filled with hydrogen atoms.

A positive value of adsorption energy is obtained for this case (+ 0.056 eV/H₂), and the top layer of Pd-atoms are spilt up by H-atoms on the hollow sites (SI.Fig.3). This indicate that the Pd-surface (100) cannot hold high coverage of H-atoms (3.0 ML).

A comparison of hydrogen chemisorption at other surfaces (110), (111), and (210) is also demonstrated in Figure 35. At very low coverage value, the adsorption energy of H-atom is weaker in surface (100) compared to the surface (111). At a coverage of 1.0 ML all surfaces have a comparable adsorption energy of around 0.50 eV. For instance our results of surface (100) showed an adsorption energy of 0.47 eV, while the result of Pasti et al [94] showed a value of 0.48 eV for the surface (111). For higher coverage (> 1.0), the adsorption energy becomes weaker due to the mutual repulsion. Besides, the most favorable hydrogen chemisorption site is the hollow site as stated in this work and in literature [89].

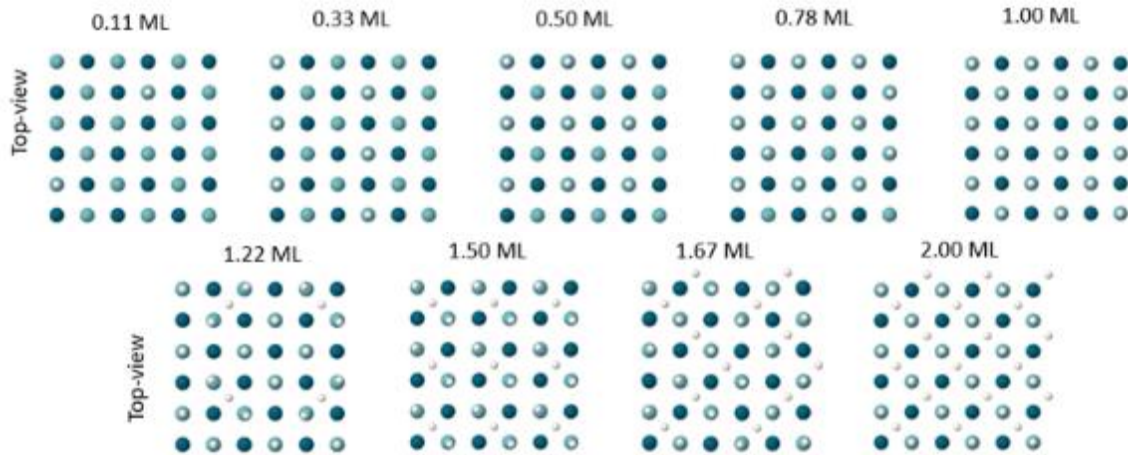


Figure 34. Relaxed locations of H-atoms at various coverage on Pd-surface (100).

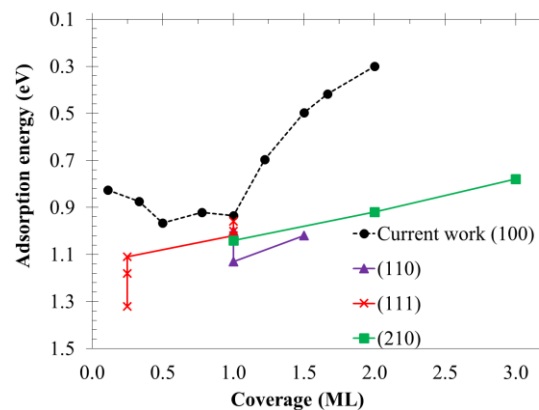


Figure 35. Chemisorption energy of H-atoms on Pd-surface (100) at various coverage (data are normalized to pair of H-atoms).

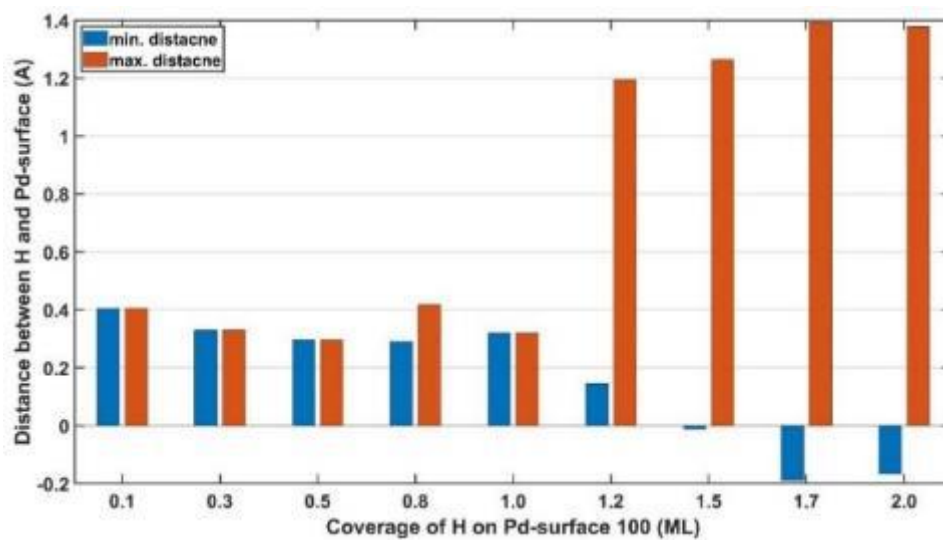


Figure 36. Chemisorption distance of H-atoms from Pd-surface at various OH-atoms.

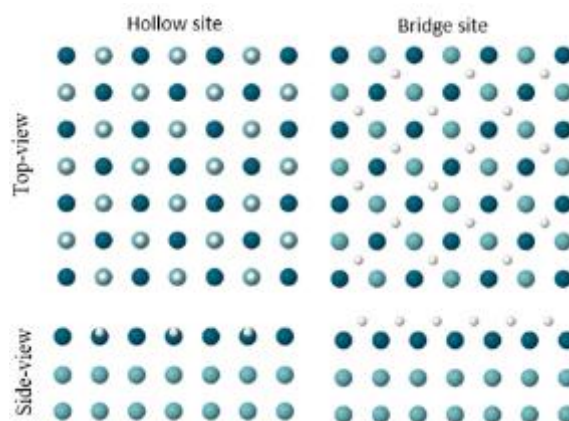


Figure 37. Comparison of hydrogen chemisorption at hollow and bridge sites of Pd-surface (100) with 1.0 ML coverage (side-view shows only 3 Pd-layers out of 7-layers).

5.3 Effect of Hydrogen Coverage on Adsorption of H₂ Molecule

It was shown previously that the hydrogen molecule get adsorbed at a Pd-top-site with horizontal orientation (Figure 32, case T.H045). The adsorption energy for that case was about -0.343 eV, and it get adsorbed at 1.83 Å above the Pd-surface. Figure 38 explore the impact of pre-existing H-atoms (with various coverage) on the adsorption energy of H₂ molecule (i.e. physisorption and chemisorption processes). Each case in Figure 38 was examined at various distance between palladium and hydrogen atoms in an attempt to capture the physisorption of H₂ at Pd-surface covered by various coverage of H-atoms. Here, only successful physisorption cases with the most negative adsorption energy are reported, while more details can be found in the supplementary information file. At low coverage ($\Theta_{\text{H-atoms}} = 0.1 \text{ ML}$), the H₂ molecule get physisorbed with binding energy (-0.302 eV) smaller than that of pure Pd (-0.343 eV). The Pd-atoms on the surface have more interaction with the H-atoms because they are very close to the Pd-surface ($< 0.5 \text{ Å}$) while the H₂ molecule get adsorbed at 1.8 Å above the Pd-surface. Also, it was noticed that the presence of H-atoms make H₂ not perfectly adsorbed at the Pd-top-site (Figure 39), where H₂ molecule oriented away from Pd-atom on opposite side to H-atom. Increasing $\Theta_{\text{H-atoms}}$ results in less adsorption energy of H₂ molecule. At coverage $\geq 0.33 \text{ ML}$, the H₂ adsorption energy drops significantly to about -0.206 eV.

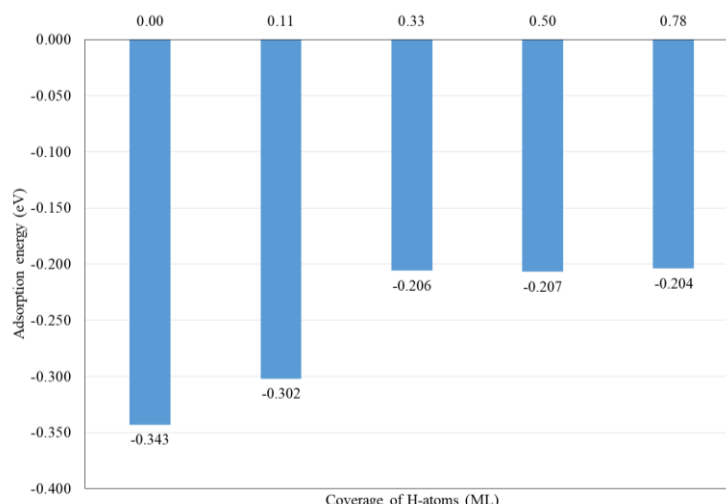


Figure 38. Effect of pre-existing H-atoms coverage on the adsorption energy of H₂ molecule.

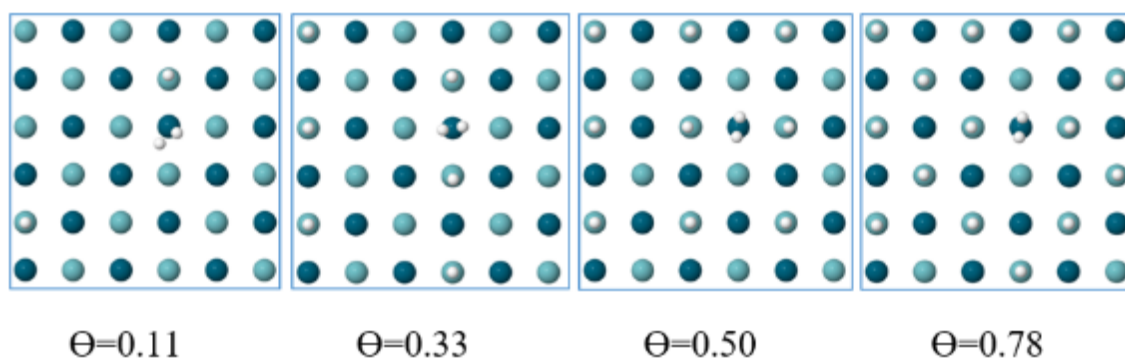


Figure 39. Relaxed location of H₂ molecule at different coverage of H-atoms (top-view).

It was noticed that the cases of $\Theta_{\text{H-atoms}}$ 0.33, 0.50, and 0.78 ML are all surrounded by two hydrogen atoms. That might be the reason why they got similar adsorption energy. Thus, another approach was adopted to reflect impact of $\Theta_{\text{H-atoms}}$ on H₂ adsorption energy. In this approach, the hollow sites surrounding the Pd-atom, at which H₂ molecule is adsorbed, are filled with H-atoms instead of distributing them across the Pd-surface (Figure 40). As expected, the adsorption of H₂ molecule is highly depends on how many H-atoms surround the adsorption sites of H₂ molecule. The adsorption energy reduced dramatically from -0.343 eV at $\Theta_{\text{H-atoms}}=0.0$ ML to -0.296, -0.189, -0.155, and -0.085 eV when the H₂ is surrounded by $\Theta_{\text{H-atoms}}=0.06, 0.11, 0.17$ and 0.22 ML, respectively. Increasing the H-atoms

coverage value while keeping the all the nearest hollow site filled by H-atoms would not make further change on the adsorption energy of H₂. For example, at 1.0 ML coverage of H-atoms, the adsorption energy of H₂ (-0.080 eV) is very close to that at 0.22 ML coverage (-0.085 eV). From the result of Figure 38 and Figure 41, one can conclude that higher value of H₂ adsorption energy could be obtained at high $\Theta_{\text{H-atoms}}$ if those H-atoms are distributed through the surface and are not surrounding the adsorption site of H₂ molecule. The vice versa is also true, i.e. lower H₂ adsorption energy can be obtained even at low $\Theta_{\text{H-atoms}}$ if those H-atoms surround all nearest hollow sites around the adsorption site of H₂ molecule.

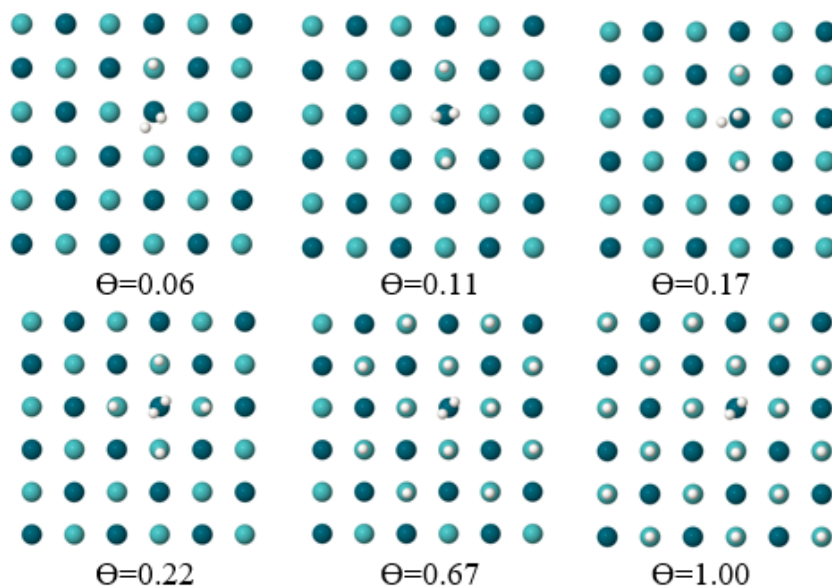


Figure 40. Relaxed location of co-adsorption of H₂ molecule with different coverage of H-atoms based on nearest site to the H₂ (top-view).

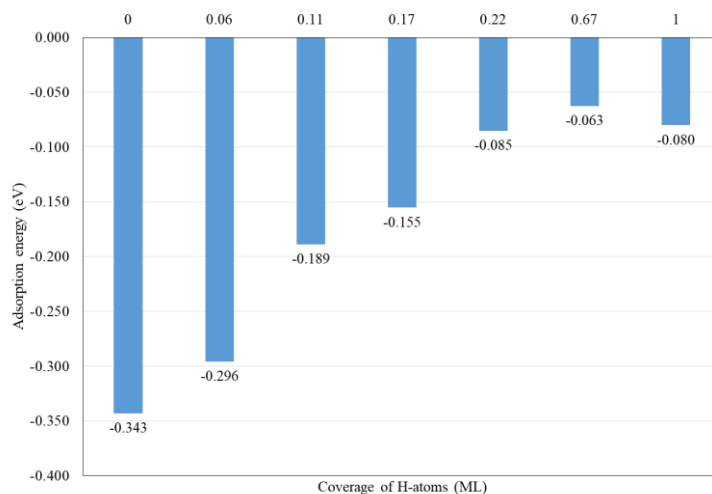


Figure 41. Effect of pre-existing H-atoms coverage on the adsorption energy of H₂ molecule based on filling nearest empty site firstly.

5.4 Adsorption of Poisoning Gases (CO₂, CO, and CH₄)

The presence of poisoning gases might impact the adsorption of hydrogen molecule either by affecting its binding energy to Pd-membrane or by blocking the available adsorption sites. To study this impact we need firstly to know the most probable site and orientation at which these poisoning gases will site on the Pd surface. Figure 42 shows the relaxed structure of CO₂ gas on Pd-surface (100) at different site/orientation. The calculation was performed on slab size of 3x3, but only part of the slab is shown in the picture to get it clear. The corresponding global adsorption energy is displayed in Figure 43. Similar to the physisorption case of H₂, each site/orientation case was evaluated at different distance between the gas and Pd-surface (see SI.Fig.8) seeking for the global adsorption energy (i.e. system with most negative adsorption energy). It noticed that the most negative $E_{\text{ads,CO}_2}$ (-0.255 to -0.250 eV) occurs when C-atom located at hollow sit at a horizontal orientation (i.e. the line connecting O-C-O is parallel to the plane of Pd-surface), followed by cases where C-atom sit at bridge-sit (-0.241 to -0.223 eV), then at top-sit with horizontal

orientation too (-0.215 to -0.212 eV). The vertical orientation (Vz) has the least negative $E_{\text{ads,CO}_2}$ (-0.138 to -0.145 eV). Considering the horizontal orientation of O-C-O, the cases of O-atoms get close to the Pd-atoms (i.e. B.H045, H.H000, and T.H045) give higher $E_{\text{ads,CO}_2}$ compared to cases where O-atoms far away from Pd-atoms. So, if CO_2 is allowed to site freely on Pd-surface (100) would prefer site/orientation of case H.H000 (Figure 42) because it has the most adsorption energy (-0.255 eV). At this location it has a distance of 3.07 Å above the slab. The gas phase of CO_2 has bond length C-O about 1.174 Å and angle of O-C-O around 180°. After the adsorption the bond length remain almost the same (only 0.001 Å variation), while the angle O-C-O shrink slightly by 0.5°.

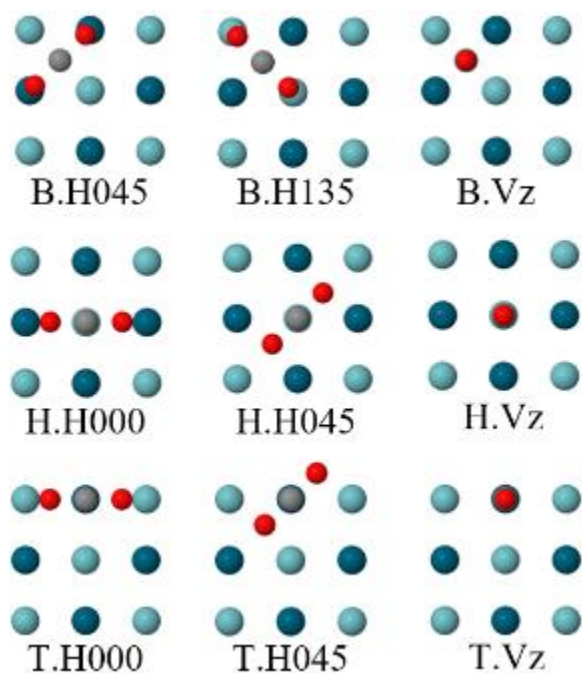


Figure 42. Relaxed structure of CO_2 physisorption on Pd-surface (100) at various site/orientation (top-view).

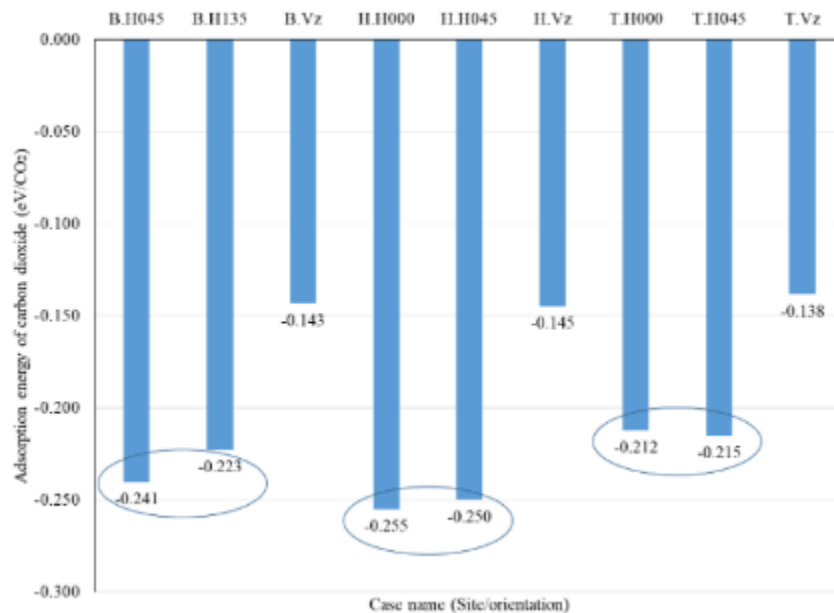


Figure 43. Adsorption energy of CO₂ at various site/orientation (eV/moleculeCO₂).

Another gas that considered highly poisoning for the Pd-membrane is the carbon monoxide (CO). Thus, the adsorption of CO on Pd- surface (100) is also examined at different adsorption sites/orientation (Figure 44.a) and $E_{ads,CO}$ results are summarized in Figure 45. It was noticed that the binding energy of CO on Pd surface become small when the carbon monoxide get adsorbed at vertical orientation with oxygen atom oriented close to Pd-surface (cases on last column of Figure 44.a). For the three adsorption sites of bridge, hollow and top, this vertical orientation gives a binding energy of only 0.117 eV. Meaning that it is less likely for CO to get adsorbed at those sites/orientation. Furthermore, all initial structure of CO at horizontal orientation are relaxed to a vertical orientation with carbon atom close to the Pd surface (see 1st and 2nd columns of Figure 44.a and b). The most negative adsorption energy of CO is about -1.887 eV. It achieved at the bridge site and vertical CO orientation with C-atoms close to the Pd surface (case B.VCdwn) where CO relaxed at 1.51 Å above the Pd-surface. The bond length of C-O slightly elongates after the physisorption process from around 1.140 Å (at gas phase) to about 1.175 Å. Moreover, the

hollow and top sites are also have large adsorption energy, they recorded values of -1.794 and -1.521 eV. Comparing E_{ads} of CO and CO₂, the former has much E_{ads} (-1.887 eV) than the later (-0.255 eV). Thus, CO gas strongly sticks to the Pd-surface than CO₂. The CO gas can stick to the Pd-surface not only at the bridge site, but also at the hollow and the top sites since the adsorption energy is almost equal at the three sites (bridge, hollow, and top). Furthermore, the CO gas get adsorbed at a distance of only 1.1 to 1.5 Å above Pd-surface which is much closer to the membrane than in the case of CO₂ (3.07 Å). When the CO get adsorbed at vertical orientation with O-atoms close to Pd-surface, the distance between CO and Pd-surface become larger (3.0 Å). So, it has low adsorption energy -0.116 eV (Figure 45). In addition, the most $E_{ads, CO}$ on (100) surface of current work is 1.887 eV and it obtained at bridge site, which is slightly smaller than $E_{ads, CO}$ on (111), 2.15 - 2.33 eV [64] for bridge, hollow hcp and hollow fcc sites. Furthermore, the CO adsorption energy (1.68 eV [64]) at top-site of surface (111) seems to be much greater than in surface (100), 0.117 eV. This means that condense Pd-surface of (111) is more vulnerable to carbon monoxide poisoning than surface (100).

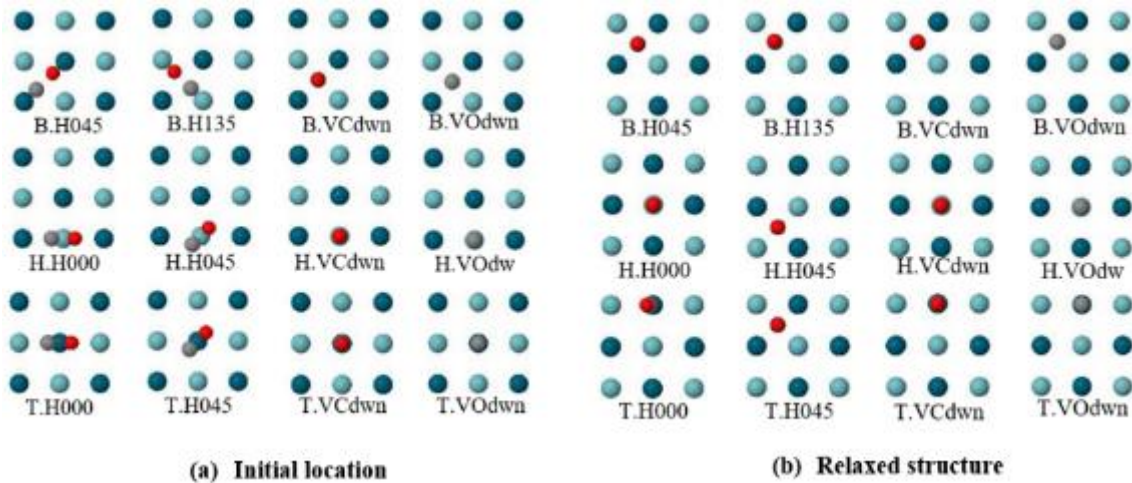


Figure 44. Initial and relaxed structure of CO on Pd-surface (100) at different site/orientation (top-view).

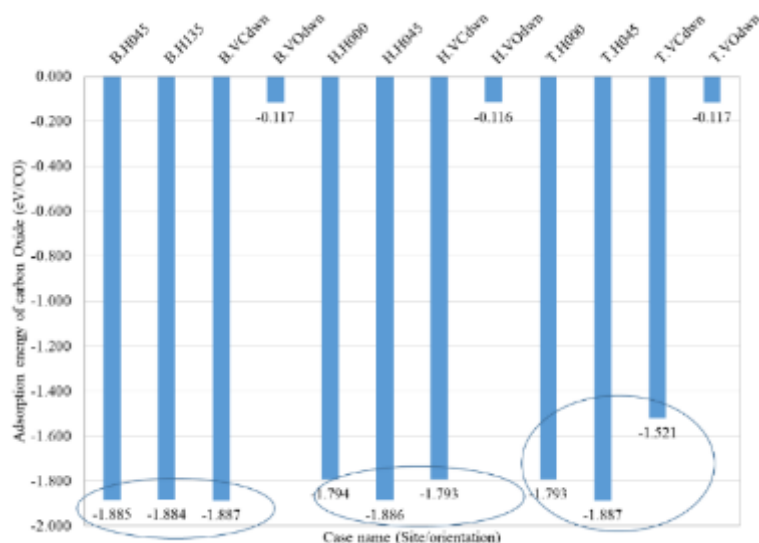


Figure 45. Adsorption energy of CO at various site/orientation (eV/CO)

Further poisoning gas that might affect the adsorption of H_2 is the methane gas (CH_4). The adsorption of this gas could happen at different orientation as depicted in Figure 46. Also, the adsorption of CH_4 was examined at different distance from the Pd-surface (0.5 – 2.00 Å) seeking for the global minimal energy. All cases of various initial distance between Pd-surface and CH_4 are relaxed to produce almost similar results (SI.Table.4).

The results show that regardless of the adsorption sites (B, T, or H), putting the methane molecule in an orientation that have only one hydrogen atom close to the Pd-surface would result in less E_{ads,CH_4} (Figure 46.c and Figure 47). These values are around -0.17 eV for the bridge and hollow-sites and -0.18 eV for the top-site. When the methane gas get adsorbed at the Pd-surface with two or three of its H-atoms facing the Pd-surface, the adsorption energy reach to nearly -0.19 eV. The highest adsorption energy was obtained at the hollow site of the Pd-membrane with three H-atoms close to the membrane (-0.194 eV). Figure 48 shows the site/orientation that gives the most negative adsorption energy of CH_4 . The final

relaxed orientation of other cases are shown in the SI.Fig.10. Jiang et al. [92] reported a very weak adsorption energy for CH₄ at Pd-surface (100), 0.06 eV (top), 0.04 eV (bridge) and 0.03 eV (hollow). For same CH₄ orientation as in [92] (i.e. at top-site with only 1 H-atom close to the Pd-surface, case T.1Hdwn on this paper, see SI.Fig.10) the obtained adsorption energy in current study is much larger (-0.182 eV). They rely weak adsorption energy to ignoring the van der Waal force, which is considered in present work. Comparing the adsorption of CH₄ with CO₂, and CO gas, one can notice that both CH₄ and CO₂ gases get adsorbed at relatively far distance from the Pd-surface, around 2.6 and 3.0 Å, respectively. At these distances, they have low adsorption energy (-0.194 and -0.255 eV, respectively) compared to the CO which get adsorbed at close distance of around (1.1 -1.5 Å) with an adsorption energy of around -1.887 eV. Also, as the methane and carbon dioxide get adsorbed at face distance, there are no any change in their bond lengths or boning angle. The CH₄ keep the bond length of C-H at around 1.1 Å with 109.5° between the H-C-H angles. Similarly, the CO₂ maintains the bond length of 1.174 Å and the angle of 180° between the O-C-O. While for CO, as it interact with the Pd closely, the C-O bond length slightly elongated by around 0.035 Å from its original value of 1.14 Å when the CO is isolated.

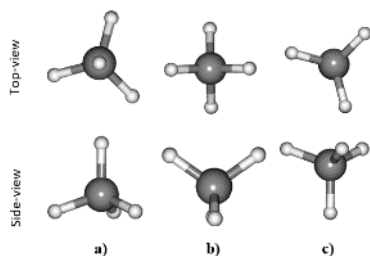


Figure 46. Different orientations of CH₄ gas a) 3-H-atoms down, b) 2-H-atoms down, 3) 1-H-atom down.

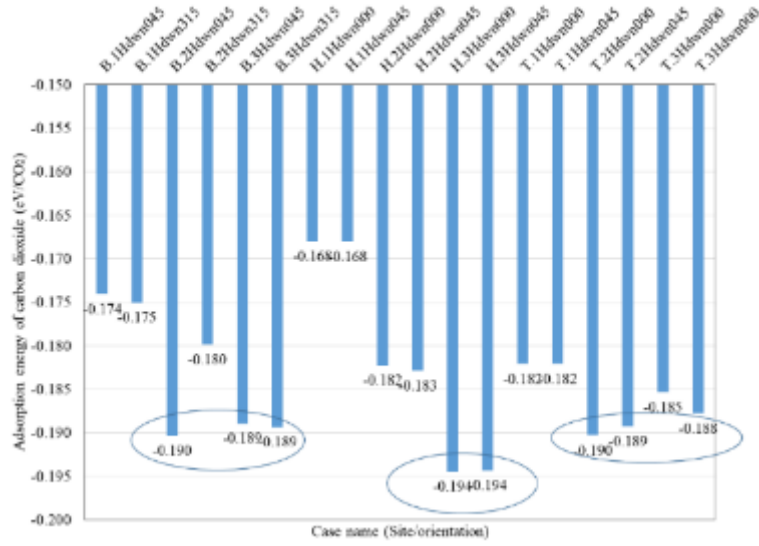


Figure 47. Adsorption energy of CH₄ at various site/orientation (eV/CH₄).

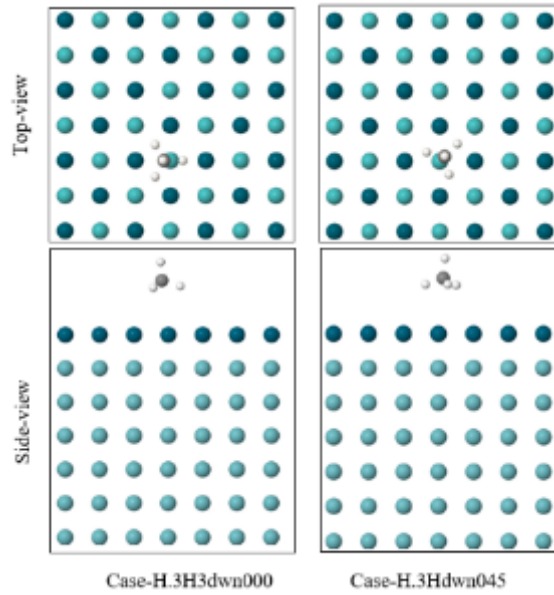


Figure 48. Orientation of relaxed CH₄ on Pd-surface (100) that gives most negative adsorption energy (cases H.3Hdwn000 and H.3Hdwn045)

5.5 Effect of Poisoning Gases on H₂ adsorption Process

In order to study the impact of poisoning gases on adsorption process of hydrogen molecule ($E_{\text{ads,H}_2}$), a slab of Pd-membrane contains both H₂ and one of poisoning gases (CO₂, CO, or CH₄) is prepared. Not only poisoning gases could impact the adsorption of H₂, but also the

pre-dissociated H-atoms have an influence of $E_{\text{ads,H}_2}$. Thus, the study is extended to include both effects (poisoning gases and H-atoms coverage) on $E_{\text{ads,H}_2}$. In previous section, it was shown that the influence of H-atoms coverage appears when H-atoms get adsorbed at the first hollow site to the adsorption site of H_2 . Accordingly, influence of poisoning gas on the $E_{\text{ads,H}_2}$ was constructed by filling the first nearest hollow site to the adsorption site of H_2 by poisoning gas and H-atoms. The adsorption of H_2 at presence of CO_2 , CO , or CH_4 at various coverage of H-atoms is shown in SI.Fig.11,13, and 15. Here, only cases of CO poisoning are presented as it showed the most influence on $E_{\text{ads,H}_2}$.

Figure 49 shows the adsorption of H_2 at presence of CO along with various coverage of H-atoms, while the corresponding adsorption energy of H_2 is shown in Figure 50, and it compared to cases of no-poisoning gases. Highest adsorption energy for H_2 is obtained at absence of any CO or H-atoms (-0.343 eV). In this case, the H_2 molecule is perfectly physisorbed at a top of Pd-atom and interact only with it (Figure 51.a). Once CO gas get present at the Pd-surface, it push the H_2 molecule from the top-Pd-site resulting in an $E_{\text{ads,H}_2}$ of -0.222 eV (34% reduction), where it interacts with two Pd-atoms to reduce system's energy according to the new adsorption site (Figure 51.b). Furthermore, the presence of both CO and H-atoms at the Pd-surface leads to more drop in $E_{\text{ads,H}_2}$. The most significant reduction in $E_{\text{ads,H}_2}$ (56%) occurs when hydrogen molecule get adsorbed between CO gas and two H-atoms ($\Theta_{\text{H-atoms}}=0.11$), where the H_2 adsorption energy recorded only -0.083 eV. When the H_2 get surrounded by 3 H-atoms ($\Theta_{\text{H-atoms}}=0.17$) and one CO gas, the CO gas relaxed at the 2nd nearest bridge site instead of 1st NN hollow site as in other cases. This shifting in adsorption site of CO slightly reduces its impact on adsorption of H_2 and makes $E_{\text{ads,H}_2}$ mainly affected by $\Theta_{\text{H-atoms}}$ rather than poisoning gas. There is only 16% reduction

in $E_{\text{ads,H}_2}$ due to presence of CO at the slab, while the $\Theta_{\text{H-atoms}}$ of 0.17 ML is responsible for 55% reduction in $E_{\text{ads,H}_2}$ as compared to the bare case ($E_{\text{ads,H}_2}$ (no CO & $\Theta_{\text{H-atoms}}=0$) = -0.343 eV). Accordingly, the $E_{\text{ads,H}_2}$ at presence of CO and $\Theta_{\text{H-atoms}}=0.17$ (-0.130 eV) showed greater value corresponding value at $\Theta_{\text{H-atoms}}=0.11$ (-0.083 eV) because of the site shifting of CO from hollow site to bridge site.

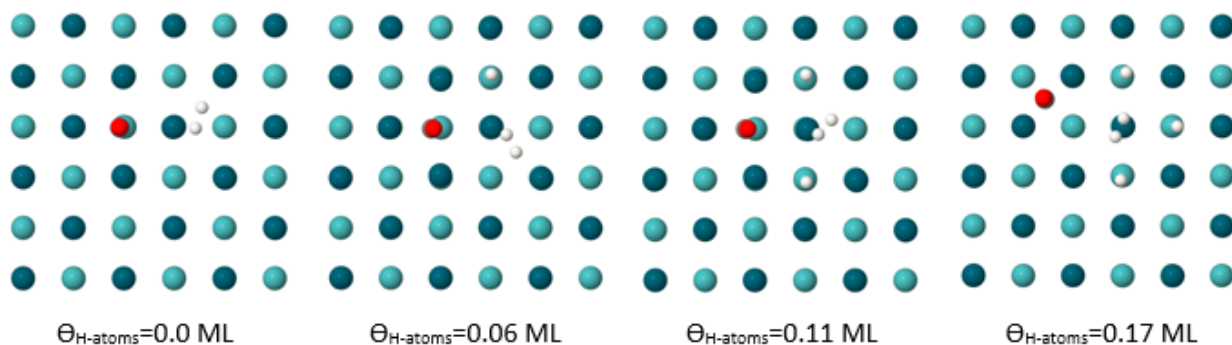


Figure 49. Relaxed locations of co-adsorption of H₂ with CO at various coverage of H-atoms.

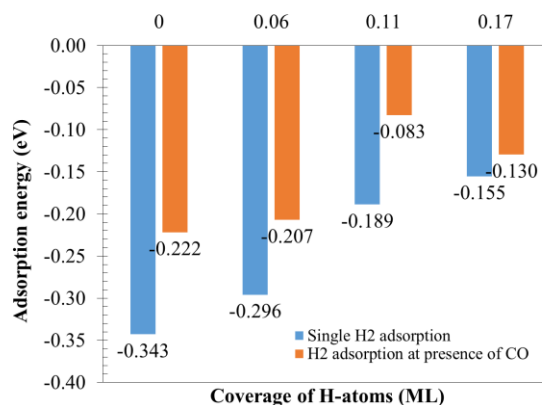


Figure 50. Comparison of $E_{\text{ads,H}_2}$ with and without poisoning of CO at various coverage of H-atoms.

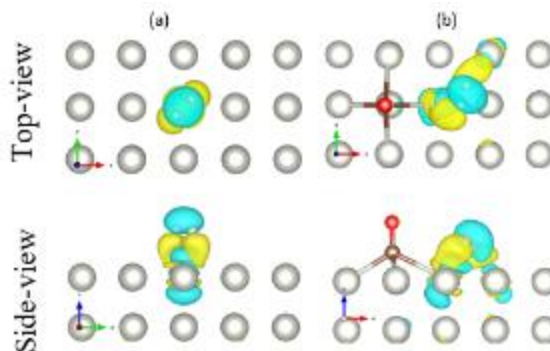


Figure 51. Charge density difference of H₂ at absence/presence of CO (Isosurface at 0.003).

Moreover, similar analysis of H₂ adsorption was performed at presence of CO₂ and CH₄ and the results are summarized in Figure 52. Among the three poisoning gases (CO, CO₂ and CH₄), carbon monoxide has the most negative impact on reducing E_{ads,H2}. Expect at high hydrogen coverage ($\Theta_{\text{H-atoms}}=0.17$ ML) where both CO₂ and CH₄ has more influence in reducing E_{ads,H2} than CO which moves away from H₂ adsorption site, so it has less impact as discussed previously. At $\Theta_{\text{H-atoms}}=0$ ML, the presence of CO₂ or CH₄ slightly diminishes the E_{ads,H2} by about 7.5% as compared to the case of single H₂ adsorption. While at high value of $\Theta_{\text{H-atoms}}=0.17$ ML, CO₂ reduces the E_{ads,H2} by 23% and CH₄ by 57%. At this coverage value of H-atoms, the methane gas relaxed approximately at the 1st NN hollow site to H₂ adsorption site, not like CO and CO₂ which tend to move away from the hollow site (see SI.Fig.11, 13, 14). The case of H₂ adsorption at presence of CH₄ with $\Theta_{\text{H-atoms}}=0.11$ ML shows an exceptional value of E_{ads,H2}, where it deceptively reflects that the presence of CH₄ could increase the adsorption of H₂ (from -0.189 to -0.261 eV). In fact, one of the H-atoms was not relaxed at the hollow site, instead, it get relaxed at the bridge site after the adsorption of H₂ molecule on the surface (Figure 53). Also, it worth to mention that when CO₂ is oriented as in Figure 42, case H.H000, the physisorption of H₂ molecule didn't detected. Instead, one of the hydrogen atoms of H₂ molecule interacted with the CO₂ while the other got relaxed at the Pd-surface (SI.Fig9). This indicates that poisoning gases do not only reduce the adsorption energy of H₂ molecule or blocking available adsorption sites, but it can poison the surface by means of capturing H-atoms and prevent them to diffuse to the bulk material.

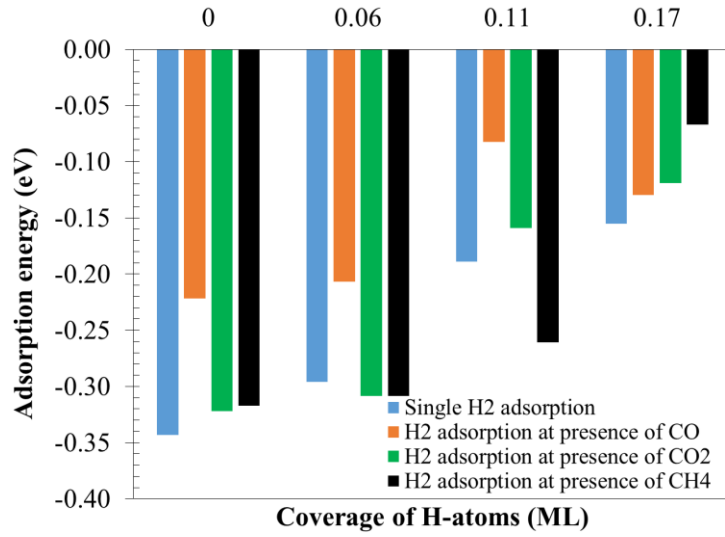


Figure 52. Impact of different poisoning gases on E_{ads,H_2} at various coverage of H-atoms.

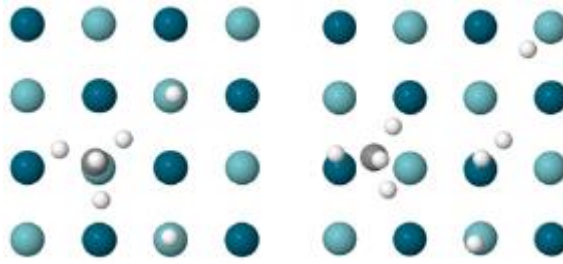


Figure 53. Relaxed structure before and after H₂ adsorption at presence of CH₄ and $\Theta_{H-atoms}=0.11$ ML.

5.6 Effect of CO Coverage of H₂ Adsorption Process

Furthermore, the impact of carbon dioxide coverage on adsorption of hydrogen molecule was investigated. In previous sections, it was shown that the effect of hydrogen coverage becomes significant when hydrogen atoms located at nearest neighboring sites to adsorption site of H₂ molecule. Accordingly, to reflect the impact of CO coverage (θ_{CO}) on H₂ adsorption energy (E_{ads,H_2}), the CO molecules are initially distributed at the first nearest neighbor of hollow sites surrounding the H₂ molecule as indicated in Figure 54. However after atoms relaxation, some of CO molecules change their initial located sites (i.e. hollow-site) to a bridge-sits Figure 55. The results of hydrogen adsorption energy for various

coverage of carbon monoxide are summarized in Figure 56. At bare slab (i.e. no poisoning gas), the H_2 molecule get adsorbed perfectly at Pd-top site and the E_{ads,H_2} is the highest (-0.343 eV). The presence of only one molecule of CO, which corresponds to $\theta_{CO} = 0.06$ ML, reduces the E_{ads,H_2} to -0.222 eV as CO relaxed at 1st NN hollow site. This site is very close to the H_2 molecule, hence, CO gas force the hydrogen molecule to slightly moves away from Pd-stop site (Figure 55, $\theta_{CO}=0.06$ ML). Increasing the number of CO that surrounding the H_2 to be two molecule of CO, results in balancing the H_2 molecule around the Pd-top site as each CO molecule try to push the H_2 toward the other side (Figure 55, $\theta_{CO}=0.11$ ML). So, the hydrogen adsorption energy jumps to -0.303 to -0.319 eV. The higher value belongs to the case where the three molecule align at straight line. In this case, the H_2 molecule perfectly physisorbed at Pd-top site and the CO molecules relaxed the 2nd NN bridge-site, so it would have more interaction with Pd-atom leading to higher adsorption energy. Moreover, doubling the number of CO gas to be 4 molecules sustain the balance of H_2 molecule to be physisorbed perfectly at Pd-top site (Figure 55, $\theta_{CO}=0.22$ ML). All of the four molecule of CO gas relaxed the 2nd NN bridge-site, but it still affecting the interaction of H_2 molecule with Pd-atom. Thus, the E_{ads,H_2} reduces to -0.280 eV which is lower than in case of bare Pd-slab by around 0.063 eV. On other hand, if the hydrogen molecule physisorbed at a middle of three CO molecules, which corresponds to $\theta_{CO} = 0.17$ ML, the H_2 molecule deviate from the Pd-top site as one of the three CO molecules relaxed at the 1st NN hollow site close the H_2 molecule. This case is the worst scenario for hydrogen physisorption where only -0.095 eV is obtained as adsorption energy.

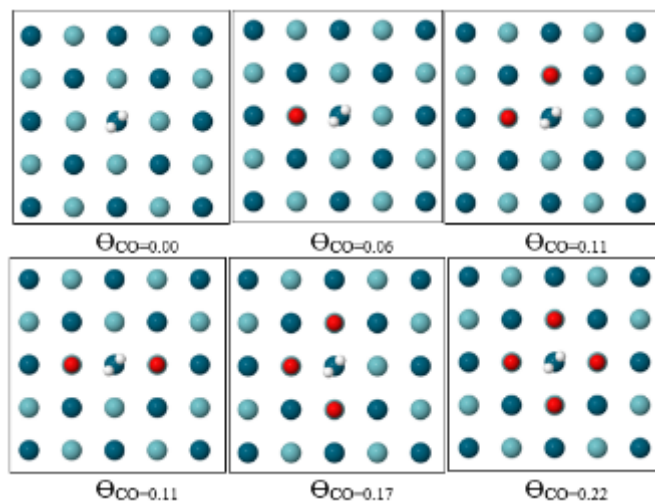


Figure 54. Initial locations of H₂ adsorption at various coverage of CO (ML).

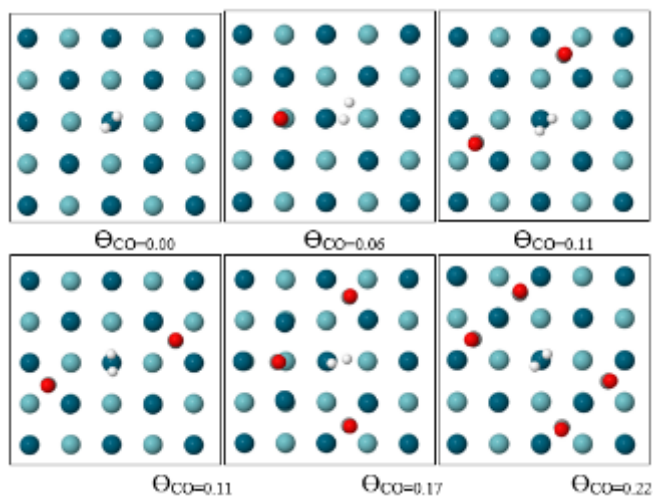


Figure 55. Relaxed structure of H₂ adsorption at various coverage of CO (ML).

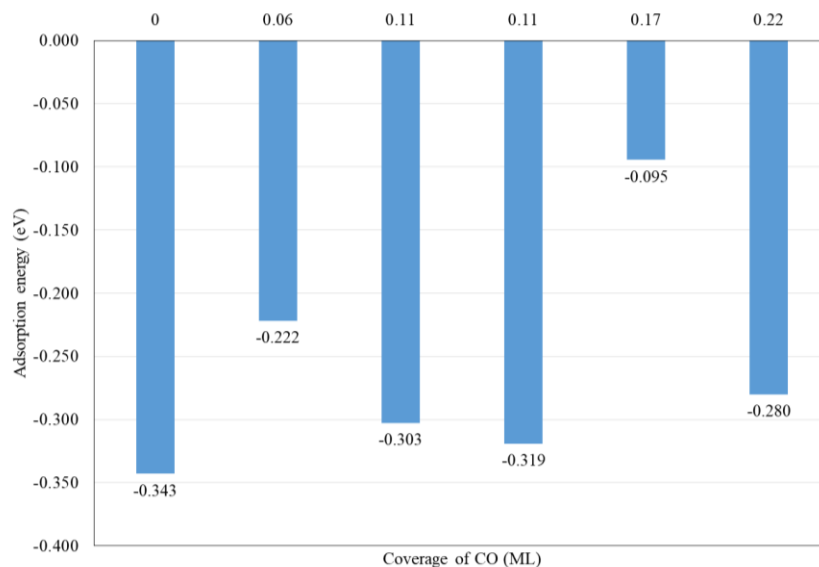


Figure 56. Adsorption energy of H₂ at various coverage of CO.

5.7 Dissociation of H₂ molecule on Pd-Surface

The dissociative process of hydrogen molecule (H₂) to two hydrogen atoms is investigated through nudged elastic band method, so the minimum energy barriers required for the process could be obtained. This method is used to catch saddle points and minimum energy paths between known reactants and products by optimizing a number of intermediate images along the reaction path. Each reaction image along the pathway of the dissociation process would have the lowest possible energy. Accordingly, the initial and final states of the hydrogen dissociation process have to be known. The initial state, or the reactants, is the physisorption of H₂ molecule on the Pd-surface, while the final state of H₂ dissociation process is the chemisorption of two H-atoms (products) on the Pd-surface. The initial state is considered to be the case with most negative physisorption energy (i.e. case T.Hxy). Regarding the final state of H₂ dissociation process, there are various combination for the dissociated atoms to site on the empty neighboring sites surrounding the H₂ adsorption-site

(Figure 57). In total, there are 14 combinations where two H-atoms can fill those 16 sites (shown in Figure 57) after eliminating symmetrical cases. The case with the most negative chemisorption energy is selected as the final state for the H₂ dissociation process. This method will give the maximum energy barriers for dissociation and association process. Table 7 summarizes the chemisorption energy of two hydrogen atoms at different sites shown in Figure 57. It can be noticed that the most preferable chemisorption sites for two hydrogen atoms are hollow sites that opposite each other's (site 1 & 5 on Figure 57). It has an adsorption energy of -0.857 eV. Then, it followed by adsorption energy of -0.833 eV, where one of the H-atom is located hollow sites close to each other's (site 1 & 3 on Figure 57) or one H-atom at a hollow site and the next one at far edge site (site 1 & 11, and 1 & 12 on Figure 57). When the two hydrogen atoms are located very close to each other, at a hollow site and its 1st neighbor bridge site (site 1 & 2 on Figure 57), the H-atom on the bridge site move to the next hollow site (site 1 & 3) and shows similar adsorption energy (-0.833 eV). All other cases has an adsorption energy of around -0.827 eV, except the configuration where the two H-atoms are located at bridge site opposite to each other (site 2 & 6 on Figure 57) which showed the lowest adsorption energy of -0.807 eV. The relaxed structures for all 14 combinations are represented in SI.Fig.17. Accordingly, the H₂ dissociation process is considered to start from the H₂ physisorption (case T.Hxy) and finished by chemisorption of two H-atoms at hollow sites as in the configuration of (site 1 & 5).

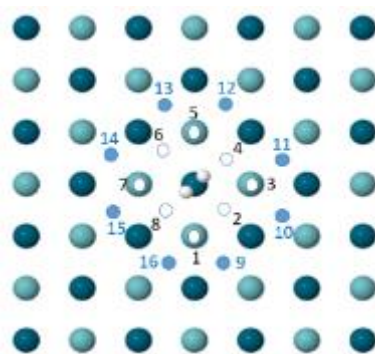


Figure 57. Available local sites for final stage of dissociation process on Pd(100).

Table 7. Chemisorption energy of two H-atoms at various sites shown on Figure 57.

Site	$E_{\text{adsorption}}$ (eV/H ₂ molecule)	Site	$E_{\text{adsorption}}$ (eV/H ₂ molecule)
1 & 05	-0.857	2 & 12	-0.827
1 & 2	-0.833	9 & 14	-0.827
1 & 11	-0.833	9 & 11	-0.827
1 & 12	-0.832	2 & 13	-0.827
1 & 3	-0.832	9 & 13	-0.826
1 & 10	-0.828	9 & 12	-0.826
1 & 4	-0.828	02 & 06	-0.807

Figure 58 shows the energy curve for 10 images of reaction coordinates starting from H₂ as a molecule (image 1) until it fully dissociated to two H-atoms (image 10). The adsorption energy of the hydrogen at image 1 is -0.343 eV (physisorption of H₂) while at image 10 it is -0.857 eV. The transition state for this dissociation reaction is image 3 which has the least stable state (-0.11 eV). It is required for the hydrogen molecule to have a 0.233 eV as an activation energy to overcome this barrier state and dissociate to a more stable state (image 10). Before the dissociation process reach to final state of image 10, it counters another small barrier (0.022 eV) at reaction coordinate of image 7. In order to understand reasons behind the energy barriers appears the dissociation process, all the reaction coordinates are drawn in one figure and the electron density of each reaction coordinate is

calculated and presented in Figure 59 and Figure 60 (and SI.Fig.18), respectively. At the beginning of the process, image 1, there is a positive charge density difference around the hydrogen molecule indicating that the electron is exchanging between the H-atoms of H₂ molecule. As the dissociation reaction continue, the distance between hydrogen atoms increases. As we move from image1 to image3 of reaction coordinates, the size of positive charge density difference around H₂ molecule increases due to the increase in the bond-length between H-atoms. This means, up to image3, the two hydrogen can see each other and interact together, however, that state is not stable. By reaction coordinate of image4, the positive charge starts to decrease indicating that we are losing the interaction between the H-atoms. Thus, H₂ is dissociated and each one of the hydrogen atom is seeking for a new stable location in the Pd surface. With refer to Figure 59, after the H₂ molecule get dissociated, the H-atoms keep move in a direction aligned with the bridge line connecting the Pd-atoms, and at same time it interacts with Pd-atom at the 1st nearest neighbor on that direction. Once the dissociation process reaches a reaction coordinate of image7, the hydrogen atom changes its direction and moves toward the hollow site. This change in direction has to overcome the interaction that have been built between H-atom and Pd-atom of 1st nearest neighbor. Accordingly, a small energy barrier appear at that point. On other hand, large value of activation energy is required to associate the two H-atoms to form H₂ molecule (0.748 eV). It is logical because hydrogen atoms are moving from most stable state (image10 which represent a chemisorption state) to a less energy state (image1 which is physisorption state). This process happens on the other side of the Pd-membrane which is a reverse process of H₂ dissociation.

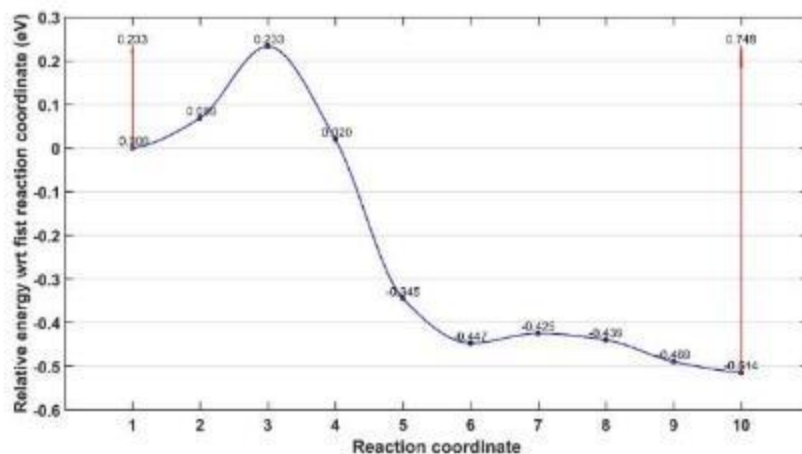


Figure 58. Energy curve during dissociation process of H_2 to two of H-atom on bare Pd-surface (100).

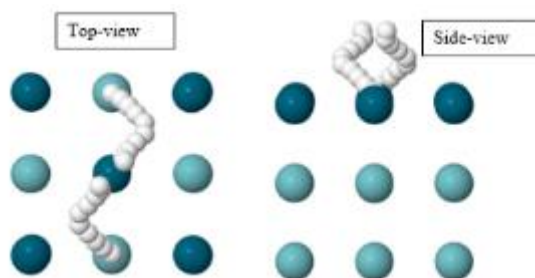


Figure 59. Pathway of H_2 dissociation process on bare Pd-surface (100).

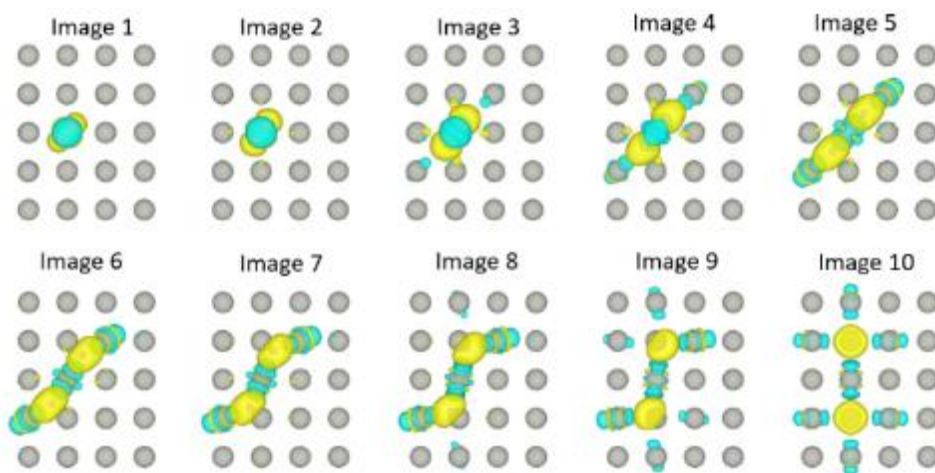


Figure 60. Isosurface of charge density difference for reaction coordinates of H_2 dissociation “blue: +ve charge, and yellow: -ve charge” (top-view).

The dissociation process of hydrogen molecule is highly affected by presence of poisoning gases.

In addition, the dissociation of hydrogen molecule at presence of CO poisoning gas is investigated. The atom structure pathway for this process is illustrated in the SI.Fig.20 while the reaction coordinates for the process is indicated in Figure 61. The first reaction coordinate (image1) in the figure refer to the physisorption of H₂ molecule on the Pd-surface that poisoned by CO gas. At this state, the H₂ molecule has weak adsorption energy (-0.222 eV). At image1, the bond length between H-H is around (0.90 Å) which is slightly stretched out compared to the case of physisorption at bare Pd-surface (0.85 Å) and it is little bit longer H₂ bond length in gas phase (0.75 Å). However, the two H-atoms remain as H₂ molecule as it can be seen from their charge density (Figure 62). As the H₂ molecule dissociates, no energy barrier appears until reaction coordinate of image5 where the H₂ molecule splits completely to two separate H-atoms. Similar to the case of H₂ dissociation at bare Pd-surface, a small energy barriers of 0.016 eV occurs at image7 when the H-atoms change their direction in the dissociation process and move toward hollow-sites (SI.Fig.21). This barrier is required to break the interaction that developed between dissociated H-atoms and Pd-atoms when H-atoms are located in the bridge-site. The dissociation of H₂ molecule on Pd-surface poisoned by CH₄, also show similar phenomenon. Around 0.018 eV is required to break the interaction developed between H-atoms and Pd-atoms when H-atoms move from bridge-site to the hollow-site. Also, a small energy barrier is required to break the H₂ bond during the dissociation (0.024 eV). In contrast the energy barrier required for the association process is very large whether the surface is clear or poisoned by a gas. These energy barriers for hydrogen association are

0.748, 0.600 and 0.561 eV for clean Pd-surface, CO and CH₄ poisoned surface, respectively.

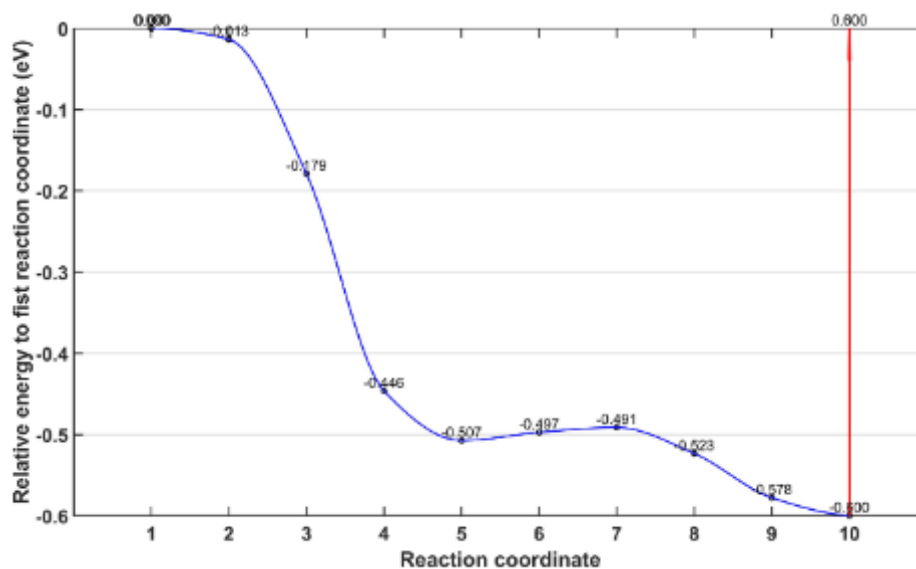


Figure 61. Energy curve during dissociation process of H₂ to two of H-atom on bare d-surface poisoned by CO gas.

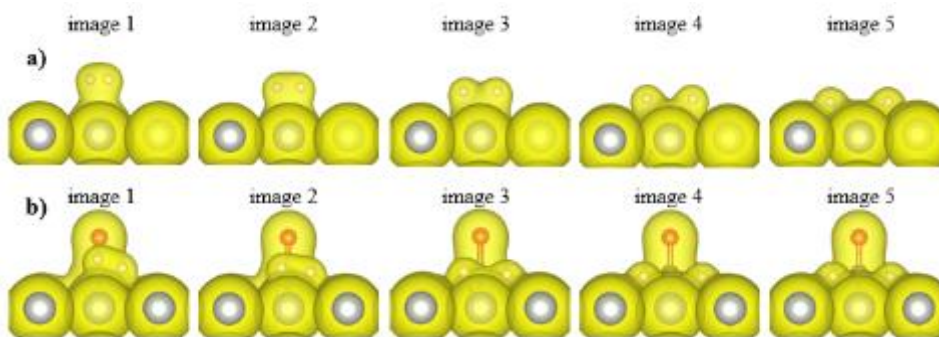


Figure 62. Charge density difference for dissociation process on a) bare Pd-surface b) Pd-surface poisoned by CO (iso-surface at 0.05).

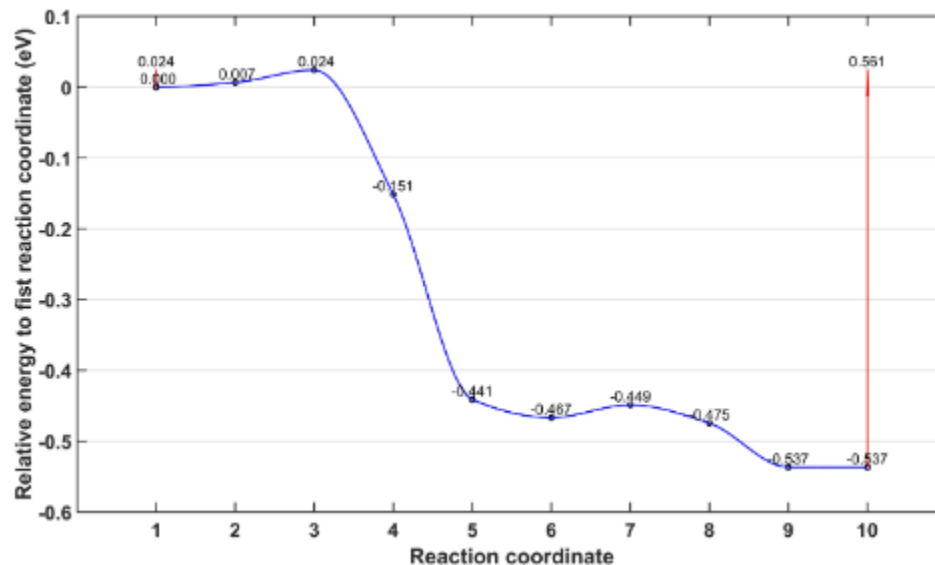


Figure 63. Energy curve during dissociation process of H_2 to two of H-atom on bare d-surface poisoned by CH_4 gas.

5.8 Diffusion of H-atom on Pd-bulk Membrane

In order to study the diffusion of hydrogen atom through a Pd-bulk, a super-cell (3x3x3) is prepared. The study considered the hydrogen diffusion at a Pd-bulk membrane at low and high concentration of hydrogen (1% and 25% at.). There are three possible pathways where hydrogen atom may follow to diffuse through the FCC bulk material of Pd-membrane; it may jump between two octahedral sites (O-O pathway), jump between two tetrahedral sites (T-T pathway), or jump between octahedral-and-tetrahedral sites (O-T pathway) until it pass all the bulk material. Figure 64 shows the O-T pathway of hydrogen diffusion at 1 and 25% at. concentration of hydrogen. Detailed pathways of O-O, T-T, and O-T are shown in SI.Fig.23. To make the picture clear in Figure 64, a small cell of Pd-atoms centered at the middle of the super-cell is highlight by dark color while others Pd-atoms are

presented in translucent light color to show the H-atoms inside the bulk membrane. It was noticed that the three pathways are almost straight line and they have length of 2.792, 1.974, and 1.710 Å for O-O, T-T, and O-T pathways. While the H-atom moves between the two sites it interact with Pd atoms resulting in slightly movement of Pd atom located around hydrogen atom. The energy curves at low hydrogen concentration (1% at.) for the three pathways are depicted in Figure 65. These energy values are referenced to the system energy when H-atom is located in O-site. According to the reaction pathway, the activation energy required for hydrogen atom to move between octahedral sites of Pd atoms, O-O, is 0.477 eV which is slightly greater than the barrier required for the movement between tetrahedral sites, T-T pathway, (0.434eV). On the other hand, the pathway of O-T shows lower energy barrier than both cases of O-O and T-T. Also, it is clear from the curve that moving from the octahedral site to tetrahedral site (O-T) required 0.166 eV, while the reverse pathway from tetrahedral to octahedral site (T-O) required only 0.123 eV which is smaller than energy barrier for (O-T). This happens because tetrahedral site is more energetic than octahedral site. Moreover, the diffusion of hydrogen under high concentrations (25% at.) was carried out by placing 27 H-atoms in the 3x3x3 super-cell. Those H-atoms are placed at the O-site as it is more favorable than T-site. Only one H-atom is allowed to diffuse through O-O, T-T, or O-T pathways while the other H-atoms as relaxed at the O-site. The activation energy values for the three pathways are increased compared to corresponding cases at low hydrogen concentration. The recorded values are 0.557, 0.422, and 0.249 eV for O-O, T-T, and O-T pathways, respectively (Figure 66).

The presence of many H-atoms distributed through the bulk material limit the movement of Pd-atoms when H-atom jumps between sites. Accordingly, higher repulsive force occurs at high hydrogen concentration which leads to higher energy barriers. In addition, a rigorous case of hydrogen diffusion at high concentration (25% at.) is investigated. In this case, all the 27 H-atoms in the 3x3x3 super-cell are moving synchronously at the same pathway. This will generate high repulsive force between Pd and H-atoms, and hence, the obtained energy barrier could represent the limit energy barrier at 25% at. concentration of H-atoms. This case can be simulated by a unite cell containing 4 Pd-atoms and 1 H-atom with periodic boundary condition in the three directions as shown in Figure 67. The reaction coordinates for the three pathways when all hydrogen atoms move synchronously are indicated in Figure 68. The energy barrier increase by about 34% and 55% for O-O and T-T pathways as compared to the case with same atomic concentration but only one H-atom is moving. On other hand, only 2% increase in barrier energy is recorded for the O-T pathway due to rigorous assumption of all H-atoms move synchronously. In all investigated cases the pathway of O-T has the lowest energy barrier so it is the more likely pathway for hydrogen diffusion. Comparing the energy barrier for this pathway to the experimental value of 0.23 eV [43], we estimated an energy barrier of 0.166 eV at low hydrogen concentration (1% at.), which less than the experimental value. Considering higher hydrogen concentration (25% at.) leads to over estimation for the diffusion barrier (0.254 eV) if all H-atoms are assumed to be moving at synchronize way. When only one H-atom is allowed

to move while the rest H-atoms are fixed in the O-sites, the predicted activation barrier is very close to the experimental value (0.249 eV, 8% error).

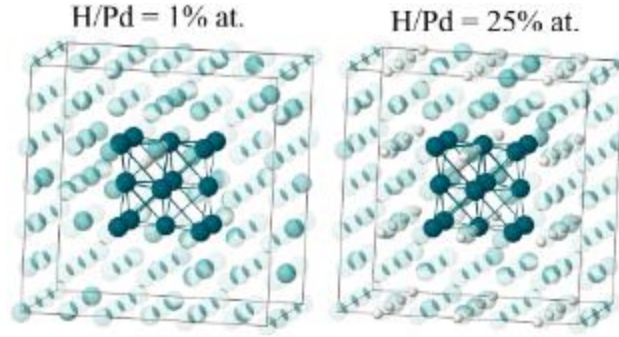


Figure 64. Hydrogen diffusion through O-T pathway at different concentrations (3x3x3 cell size).

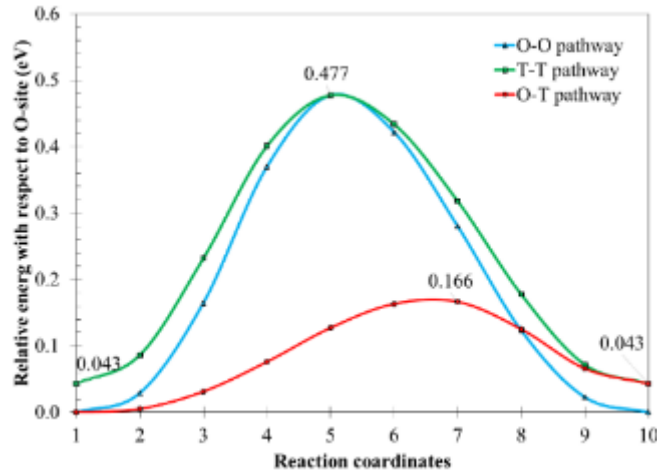


Figure 65. Comparison of energy curves for H-atom diffusion through different pathways at 1% at. concentration (cell size 3x3x3).

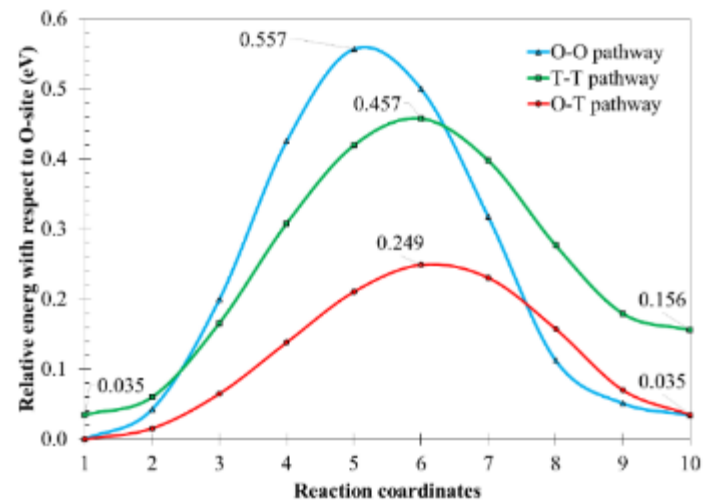


Figure 66. Comparison of energy curves for H-atom diffusion through different pathways at 25% at. concentration (cell size 3x3x3).

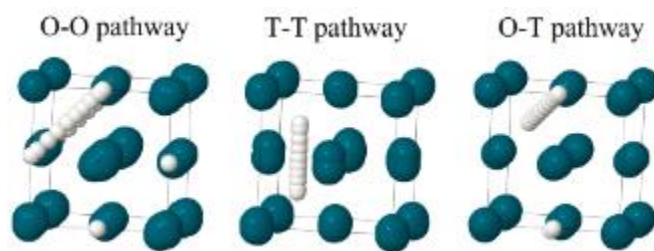


Figure 67. Hydrogen diffusion through various pathways at 25% at. concentration (cell size 1x1x1).

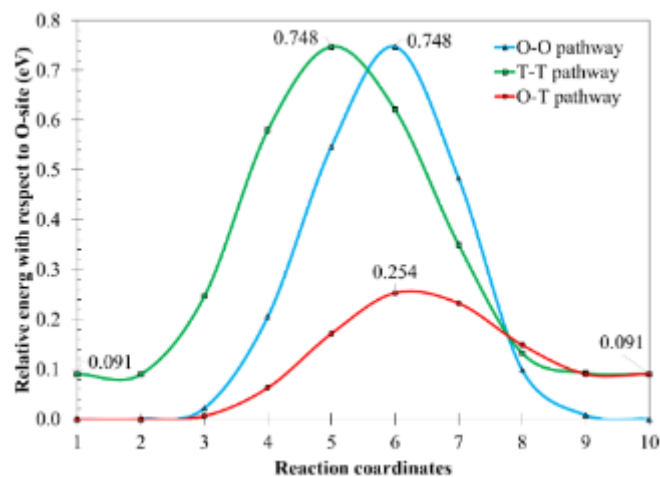


Figure 68. Comparison of energy curves for 25% at. concentration H-atom all diffusion synchronously through different pathways (cell size 1x1x1).

CHAPTER 6

HYDROGEN PERMEATION ON PdAu-MEMBRANE

This chapter deal with the permeation processes on PdAu-alloy. The surface processes of adsorption and dissociation are considered along with their reversed processes of hydrogen desorption and association. Furthermore, the bulk process of hydrogen diffusion through the bulk alloy of PdAu is investigated.

6.1 Adsorption of H₂ molecule on PdAu-Surface

The physisorption of H₂ molecule on a dilute surface of Pd-Au-alloy containing 5% Au is evaluated at different sites (bridge, hollow, and Pd-top) and various molecule orientations. The adsorption energy of H₂ molecule is evaluated based on how far the adsorption site from the Au-atom (i.e. based on nearest neighbor site to Au-atom) as shown in Figure 69. Also, the adsorption of H₂ molecule on Au-top is considered and compared to other cases. For each one of the sites shown in Figure 69, different molecule orientation is examined (Figure 70) at various distance from the PdAu-surface. The results of adsorption energy at various site/orientation/distance-from-surface and their corresponding bonding length of H₂ are summarized in Table 8 and Table 9.

It was noticed from the results that putting the H₂ molecule initially at the hollow sites do not capture the physisorption of the H₂. Considering that the bonding length of H₂ molecule in gas phase (0.75 Å) and after physisorption this bonding length might get elongated up to 0.90 Å. Thus, any bonding length of H₂ molecule greater than this range indicates that either the hydrogen molecule is dissociated or in a transition state of dissociation process.

Locating the hydrogen molecule initially at the hollow sites (H1, H2, and H3 Figure 69) results on bonding length greater than 2.4 Å for most of the studied cases. Only three cases of H₂ physisorption on 1st nearest hollow site to Au-atom (H1 Figure 69) was capable of capturing the H₂ molecule physisorption (adsorption energy around -0.340 eV). These cases are H1.H000, H1.H045, and H1.Vz with initial distance between H₂ molecule and PdAu-surface ($d_{z-PdAu-H_2}$) of 1.5, 1.5, and 0.5 Å. However, the H₂ molecule moves to the Pd-top-site instead of being relaxed within the hollow site (Figure 71). Relaxing the system structure with an initial value of $d_{z-PdAu-H_2}$ other than values stated above leads to either a dissociated H₂ molecule to two H-atoms or a weak adsorption of H₂ (-0.065 to -0.095 eV). Similar notice was observed when H₂ molecule was initially located at bridge sites (B1, B2, and B3). In all cases that showed strong physisorption of H₂ molecule (~ 0.30 eV), the H₂ molecule get relaxed at a Pd-top-site however it was initially located at bridge-site (Figure 72). The other cases in which H₂ molecule physisorped at the bridge-site reflected a weak value adsorption energy (-0.083 to -0.175 eV) with some exceptional cases. For instant, locating the H₂ molecule initially at second nearest bridge site (B2) with horizontal molecule orientation perpendicular to the bridge line (case B2.H135) at initial distance of 1.0 Å from the surface (i.e. $d_{z-PdAu-H_2}$) results in an adsorption energy of -0.32 eV. For the same site (B2) with the horizontal molecule orientation, if the hydrogen molecule is aligned to the bridge-line instead of being perpendicular to it (case B2.H045), the adsorption energy become very small (-0.17 eV). On the other hand, when the hydrogen molecule is located at Pd-top-site (T1, T2, T3), strong physisorption (-0.334 to -0.347 eV) was detected. The highest H₂ adsorption energy (-0.347 eV) was recorded at 2nd nearest Pd-top-site with horizontal orientation (case T2.H045).

To identify the impact of alloying top-layer of Pd-surface with Au-atom on H₂ adsorption energy, the most negative adsorption energy of each site/orientation case on PdAu-surface is compared to that on pure-Pd-surface. Starting by the bridge-site, all molecule orientations cases on pure-Pd-surface recorded weak physisorption energy (-0.095 and -0.170 eV for vertical orientation and horizontal orientation with H₂ molecule aligned to the bridge-line, respectively). While the horizontal molecule orientation with H₂ perpendicular to the bridge-line has less stable configuration, since the relaxed structure showed a dissociation to two hydrogen atoms instead being physisorbed even at different distances between H₂ and the slab ($d_{z-PdAu-H_2}$). In the PdAu-surface, the vertical orientation of H₂ has also small adsorption energy (-0.095 eV) at 1st, 2nd, and 3rd nearest bridge sites (i.e. B1, B2, and B3-sites), and it becomes weaker at the first nearest bridge site (B1) (-0.089 eV). Also, locating the hydrogen molecule at B1 make it has a tendency to get adsorbed close to the nearest Pd-top site. Only the second nearest bridge site was able to get higher physisorption energy (-0.320 eV). Regarding the physisorption of H₂ on the hollow-site, both pure-Pd and PdAu surfaces showed weak adsorption energy (-0.095 eV). Nevertheless, on the PdAu surface some cases on the first nearest hollow site (H1) showed stronger physisorption energy, but the hydrogen molecule was relaxed at location close to Pd-top-site rather than on a hollow-site. On the other hand, the Pd-top-site showed the most negative adsorption energy for both pure-Pd and PdAu surfaces. The adsorption energy on the second nearest Pd-top-site on PdAu surface (-0.347 eV) is slightly larger than corresponding values at first nearest Pd-top-site (-0.336 eV), third nearest top-site (-0.343 eV) or on top-site on pure-Pd-surface (-0.343 eV). While the adsorption energy on the Au-top-site is very weak (-0.056 to -0.076 eV) depending on the H₂ orientation. Accordingly, it can be concluded that

the presence of Au-atom on the top-layer of the Pd-surface leads to slightly increase in the adsorption energy on the second nearest Pd-top-site and it offer a possibility for hydrogen molecule to be physisorbed at the second nearest bridge site.

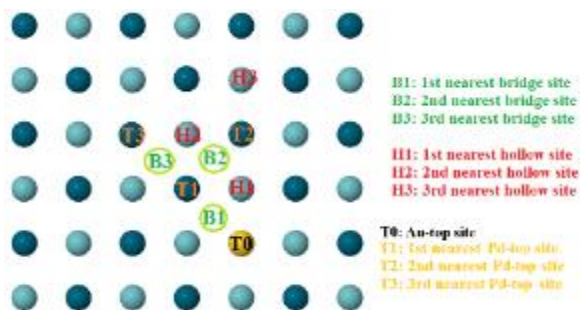


Figure 69. Adsorption sites location on PdAu surface.

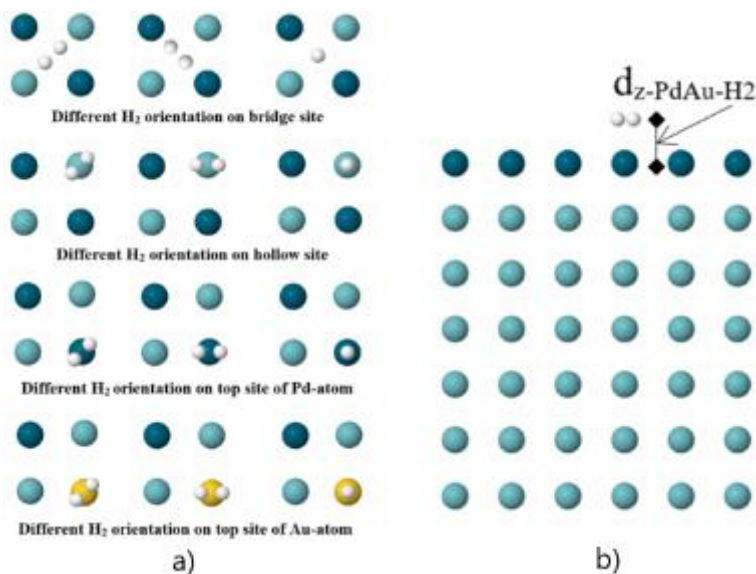


Figure 70. Available adsorption site/orientation of H₂ molecule on PdAu surface a) Top-view; only part of the slab is shown. b) Side-view.

Table 8. Adsorption energy (eV) of H₂ on PdAu-surface (100) at various sites and orientations.

Site/orientation	H ₂ initial distance from PdAu-surface (Å)				
	0.0	0.5	1.0	1.5	2.0
B1.H045	-	-	<u>-0.334</u>	-0.328	-0.083
B1.H135	-	-0.336	-0.338	<u>-0.339</u>	-
B1.Vz	-	<u>-0.337</u>	-	-0.089	-0.086

B2.H045	-	-	-	-0.170	-0.171
B2.H135	-	-	-0.320	-	-
B2.Vz	-0.363	-	-0.095	-0.095	-0.099
B3.H045	-0.846	-0.845	-0.845	-	-
B3.H135	-	-0.330	-0.174	-0.175	-0.336
B3.Vz	-0.370	-	-0.096	-0.096	-0.100
H1.H000	-0.779	-0.776	-0.776	-0.342	-0.065
H1.H045	-0.659	-0.658	-0.659	-0.338	-0.069
H1.Vz	-	-0.342	-0.097	-0.087	-0.090
H2.H000	-	-0.771	-0.771	-	-0.071
H2.H045	-0.813	-0.812	-0.814	-0.813	-0.069
H2.Vz	-	-	-0.095	-0.093	-0.095
H3.H000	-	-	-0.781	-	-0.069
H3.H045	-0.812	-0.812	-0.812	-0.812	-0.069
H3.Vz	0.249	-	-0.095	-0.093	-0.093
T0.H000	-	-0.061	-0.061	-0.056	-
T0.H045	-	-	-0.061	-0.056	-
T0.Vz	-	-0.078	-0.074	-0.075	-
T1.H000	-0.336	-0.335	-0.337	-0.334	-
T1.H045	-0.334	-0.335	-0.336	-0.334	-
T1.Vz	-0.339	-0.115	-0.116	-0.119	-
T2.H000	-0.344	-0.345	-0.346	-0.346	-
T2.H045	-0.345	-0.345	-0.347	-0.347	-
T2.Vz	-0.345	-0.114	-0.116	-0.118	-
T3.H000	-0.341	-0.341	-0.342	-0.342	-
T3.H045	-0.34121	-0.342	-0.343	-0.343	-
T3.Vz	-0.3413	-0.113	-0.115	-0.118	-

Table 9. Bonding length (Å) of H₂ on PdAu-surface (100) at various sites and orientations.

Site/orientation	H ₂ Initial distance from PdAu-surface (Å)				
	0.0	0.5	1.0	1.5	2.0
B1.H045	-	-	0.84	0.84	0.76
B1.H135	-	0.84	0.84	0.84	-
B1.Vz	-	0.84	-	0.76	0.76
B2.H045	-	-	-	0.87	0.87
B2.H135	-	-	1.04	-	-
B2.Vz	2.04	-	0.76	0.77	0.77
B3.H045	3.09	3.10	3.10	-	-
B3.H135	-	0.90	0.87	0.88	0.89
B3.Vz	2.05	-	0.77	0.77	0.77

H1.H000	2.48	2.43	2.45	0.84	0.75
H1.H045	3.24	3.23	3.31	0.85	0.75
H1.Vz	-	0.84	0.76	0.76	0.76
H2.H000	-	2.38	2.37	-	0.75
H2.H045	3.19	3.21	3.29	3.22	0.75
H2.Vz	-	-	0.76	0.76	0.76
H3.H000	-	-	2.44	-	0.75
H3.H045	3.21	3.25	3.29	3.24	0.75
H3.Vz	1.07	-	0.76	0.76	0.76
T0.H000	-	-	0.75	0.75	0.75
T0.H045	-	-	-	0.75	0.75
T0.Vz	-	-	0.76	0.76	0.76
T1.H000	-	0.84	0.84	0.84	0.84
T1.H045	-	0.84	0.84	0.84	0.84
T1.Vz	-	0.85	0.77	0.77	0.77
T2.H000	-	0.85	0.85	0.84	0.85
T2.H045	-	0.85	0.84	0.85	0.85
T2.Vz	-	0.85	0.77	0.77	0.77
T3.H000	-	0.84	0.85	0.84	0.84
T3.H045	-	0.85	0.85	0.85	0.85
T3.Vz	-	0.85	0.77	0.77	0.77

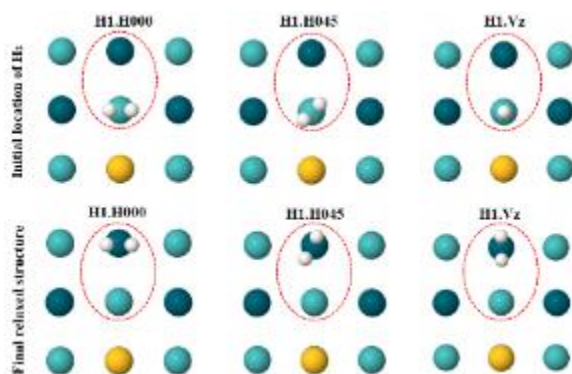


Figure 71. Initial and relaxed structure of selected cases for H₂ physisorption on 1st nearest hollow-site at PdAu surface

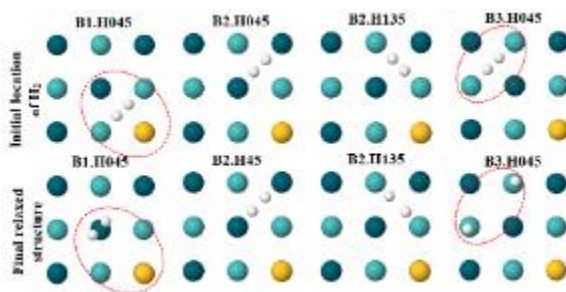


Figure 72. Initial/Final locations of selected cases of H₂ adsorption on bridge-site at PdAu surface

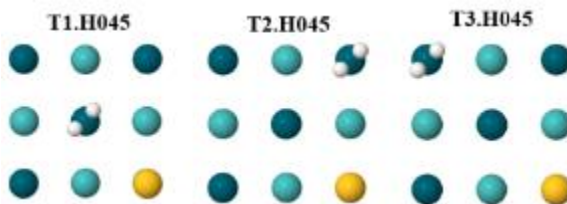


Figure 73. Relaxed positions of H₂ molecule on Pd-top-site on PdAu surface

6.2 Adsorption of Poisoning Gases (CO₂, CO, and CH₄) on PdAu-Surface

In this section, the adsorption of poisoning gases (CO₂, CO, and CH₄) is evaluated at the PdAu membrane surface. The adsorption energy of poisoning gases is examined at various adsorption-sites seeking for the most negative adsorption energy. These sites are based on their nearest to Au-atom (Figure 69). Due to computational expense of examining various combination of adsorption-site and molecule-orientations, few cases of this combination is considered. For each poisoning gas (CO₂, CO, and CH₄), only the adsorption-site and molecule orientation that showed higher negative adsorption energy at pure-Pd-surface is evaluated on the PdAu-surface at different nearest neighbor of that site from Au-atom. On pure-Pd-surface, the sites/orientations of the most negative adsorption energy for CO₂, CO, and CH₄ are H.H045, B.VCdwn, and H.3Hdwn, respectively (Figure 74). Accordingly, these sites and orientations of poisoning gases are evaluated at PdAu surface.

The adsorption energy of carbon dioxide on dilute alloy of PdAu at different hollow-sites based on their nearest neighbor to Au-atom (Figure 69) are summarized in Table 10. Also, a comparison to corresponding values of adsorption energy at pure-Pd-surface is made at the same table. Locating the CO₂ on horizontal orientation align with lattice direction [100] on all hollow-site (either close or far away from Au-atom, cases; H1.H000, H2.H000, and H3.H000) do not make large difference in its adsorption energy when it compared to E_{ads} at pure-Pd-surface, both values are about -0.255 eV. When the orientation is change to make 45° with lattice direction [100], the adsorption energy on 2nd and 3rd NN of hollow sites (cases; H2.H045 and H3.H045) do not vary compared to adsorption energy at hollow site on pure-Pd-surface (still around -0.250 eV). On other hand, at the 1st NN of hollow site (case H1.H045) the adsorption energy reduced dramatically to a value of -0.091 eV (64% reduction compared to E_{ads,CO_2} on pure-Pd-surface), however, if the CO molecule changes to (H1.H000) it is orientation it would have higher adsorption energy (-0.259 eV) close to that on pure-Pd-surface. Also, the CO₂ molecule did not stayed at the hollow-site, instead, it moved to the next bridge site (Figure 75) and the angle between O-C-O changed from 179.98° to around 145°. Figure 76 shows the adsorption of CO₂ on Au-top-site at different orientations of CO₂ molecule. The horizontal orientation of CO₂ on this site has an adsorption energy slightly smaller than corresponding value on a Pd-top-site (by about 5%). While in the vertical orientation, the adsorption energy becomes weaker by 14% Au-top-site compared to Pd-top-site. Furthermore, adsorption of carbon dioxide on vertical orientation at Au-top-site is not perfectly align to the vertical direction like the case on Pd-top-site. It makes an angle of around 22.8° with the normal axis to the slab (direction [001]).

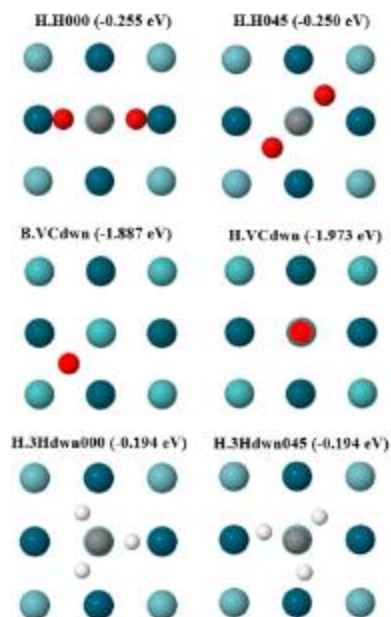


Figure 74. Adsorption-site/molecule-orientation that give most negative adsorption energy of poisoning gases at pure-Pd-surface.

Table 10. Comparison of CO₂ adsorption energy on PdAu and Pd surface.

site/orientation	E _{ads} (eV)		Difference %
	Pure-Pd	PdAu	
H1.H000	-0.255	-0.259	2%
H2.H000		-0.254	-1%
H3.H000		-0.257	1%
H1.H045	-0.250	-0.091	-64%
H2.H045		-0.249	0%
H3.H045		-0.250	0%
T0.H000	-0.212	-0.204	-4%
T0.H045	-0.215	-0.206	-5%
T0.Vz	-0.138	-0.119	-14%

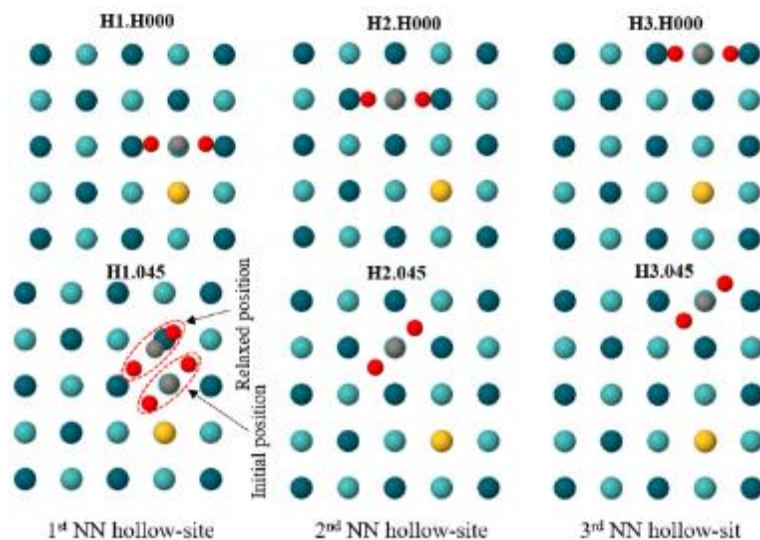


Figure 75. Relaxed locations of CO₂ adsorption at PdAu surface on hollow-site based on nearest neighbor (NN) to Au-atom (top-view)



Figure 76. Final locations of CO₂ adsorption on a top-site of Au-atom at PdAu surface (top-view).

The adsorption of CO on pure-Pd-surface showed higher values of E_{ads} at the three sites; bridge, hollow and Pd-top (-1.973 to -1.887 eV). Thus to reflect the impact of alloying Pd-surface by Au-atom, the adsorption of CO was evaluated at the three sites (B, H, T-sites) based on their nearest neighbor to Au-atom. However, only one orientation for CO (vertical orientation with C-atom downside) is consider because all previous values of $E_{\text{ads,CO}}$ on pure-Pd-surface indicate that the CO molecule would get relaxed at vertical orientation where C-atom facing slab. The results of CO adsorption on PdAu-surface reveal that all sites (B, H, T) on the 2nd and 3rd nearest neighbor to Au-atom have almost similar

adsorption energy as in the corresponding site at pure-Pd-surface (Table 11). The adsorption energy of CO on 1st NN of bridge, hollow and top-sites are reduced by 24%, 10%, and 2% compared to the corresponding sites on pure-Pd-surface. Since the 1st NN bridge site is very closer to the Au-atom than 1st NN hollow- and top-sites, the adsorption of carbon monoxide is highly influenced by presence of Au-atom (24% reduction in $E_{ads,CO}$). Only 10% reduction of $E_{ads,CO}$ is recorded in the 1st NN hollow site of PdAu-surface because this site is slight far from Au-atom than bridge-site. Furthermore, it can be notice from Figure 77 that CO molecule is much attracted to Pd-atoms than Au-atom, so, when it is located in the hollow site it pulls the three neighbor Pd-atoms and moves away from the Au-atom. On other hand, the 1st NN top-site is far enough from the Au-atom, therefore, the adsorption energy is less affected by Au-atom as compared to adsorption energy on top-site of pure-Pd-surface (only 2% difference).

Furthermore, the adsorption energy of CO at the top of Au-atom is examined at different orientation of CO. Similar behavior of CO tends to get relaxed at vertical orientation on pure-Pd-surface is noticed on PdAu-surface. Where all initial structure of CO on horizontal orientation get relaxed at vertical orientation (Figure 78). Also, the adsorption energy of CO on the top of Au-atom on PdAu surface is smaller than on top of Pd-atom on pure-Pd-surface. The reduction of adsorption energy on Au-top-site reach up to around 50% compared to Pd-top-site on pure-Pd-surface, which almost double the $E_{ads,CO}$ reduction that happens on 1st NN bridge site because the CO molecule is much closer to Au-atom (just above Au-atom).

Table 11. Comparison of CO adsorption energy on PdAu and pure-Pd surfaces.

Initial site/orientation	Eads (eV)		Difference %
	PdAu	pure-Pd	
B1.VCdown	-1.439	-1.887	-24%
B2.VCdown	-1.869		-1%
B3.VCdown	-1.883		0%
H1.VCdown	-1.619	-1.793	-10%
H2.VCdown	-1.802		0%
H3.VCdown	-1.796		0%
T1.VCdown	-1.494	-1.521	-2%
T2.VCdown	-1.523		0%
T3.VCdown	-1.520		0%
T0.H000	-0.795	-1.793	-56%
T0.H045	-0.795	-1.887	-58%
T0.VCdown	-0.795	-1.521	-48%
T0.VOdown	-0.091	-0.117	-23%

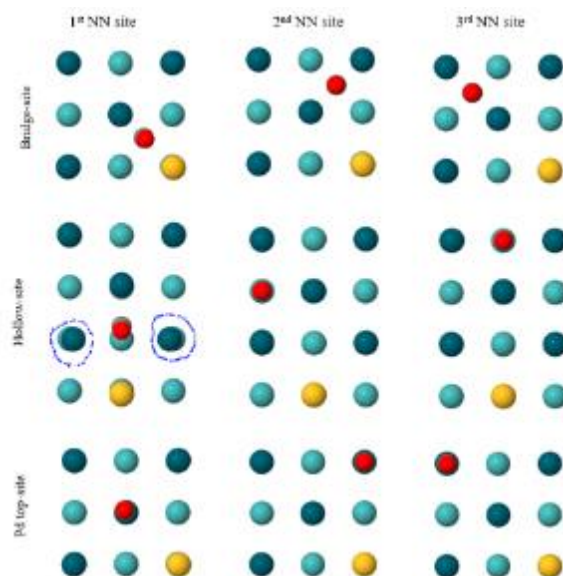


Figure 77. Final locations of CO adsorption at PdAu surface at various site based on its nearest neighbor (NN) to the Au-atom (top-view)

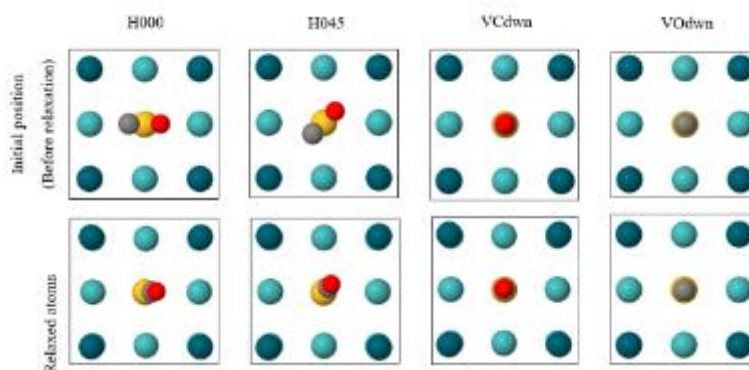


Figure 78. Initial and final locations of CO adsorption at top of Au-atom with different molecule orientation on PdAu surface (top-view)

The results of methane adsorption on pure-Pd-surface reveal that hollow site is the most favorable site. In this site, the orientation of having three H-atoms facing the slab while the fourth H-atom located opposite to the slab (case 3Hdwn000 and 3Hdwn045) has the most negative adsorption energy (-0.19445 and -0.19433 eV) (SI.Fig.0). Accordingly, this orientation is selected to evaluate adsorption of CH₄ at PdAu-surface. Figure 79 shows the relaxed position of CH₄ at PdAu-surface at different nearest neighbor hollow sites to Au-atom. Comparing adsorption energy on hollow site of pure-Pd-surface and PdAu-surface

(Table 12), the presence of Au-atom has trivial impact on the adsorption of methane gas for all hollow sites near or far away from the Au-atom. Only 1% difference in the adsorption energy is observed. Furthermore, the E_{ads} at various orientation of CH_4 was evaluated at Au-top-site (Figure 80), and they are in the range of -0.13 eV to -0.15 eV which is lower than that on Pd-top-site on pure-Pd-surface which reach up to -0.19 eV. Thus, when CH_4 get adsorbed at Au-top-site the $E_{\text{ads,CH}_4}$ would be lower by 18% - 28% than if it get adsorbed a top of Pd-atom.

Table 12. Comparison of CH_4 adsorption energy on PdAu and pure-Pd surfaces.

site/orientation	E_{ads} (eV)		Difference %
	PdAu	pure-Pd	
H1.3Hdwn000	-	-0.19445	-
H2.3Hdwn000	-0.19631		1%
H3.3Hdwn000	-0.19568		1%
H1.3Hdwn045	-0.19342	-0.19433	0%
H2.3Hdwn045	-0.19681		1%
H3.3Hdwn045	-0.19571		1%
T0.1Hdwn000	-0.13114	-0.18211	-28%
T0.1Hdwn045	-0.13108	-0.18211	-28%
T0.2Hdwn000	-0.14282	-0.19033	-25%
T0.2Hdwn045	-0.14347	-0.18926	-24%
T0.3Hdwn000	-0.15146	-0.18534	-18%
T0.3Hdwn045	-0.15148	-0.18777	-19%

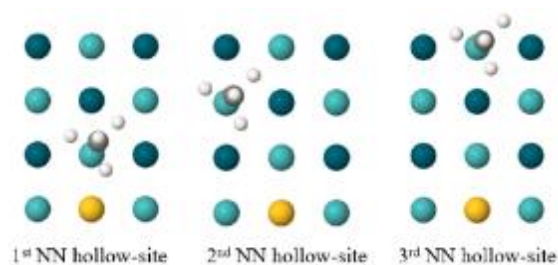


Figure 79. Final locations of CH₄ adsorption at PdAu surface at various nearest neighbor (NN) of hollow-site to Au-atom (top-view).

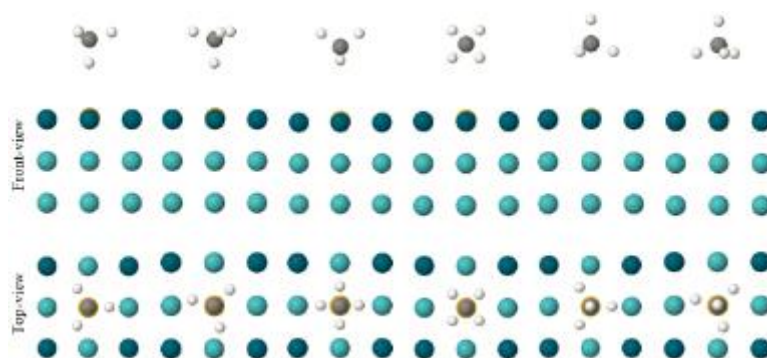


Figure 80. Final relaxed locations of CH₄ adsorption at top of Au-atom with different molecule orientation on PdAu surface.

In order to understand clearly the reasons behind the impact of alloying Pd-membrane by Au-atom, the charge density differences for selected cases of gas adsorption (H₂, CO₂, CO, and CH₄) on pure-Pd and PdAu surfaces are calculated and compared to each other's. The adsorption energy for these cases are summarized in Table 13. According to Figure 81, weak charge density is produced to the reaction of H₂ adsorption on Au-top-site. While, the charge density differences for H₂ adsorption on 1st NN Pd-top-site at PdAu-surface and on Pd-top at pure-Pd-surface are much similar. Thus, the E_{ads} for them is almost alike. Also, the charge density difference for CH₄ at hollow sites are almost identical at pure-Pd and PdAu-surfaces (cases H.3H045 and H1.3Hdwn045 on Figure 82) and there is no any sign of an interaction with the Au-atom, so, alloying the Pd-slab by Au-atom has trivial impact

on adsorption of CH₄ at hollow site. On the other hand, at Au-top-site, a very small size of positive charge is generated at the H-atoms the methane gas when three H-atoms of CH₄ are close to Au-atom (case T0.31Hdwn045). Even the other orientation of the methane gas (T0.1Hdwn045) has small charge density difference cloud at PdAu compared to the cloud at pure-Pd-surface. In Figure 83, for both pure-Pd and PdAu surfaces, the charge density difference due to adsorption reaction of CO gas is very large compare to other gases (CO₂, CH₄, and H₂) which demonstrate the high value of $E_{ads,CO}$ at different sites. Even at Au-top-site, CO can interact strongly with the PdAu-slab. The only exception is when O-atom is oriented close membrane surface. Also, the vertical orientation of CO₂ gas makes one of its O-atom interact with Pd-membrane which is weak interaction as indicated in Figure 84.

Table 13. Summary of selected cases used for the charege density difference analysis.

Gas	site/orientation	E_{ads} (eV)		Difference %
		PdAu	pure-Pd	
H ₂	T1.H045	-0.336	-0.343	-2%
	T0.H045	-0.056		-83.7%
CH ₄	H1.3Hdwn045	-0.19342	-0.19433	0%
	T0.1Hdwn045	-0.13108	-0.18211	-28%
	T0.3Hdwn045	-0.15148	-0.18777	-19%
CO	B1.VCdwn	-1.439	-1.887	-24%
	H1.VCdwn	-1.619	-1.793	-10%
	T0.VCdwn	-0.795	-1.521	-48%
	T0.VOdwn	-0.091	-0.117	-23%
CO ₂	H1.H000	-0.259	-0.255	2%

	H1.H045	-0.091	-0.250	-64%
	T0.H045	-0.206	-0.215	-5%
	T0.Vz	-0.119	-0.138	-14%

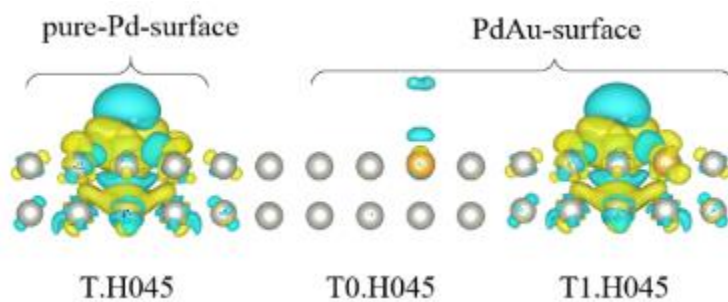


Figure 81. Charge density difference for H₂ (e/Bohr³) at various sites.

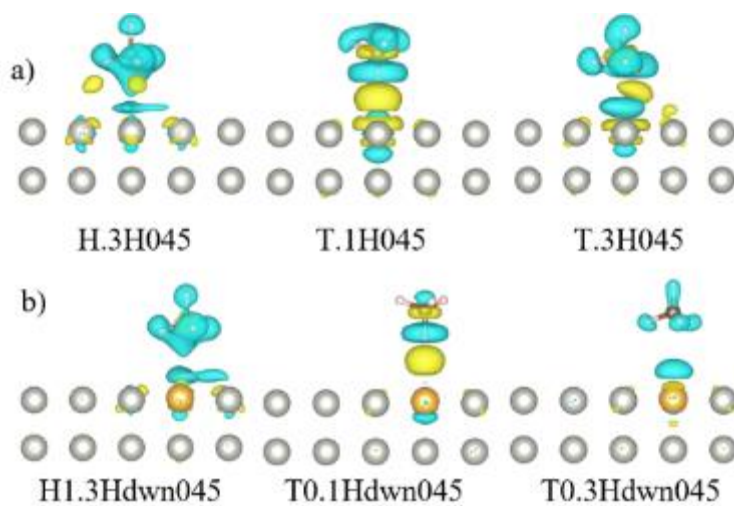


Figure 82. Charge density difference for CH₄ (iso-surface at 0.0003 e/Bohr³) at various sites on a) pure-Pd-slab
b) PdAu-slab.

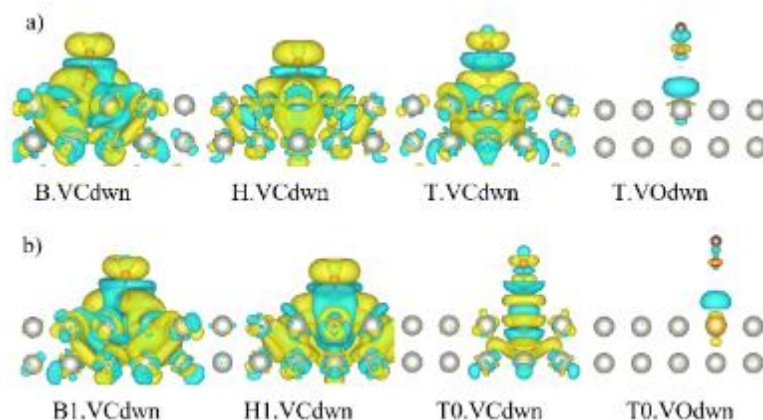


Figure 83. Charge density difference for CO (iso-surface at 0.0003 e/Bohr³) at various sites on a) pure-Pd-slab b) PdAu-slab.

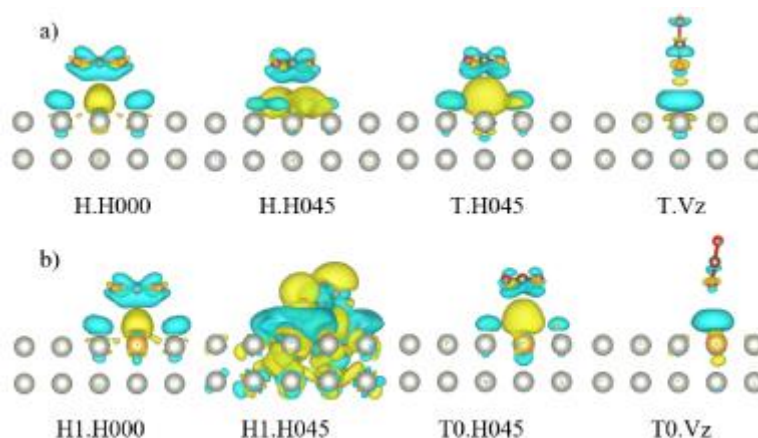


Figure 84. Charge density difference for CO₂ (iso-surface at 0.0003 e/Bohr³) at various sites on a) pure-Pd-slab b) PdAu-slab.

6.3 Effect of Poisoning Gases on H₂ Adsorption Process on PdAu-Surface

In order to study the impact of poisoning gases on adsorption process of hydrogen molecule ($E_{\text{ads},\text{H}_2}$), a slab of PdAu-membrane contains both H₂ and one of poisoning gases (CO₂, CO, or CH₄) is prepared. Firstly, a PdAu-slab structure that contains poisoning gas is relaxed, then H₂ molecule is allowed to physisorbed at that structure Figure 85. The H₂ is considered

to be adsorbed at its most favorable site close to the Au-atom, which is 1st NN of Pd-top site. While the poisoning gas (CO, CO₂, and CH₄) is located at the hollow-site that adjacent to both Au-atom and H₂ molecule Figure 85.b. The results of hydrogen adsorption energy ($E_{\text{ads,H}_2}$) are summarized in Figure 50. To reflect the impact of alloy Pd-slab by gold atom, the results of $E_{\text{ads,H}_2}$ at pure Pd-slab are added to the figure. The $E_{\text{ads,H}_2}$ at bare surface is around -0.340 eV at PdAu-slab which is very close to the value at pure Pd-slab, -0.343 eV. The presence of methane gas slightly reduces the physisorption energy of H₂ at pure Pd-slab to -0.317 eV. Alloy the Pd-slab by Au-atom has no great impact on enhancing the $E_{\text{ads,H}_2}$, where almost similar value was noticed for $E_{\text{ads,H}_2}$ on PdAu-slab with methane poisoning (-0.300 eV). Nevertheless, when the slab is poisoned by CO, a remarkable enhancement was recorded. The carbon monoxide is known to be the most poisoning gas for Pd-membrane. At pure Pd-slab, the existence of CO diminish the $E_{\text{ads,H}_2}$ from -0.343 to -0.222 eV, which is about 35% reduction in the adsorption energy. But at PdAu-slab, the $E_{\text{ads,H}_2}$ at CO poisoning is improved to reach up to -0.335 eV. This value is very close to the value at bare PdAu-slab, -0.340 eV. What refer to Figure 87, at Pd-slab the hydrogen molecule adsorption site is slightly deviated to the Pd-top. Consequently, the H₂ would have less interaction with the Pd-atom the things that demonstrate large reduction in $E_{\text{ads,H}_2}$ caused by CO on Pd-slab. While in PdAu-slab, the Au-atom push CO gas from the hollow-site to the bridge-site that far away from the adsorption site of H₂ molecule. Before the physisorption of H₂ molecule, the CO gas relaxed at the hollow-site closed to Au-atom. It is clear from Figure 85.a that Au-atom try to push the CO gas away from hollow site, but it stay and interacting with the surrounding three Pd-atoms, where CO pull Pd-atoms. When hydrogen molecule comes to the Pd-top site, the hollow-site is not any more favorable for

CO because one of the three Pd-atoms surrounding the CO gas interacts with the H₂ molecule. So, Au-atom successfully pushes the CO gas to the bridge-site away from Pd-atom where H₂ molecule adsorbed at it. Accordingly, the distance between CO and H₂ molecule becomes large, the things that demonstrate the higher value of $E_{\text{ads,H}_2}$ of -0.335 eV on PdAu at presence of CO gas. Similar phenomenon was observed with CO₂ gas. Where the adsorption energy of H₂ pure Pd-slab with CO₂ poisoning is about -0.312 eV, and when the slab is alloyed by Au the value increased to -0.362 eV as the Au-atom pushes the poisoning gas away from the H₂ molecule (Figure 88).

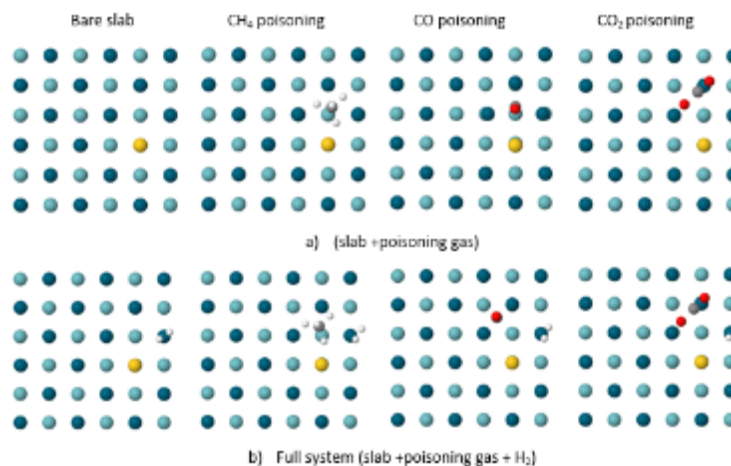


Figure 85. Relaxed structure of PdAu-slab before and after hydrogen physisorption.

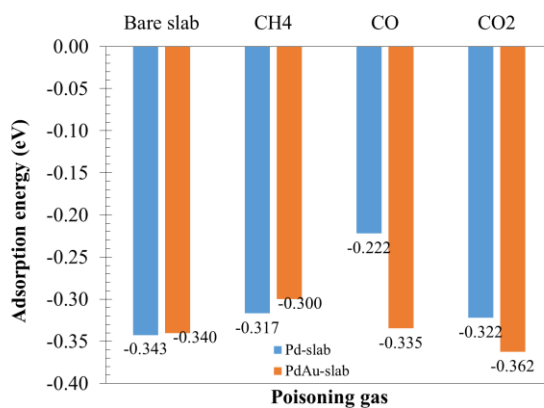


Figure 86. Comparison of hydrogen adsorption energy on Pd and PdAu slab at presence of various poisoning gases.

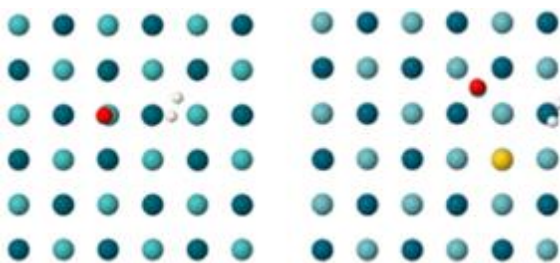


Figure 87. Comparison of hydrogen adsorption at CO poisoning on Pd-slab and PdAu-slab.



Figure 88. Comparison of hydrogen adsorption at CO₂ poisoning on Pd-slab and PdAu-slab.

6.4 Dissociation of H₂ Molecule on PdAu-Membrane.

The dissociative process of hydrogen molecule (H₂) to two hydrogen atoms is investigated through nudged elastic band method, so the minimum energy barriers required for the process could be obtained. This method is used to catch saddle points and minimum energy paths between known reactants and products by optimizing a number of intermediate images along the reaction path. Each reaction image along the pathway of the dissociation process would have the lowest possible energy. Accordingly, the initial and final states of the hydrogen dissociation process have to be known. The initial state, or the reactants, is the physisorption of H₂ molecule on the PdAu-surface. From the previous section it was shown that Pd-top site is the most preferable site for physisorption of H₂. And to reflect the impact of Au-alloying on the dissociation process, the physisorption of H₂ on the 1st NN of Pd-top site is considered the starting state for the dissociation process. The final state of H₂ dissociation process is the chemisorption of two H-atoms (products) on the PdAu-

surface. Figure 58 shows hydrogen dissociation energy curve on PdAu-dilute alloy and compares it to that on pure Pd-membrane. There are 10 images of reaction coordinates, where the first image represents the physisorption of H_2 as a molecule (image 1) and the last image represents fully dissociated of H_2 molecule to two H-atoms (image 10). The adsorption energy of the H_2 on PdAu-alloy is -0.336 eV at image 1 (physisorption of H_2), while at image 10 it is -0.748 eV. The chemisorption of H-atoms is known to have higher adsorption energy compared to physisorption of H molecule, and since the last reaction coordinates (image 10) represents a chemisorption of hydrogen it has higher adsorption energy. However, in order to reach to that state it is required for the hydrogen molecule to overcome the energy barrier of the transition state at image 3 (0.042 eV). This barrier is very small compared to the barrier required at pure Pd-membrane (0.233 eV).

Before the dissociation process reach to final state of image 10, it counters another small barrier (0.022 eV) at reaction coordinate of image 7. All of images 7, 8, and 9 have more negative energy than the last reaction coordinate (image 10). With refer to Figure 59, at these images, the H-atom that close to Au-atom stays at higher distance above the PdAu surface (around 0.82 Å) compared to the last image (0.44 Å). The chemisorption of H-atoms on PdAu is -0.748 eV which is less than at pure Pd, -0.857 eV. Thus, the presence of Au-atom makes it less preferable site for H-atom to be adsorbed near to it. Accordingly, the images 7, 8, and 9 offer more negative energy stat since the H-atom is far from the Au-atom. That is also become clear in image 10, where the H-atom close to Au-atom relaxed slightly away from hollow site on the opposite direction to Au-atom, while the other H-atom perfectly relaxed at the center of the hollow site.

On other hand, the reverse process which is the association of two hydrogen atoms to form H_2 molecule, required large value of activation energy 0.454 eV. It is logical because hydrogen atoms are moving from most stable state (image10 which represent a chemisorption state) to a less energy state (image1 which is physisorption state). This process happens on the other side of the Pd-membrane which is a reverse process of H_2 dissociation. Alloying Pd membrane by Au reduces the association energy barrier from 0.748 eV to 0.454 eV (reduced by 0.294 eV).

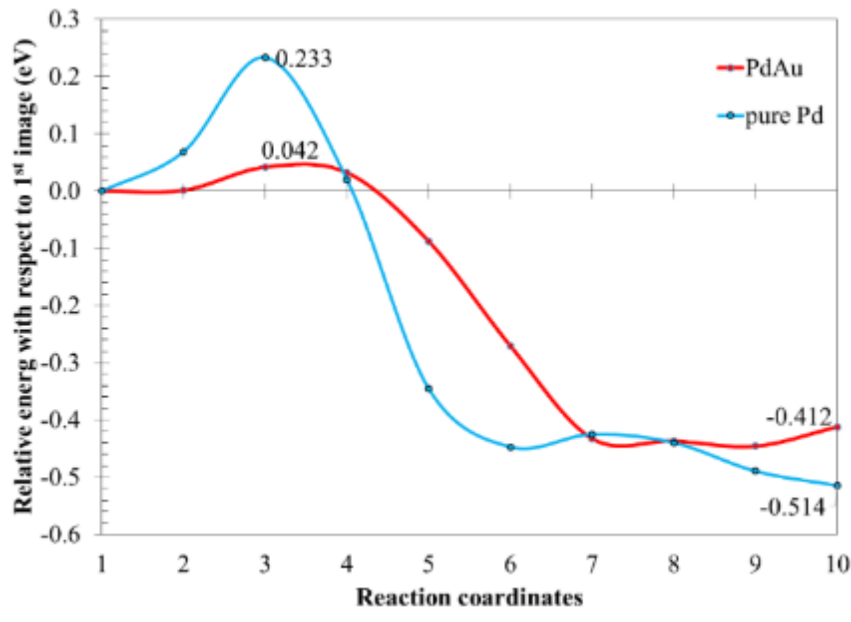


Figure 89. Energy curve during dissociation process of H_2 to two of H-atom on bare Pd-surface (100).

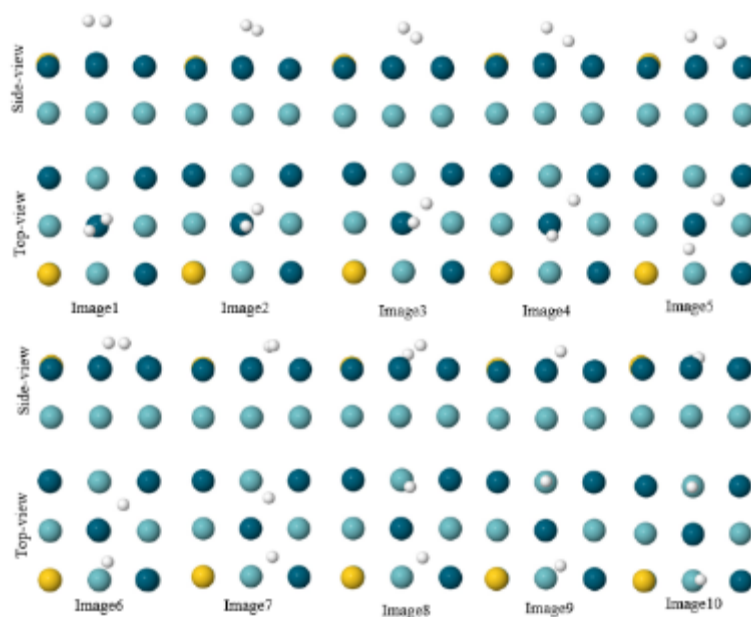


Figure 90. Pathway of H₂ dissociation process on bare Pd-surface (100).

6.5 Diffusion of H-atom on Dilute Alloy of PdAu-Membrane.

Alloying Pd-bulk membrane with gold atoms would have an impact on hydrogen diffusion energy barrier when hydrogen atom permeate through the bulk membrane near the Au-atom. In dilute alloy of Pd-Au membrane, the Au-atoms are distributed through the bulk membrane with a distance that makes not feeling the existence of other Au-atoms. Thus, any Au-atom acts as it is the only Au-atom on the bulk material. Therefore, the diffusion energy barrier can be characterized by energy barrier close to the Au-atom in a super-cell that contains only one Au-atom, Figure 91.

In order to prove the dilute PdAu-alloy assumption, the binding energy of H-atom is calculated at the nearest neighbor of octahedral-site to Au-atom. Then, another Au-atom is added to the bulk material at different distances. The idea is to get a distance at which locating another Au-atom would give similar binding energy as if that second Au-atom not

exit (see Figure 92). The distances between Au-atoms are summarized on Table 14. When the binding energy of H-atom get affected by the second Au-atom that would be the breaking point for the dilute PdAu-alloy assumption. The Au% in PdAu-alloy corresponding to dilute assumption can be obtained from (Table 15). This table shows the minimum distance that can be maintained between Au-atoms at specific Au% in PdAu-alloy, and it also shows the order of the nearest Au-atom corresponding to Au% in the Pd-alloy. The data of Table 15 are formulated by obtaining all possible arrangement of Au-atoms in a PdAu-bulk cell (3x3x3) each Au%. At specified Au%, each arrangement would have different distance between Au-atoms. Then, the arrangement that maintain the largest distance between Au-atoms is considered and the distance between Au-atoms is reported in Table 15. For instance, at 6.5% of Au, the minimum distance between Au-atoms is when one of them is located at 5th nearest neighbor, i.e. 6.8 Å, as it read from Table 14 and Table 15. It is clear that in order to get higher Au% in PdAu-alloy, the Au-atoms have to come close to each other. For instant, at Au = 9.3%, the Au atoms will be distributed through the bulk material with a distance around 4.84 Å, which means there will be another Au atom at the 3rd nearest neighbor of any Au-atom.

The impact of a second Au-atom within bulk-membrane on the binding energy of the 1st nearest octahedral is presented in Table 16. Replacing a Pd-atom on 1st NN or 2nd NN to the Au-atom by Au-atom, results in unstable site for the hydrogen atom. Those two cases gives positive binding energy and they highly influence the hydrogen binding energy, and consequently, they are violating the dilute PdAu-alloy assumption. If the distance between the Au-atoms increased up to the 3rd NN, still Au-atoms can impact the hydrogen binding energy (there is 0.010 eV difference in binding energy compared to case of only one Au-

atom). The influence of the second Au-atom disappear when it located at least at a 5th NN to the first Au-atom. This case is corresponding to about $\leq 7.4\%$ of Au-atoms in bulk material (Table 15). Thus, up to 7.8% of Au in the bulk-PdAu-membrane can be considered as dilute PdAu-alloy and the diffusion of H-atom can be studied by locating only one Au-atom, and then, analyze the hydrogen diffusion phenomena close to that Au-atom.

In the FCC membrane structure, the H-atom keep jumping between octahedral (O) and tetrahedral sites (T) until it diffuse to the other side of the membrane. Therefore, there are three possible pathways where hydrogen atom may follow which are; O-O, T-T or O-T pathway. The diffusion barrier results for the three pathways on pure Pd-bulk indicate that the O-T pathway is the most possible pathway for hydrogen to follow as it has the lowest energy barrier (0.166 eV) compared to the others. Thus, only O-T pathway is considered in current analysis of H-atom diffusion on PdAu-dilute-alloy. The diffusion is analyzed at low and high hydrogen concentrations (1% and 25% at.). These percentages are corresponding to 1 H-atom and 27 H-atoms in super-cell 3x3x3, respectively. All the 27 H-atoms are distributed on octahedral-sites through the bulk (Figure 93) because the O-site is more favorable than T-site. Only one H-atom is allowed to jump from the O-site to the T-site, while other H-atoms as relaxed at their O-site. Figure 93 shows the O-T pathway of hydrogen diffusion at 1% and 25% at. concentration of hydrogen. To make the picture clear in Figure 93, a small part of the bulk-atoms centered at the middle of the super-cell is shown while other Pd-atoms are hidden but they were included the calculation. Figure 94 compares the energy curves for hydrogen diffusion between O-T pathway for pure Pd-bulk and PdAu-bulk at 1% and 25% at. concentration of the hydrogen. These energy values are referenced to the system energy when H-atom is located in O-site. On pure Pd-bulk, the

activation energy required for hydrogen atom to move from the octahedral site to tetrahedral site (O-T) 0.166 eV, while the reverse pathway from tetrahedral to octahedral site (T-O) required only 0.123 eV which is smaller than energy barrier for (O-T). This happens because tetrahedral site is more energetic than octahedral site. Applying PdAu-dilute-alloy reduce the barrier from 0.166 to 0.150 eV when H-atom jumps from O-site to T-site, at low hydrogen concentration. However, a slightly higher energy barrier of 0.128 eV is required for the T-O pathway compared to the case of pure Pd-bulk (0.123 eV). Moreover, at high hydrogen concentrations (25% at.), the PdAu-dilute alloy shows less energy barriers (0.206 eV) compared to pure Pd (0.249 eV). Nevertheless, this energy barrier (0.206 eV) is larger than the value of at low hydrogen concentration (0.150 eV) of same PdAu material. The presence of many H-atoms distributed through the bulk material limit the movement of Pd-atoms when the H-atom jumps between the sites. Accordingly, higher repulsive force occurs at high hydrogen concentration which leads to higher energy barriers.

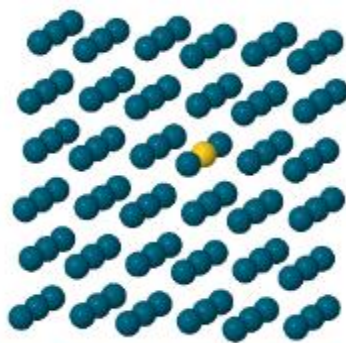


Figure 91. Dilute alloy of PdAu-bulk membrane containing one Au-atom in super-cell 3x3x3.

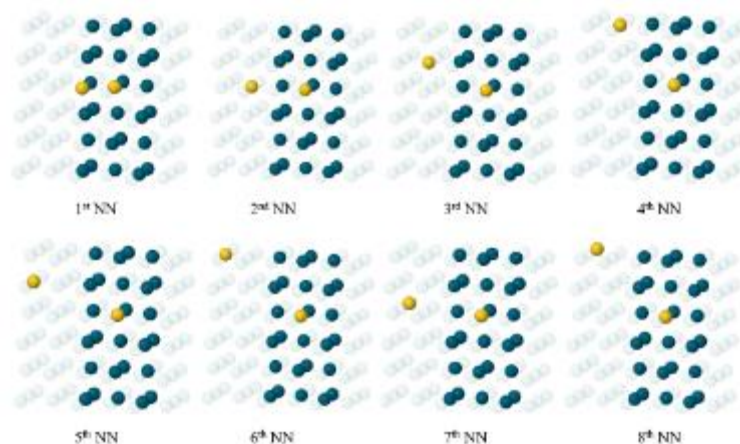


Figure 92. Location of 2nd Au atom at different distance from the 1st Au-atom (PdAu membranes used to verify the dilute alloy assumption).

Table 14. Distances between the nearest Au-atom of PdAu-alloy

Order of nearest neighbor (NN)	Distance (Å)
1st NN	2.8
2nd NN	3.9
3rd NN	4.8
4th NN	5.6
5th NN	6.8
6th NN	7.4
7th NN	8.4
8th NN	9.3

Table 15. Order of nearest neighbor of Au-atoms at different PdAu-alloy

# Au atoms	# Total atoms	Au%	Nearest neighbor (NN)
6	108	5.6%	5th NN
7	108	6.5%	5th NN
8	108	7.4%	5th NN
9	108	8.3%	4th NN
10	108	9.3%	3rd NN
11	108	10.2%	3rd NN
12	108	11.1%	3rd NN

Table 16. Difference in binding energy due to presence of a second Au-atom in bulk membrane as compared to case with single Au-atom in bulk membrane.

Location of 2 nd Au-atom	Difference in binding energy (eV)
1st NN	0.064
2nd NN	0.234
3rd NN	-0.010
4th NN	-0.005
5th NN	0.000

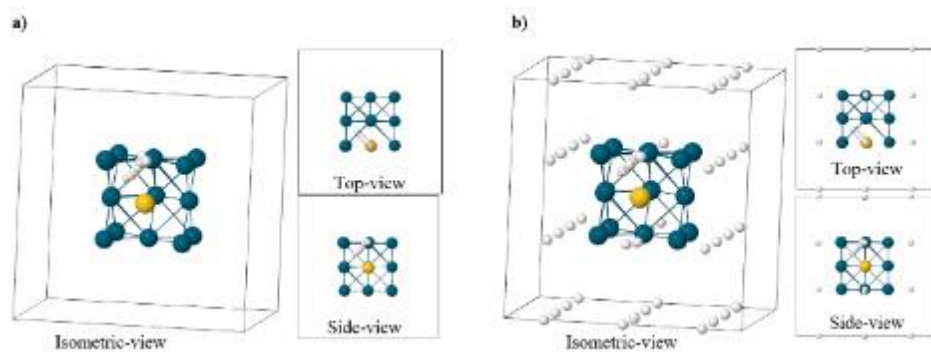


Figure 93. Diffusion of H-atom through O-T pathway. a) 1% at. b) 25% at. concentration.

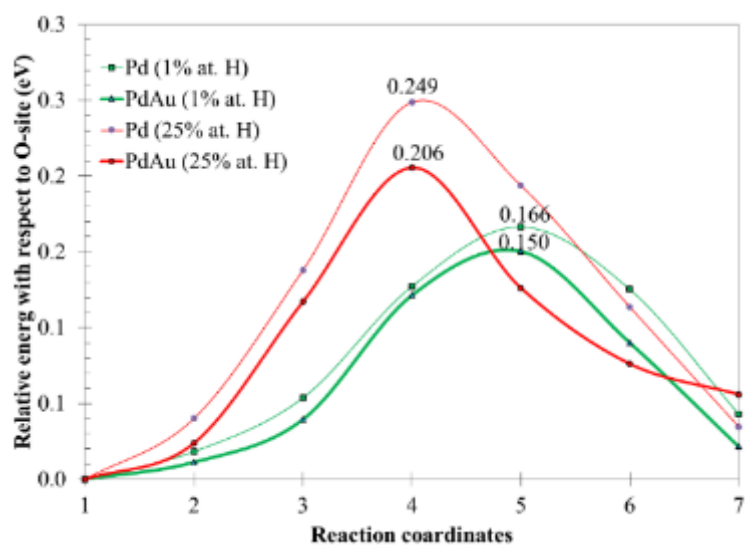


Figure 94. Energy curves for H-atom diffusion between O-T sites in bulk material of Pd and PdAu-dilute-alloy (super-cell 3x3x3).

CHAPTER 7

CONCLUSIONS & RECOMMENDATIONS

7.1 Conclusions

In this work, first-principles calculations of hydrogen permeation through Pd-based membrane was performed using density-functional theory (DFT) at quantum-level (atomic scale). Thus, series of DFT calculation for both pure Pd and Pd_{95%}Au_{5%} was conducted to reveal the characteristics of Pd-base membrane on hydrogen adsorption and dissociation at the membrane surface (100) along with the diffusion on bulk membrane material. The main conclusions can be summarized in the following points:

- The DFT can accurately predict the properties of Pd membrane and gas molecules, where it estimated lattice constant for Pd-membrane is found to be 3.948 Angstrom (1.89% error), while its binding energy is 3.935 eV/atom (0.44% error). For the hydrogen molecule and poisoning gases, the error in binding energy is less than 2.5% and the bonding length error is less than 1.5%.
- The DFT calculations showed that the top site with horizontal orientation of hydrogen molecule that makes 45° with x- and y-axes has the most negative physisorption energy, so the hydrogen molecule is highly likely will get adsorbed at it.
- The chemisorption of hydrogen atoms is almost 2.5 times the physisorption of H₂ molecule. Also, the chemisorption energy increase proportionally with the hydrogen coverage until it reach the maximum value (around -0.966 eV) at

coverage range of 0.5 to 1.0 ML, then, it decrease gradually. Furthermore, very high coverage value (3.0 ML) is less likely to happen as the chemisorption energy becomes positive.

- Higher value of H₂ adsorption energy could be obtained at high coverage value of pre-existing H-atoms if those H-atoms are distributed through the surface and they are not surrounding the adsorption site of H₂ molecule. The vice versa is also true, i.e. the lower H₂ adsorption energy can be obtained even at low coverage of pre-existing H-atoms if those H-atoms are surrounding the nearest hollow sites around the adsorption site of H₂ molecule.
- Both CH₄ and CO₂ gases get adsorbed at relatively far distance from the Pd-surface, around 2.6 and 3.0 Å, respectively. Thus, they have low adsorption energy (-0.194 and -0.255 eV, respectively) compared to the CO which get adsorbed at close distance of around (1.1 -1.5 Å) with an adsorption energy of around -1.887 eV. Also the CO gas has high adsorption energy at various sites on the Pd-surface, consequently, it is considered as highly poisoning gas compared to CO₂ and CH₄.
- The dissociation energy of hydrogen molecule required an activation energy of 0.233 eV, while the revers process of association of two hydrogen atoms to form a hydrogen molecule require 0.738 eV.
- The activation barriers for the hydrogen atom to jump between two consecutive octahedral site, or consecutive tetrahedral sites, are very high. Thus, it will be jumping from octahedral site to the nearest tetrahedral site then to another octahedral site and so on until it diffuse through all the membrane material.

- Alloying Pd with a dilute alloy of Au would reduce the diffusion energy barrier from 0.166 to around 0.150 eV. Additionally, it has positive impact on reducing the dissociation barrier from 0.233 eV to 0.042 eV, and it also reduce the association barrier from 0.748 eV to 0.454 eV.
- Higher concentration of hydrogen atoms would increase the energy barriers required for the diffusion. At 25% atomic concentration, the required energy barrier is 0.249 eV. While it reduced to 0.206 eV when Pd-membrane is alloyed by Au-atom.
- PdAu-alloy with up to 7.4% Au, can be considered as dilute alloy, where the nearest distances between Au-atoms within the bulk material is 5th NN.

7.2 Recommendations and Future Work

An enormous effort was done in this study to achieve the research objectives. However, there is always a room for improvement. Therefore, here are some suggestions on how the work can be extended:

- Explore the hydrogen permeation at higher gold concentration of PdAu-alloy can be investigated to judge to what extent of Au% the performance of PdAu can be improved as Au% increased.
- Investigate the permeation of hydrogen on Pd-alloy with other materials such as silver, ruthenium, and yttrium.
- Examine the performance of ternary Pd-alloy on the hydrogen permeation instead of using binary alloys of Pd-membrane.
- More poisoning gases can be investigated such as HS and H₂S.

Appendix

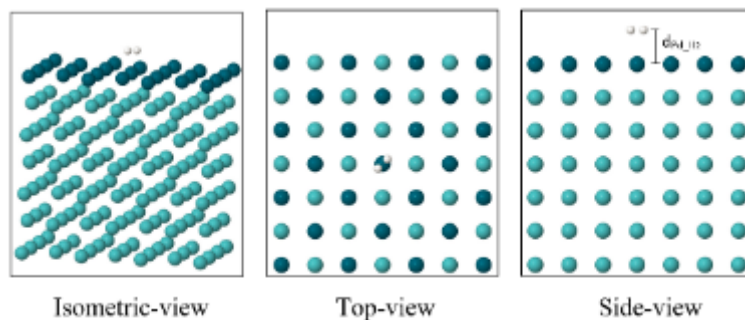


Figure 95. Super cell 3x3x1 of Pd-surface and H₂ molecule.

Table 17. Adsorption energy (eV) of H₂ on bare Pd-surface (100) at various sites/orientations and various distance from the Pd-surface (d_{Pd-H2}).

Site/orientation	d _{Pd-H2} (Å)				
	0.0	0.5	1.0	1.5	2.0
B.H045	-0.327	-0.167	-0.169	-0.171	-0.170
B.H135	-0.832	-0.832	-0.830	-0.832	-0.834
B.Vz	-0.328	-0.096	-0.094	-0.096	-0.095
H.H000	-0.229	-0.228	-0.229	-0.229	-0.067
H.H045	-0.809	-0.808	-0.810	-0.810	-0.067
H.Vz	0.249	-0.092	-0.090	-0.089	-0.093
T.H000	-	-0.339	-0.340	-0.341	-0.341
T.H045	-	-0.341	-0.341	-0.343	-0.342
T.Vz	-	-0.113	-0.111	-0.113	-0.116

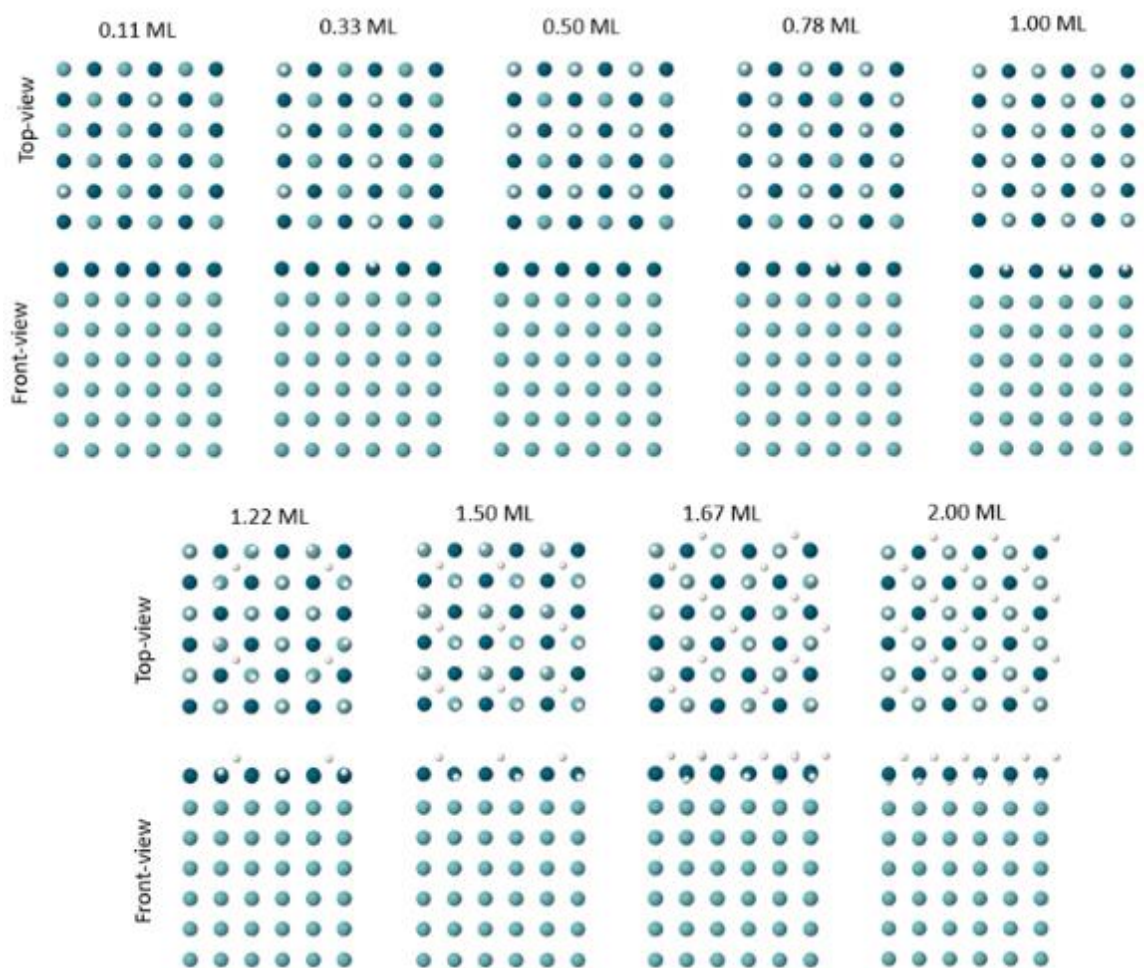


Figure 96. Relaxed locations of H-atoms at various coverage on Pd-surface (100).

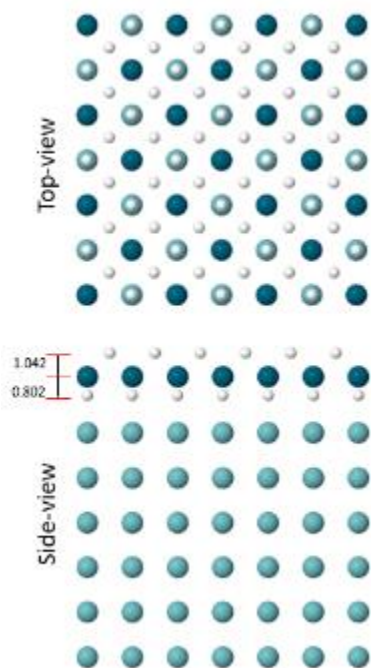


Figure 97. Chemisorption of H-atoms at high coverage (3.0 ML) on Pd-surface (100).

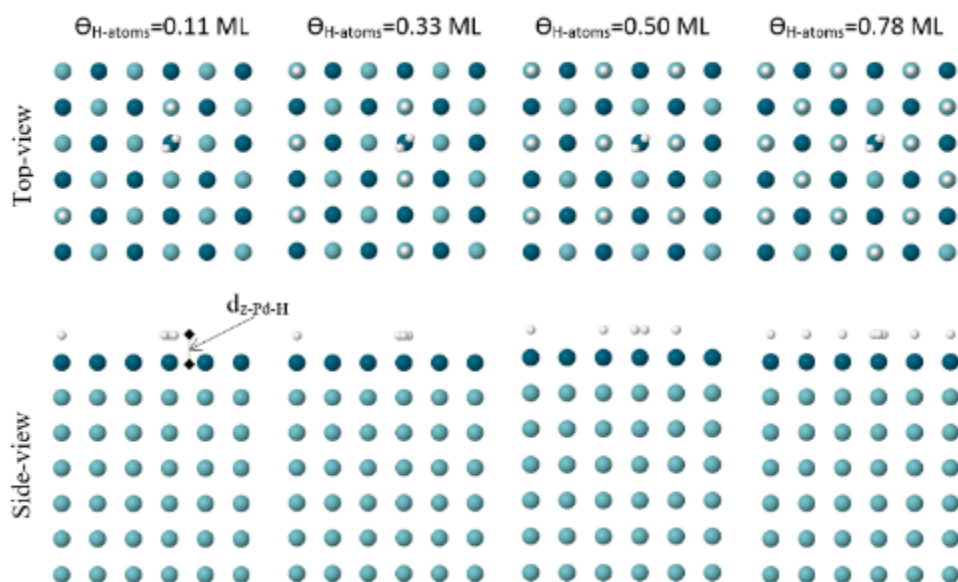


Figure 98. Initial location of H₂ molecule with different coverage of H-atoms.

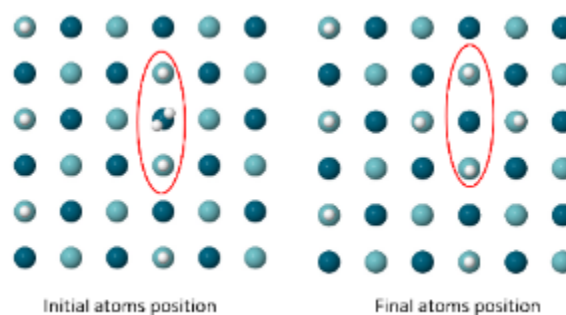


Figure 99. Dissociation of H₂ molecule when trying to capture physisorption and chemisorption of H₂/H-atoms ($\Theta_{\text{H-atoms}} = 0.3$, initial distance from Pd-surface = 2.0 Å).

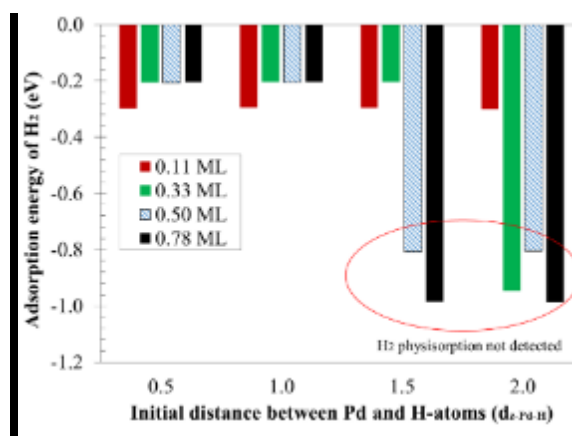


Figure 100. Physisorption of H₂ molecule at different $\Theta_{\text{H-atoms}}$ and various initial distance between Pd and H (dz-Pd-H).

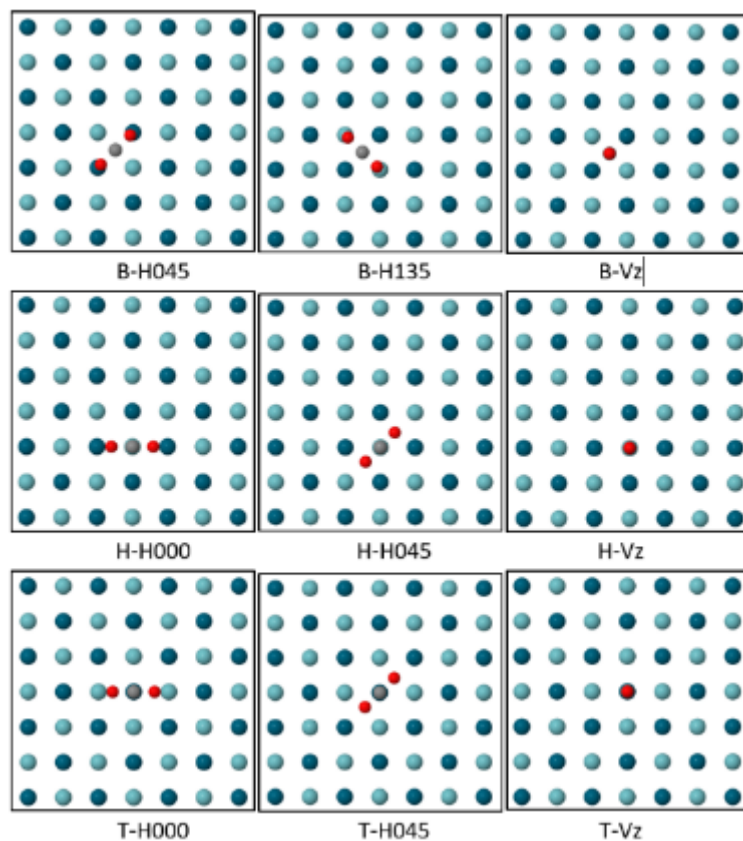


Figure 101. Top-view of CO₂ on Pd-surface (100) at different site/orientation.

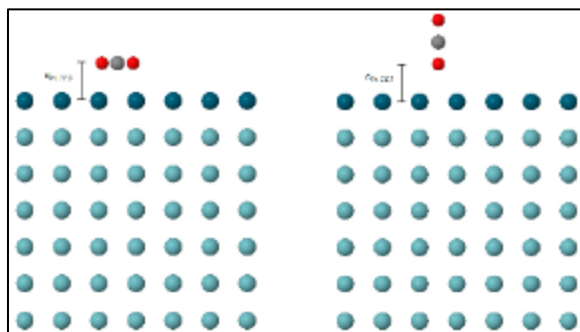


Figure 102. Side-view showing initial distance between CO₂ and Pd-surface (100) at horizontal and vertical orientation.

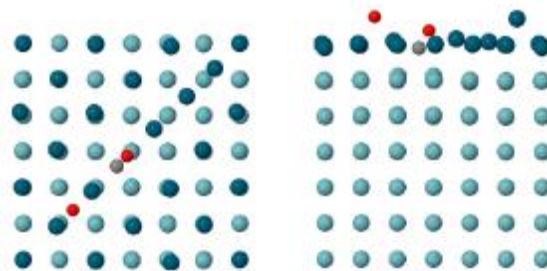


Figure 103. Relaxed structure of unsuccessful physisorption for case B.H045 (when CO₂ initially located very close to Pd-surface), (left: top-view, right: side-view).

Table 18. Summary of adsorption energy (eV) of CO₂ on Pd-surface (100) at various sites/orientations.

Site/orientation	Initial distance between Pd surface and CO ₂ molecule (Å)				
	0.0	0.5	1.0	1.5	2.0
B.H045	+3.063	+3.271	-0.241	-0.240	-0.239
B.H135	-0.220		-0.223	-0.222	-0.220
B.Vz	-0.139	-0.142	-0.143	-0.142	-0.137
H.H000	-0.255	-0.254	-0.255	-0.255	-0.255
H.H045		-0.246	-0.250	-0.246	-0.247
H.Vz	-0.145	-0.145	-0.140	-0.141	-0.142
T.H000	-	-0.212	-0.211	-0.210	-0.212
T.H045	-	-0.214	-0.215	-0.215	-0.214
T.Vz	-	-0.138	-0.138	-0.138	-0.136

Table 19. Summary of adsorption energy (eV) of CO on Pd-surface (100) at various sites/orientations.

Case	Initial distance between Pd surface and CO molecule (Å)				
	0.0	0.5	1.0	1.5	2.0
B.H045	-1.885	-1.884	-1.883	-1.885	-1.885
B.H135	-1.883	-1.878	-1.882	-1.878	-1.884
B.VCdown	-1.882	-1.882	-1.884	-1.887	-1.886
B.VOdown	-0.110	-0.117	-0.114	-0.110	-0.111
H.H000	-1.793	-1.792	-1.794	-1.793	-1.794
H.H045	-1.793	-1.886	-1.885	-1.886	-1.884
H.VCdown	-1.791	-1.792	-1.793	-1.793	-1.793
H.VOdown	-0.114	-0.116	-0.104	-0.111	-0.113
T.H000	-	-1.793	-1.519	-1.519	-1.519
T.H045	-	-1.887	-1.883	-1.520	-1.519
T.VCdown	-	-1.521	-1.519	-1.521	-1.521
T.VOdown	-	-0.116	-0.117	-0.113	-0.113

Table 20. Summary of adsorption energy (eV) of CH₄ on Pd-surface (100) at various sites/orientations.

Case	Initial distance between Pd surface and CH ₄ molecule (Å)			
	0.5	1.0	1.5	2.0
B.1Hdwn045	-0.174	-0.173	-0.168	-0.171
B.1Hdwn315	-0.175	-0.173	-0.168	-0.171
B.2Hdwn045	-0.190	-0.190	-0.189	-0.187
B.2Hdwn315	-0.180	-0.180	-0.180	-0.171
B.3Hdwn045	-0.182	-0.185	-0.187	-0.189
B.3Hdwn315	-0.182	-0.183	-0.188	-0.189
H.1Hdwn000	-0.168	-0.168	-0.167	-0.159
H.1Hdwn045	-0.168	-0.168	-0.167	-0.159
H.2Hdwn000	-0.182	-0.182	-0.181	-0.182
H.2Hdwn045	-0.182	-0.183	-0.183	-0.183
H.3Hdwn000	-0.186	-0.194	-0.194	-0.194
H.3Hdwn045	-0.186	-0.194	-0.194	-0.194
T.1Hdwn000	-0.182	-0.181	-0.178	-0.182
T.1Hdwn045	-0.182	-0.181	-0.179	-0.182
T.2Hdwn000	-0.189	-0.190	-0.190	-0.188
T.2Hdwn045	-0.189	-0.189	-0.188	-0.189
T.3Hdwn000	-0.185	-0.182	-0.183	-0.182
T.3Hdwn045	-0.188	-0.182	-0.183	-0.182

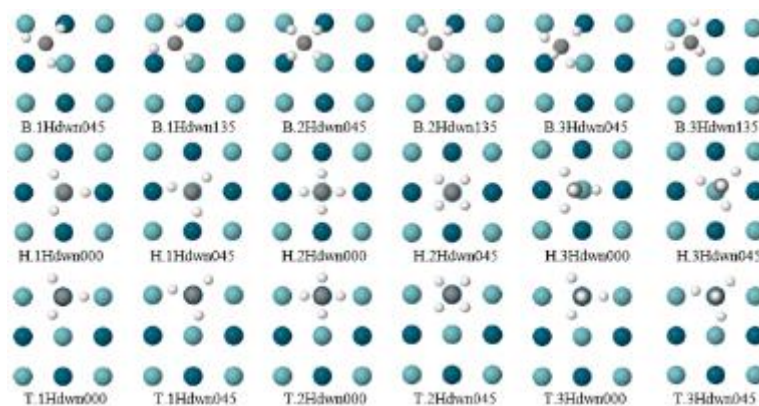


Figure 104. Top-view of relaxed CH4 on Pd-surface (100) at different sites/orientations.

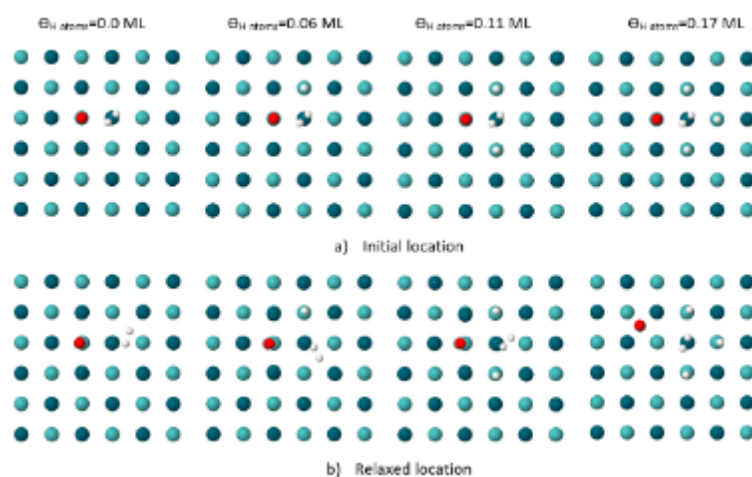


Figure 105. Initial and relaxed locations of H₂ adsorption at presence of CO and various coverage of H-atoms.

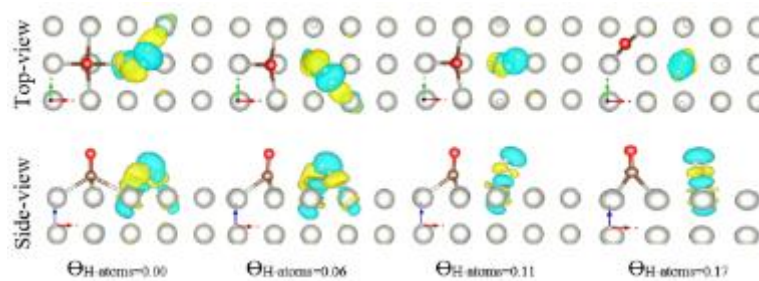


Figure 106. Charge density difference of H₂ at presence of CO with various hydrogen coverage (Isosurface at 0.003).

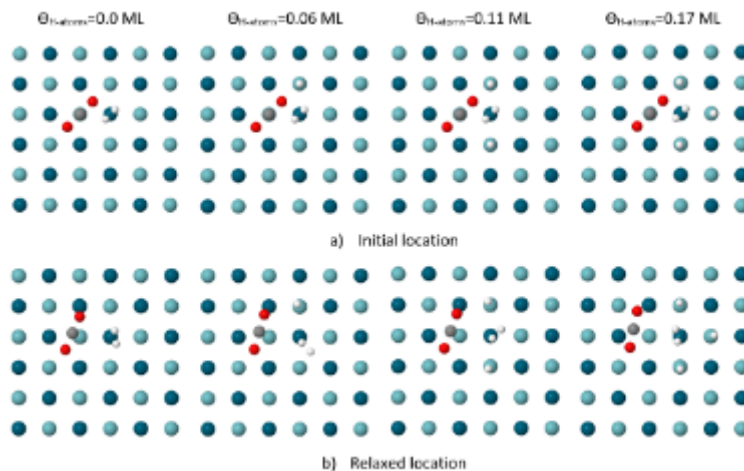


Figure 107. Initial and relaxed locations of H_2 adsorption at presence of CO_2 and various coverage of H-atoms.

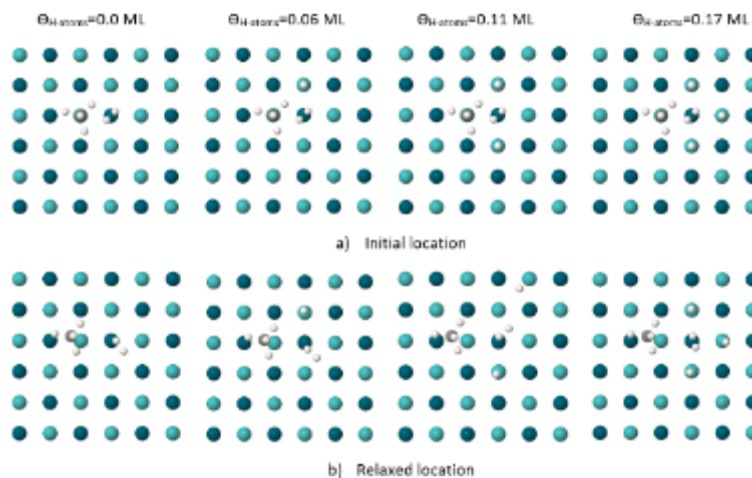


Figure 108. Initial and relaxed locations of H_2 adsorption at presence of CH_4 and various coverage of H-atoms.

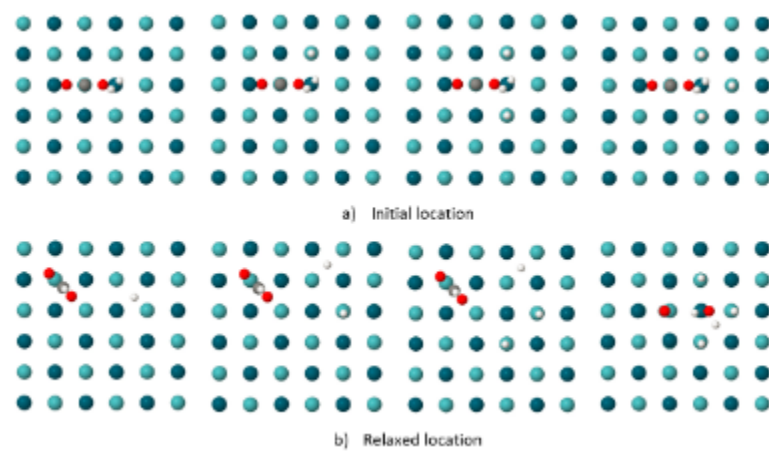


Figure 109. An attempt to capture H_2 physisorption at presence of CO_2 at orientation of H.H000.

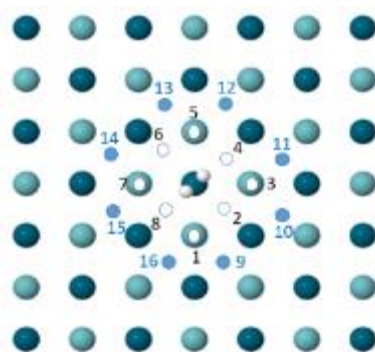


Figure 110. Available local sites for final stage of dissociation process on Pd(100).

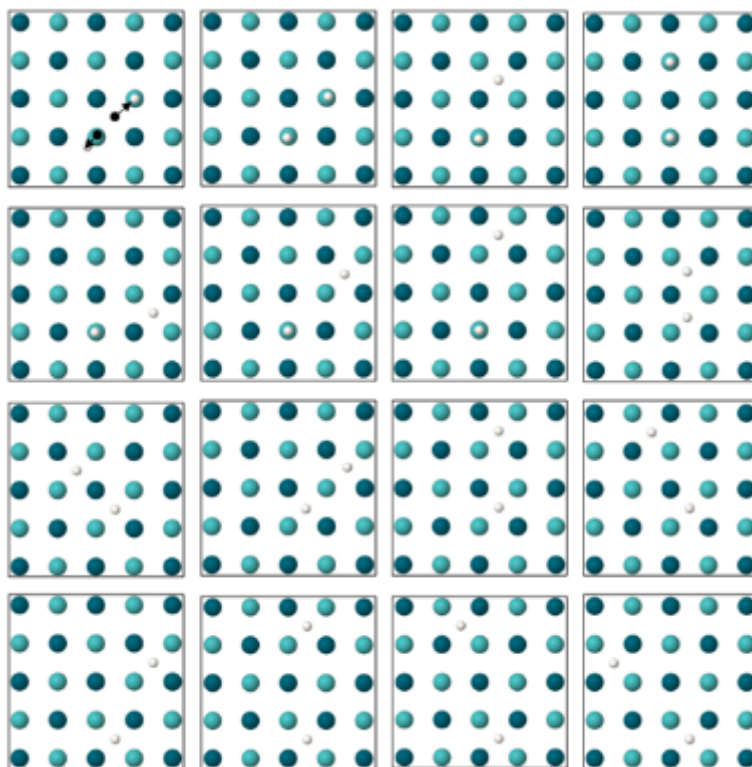


Figure 111. Relaxed positions of two hydrogen atoms located at different sites as shown in Figure 57.

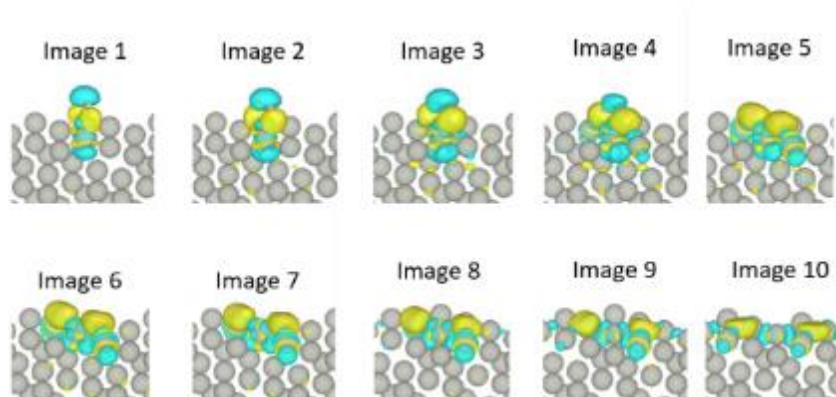


Figure 112. Isosurface of charge density difference for reaction coordinates of H₂ dissociation “blue: +ve charge, and yellow: -ve charge” (isometric-view)

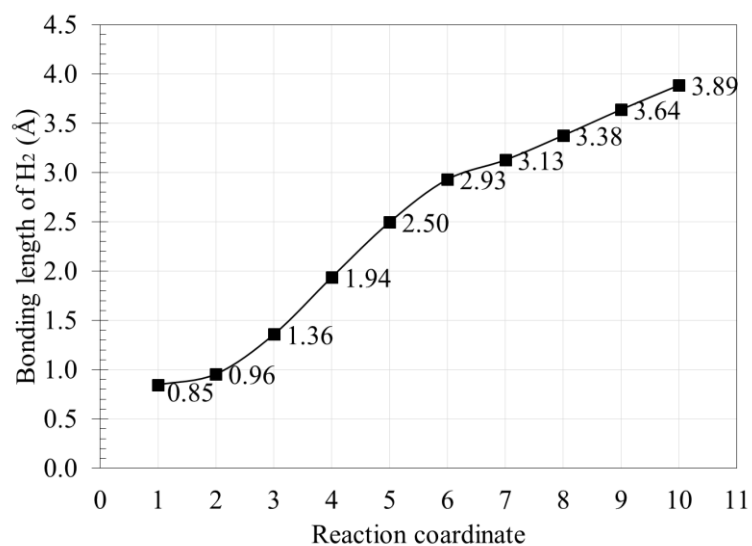


Figure 113. Bonding length of hydrogen molecule during dissociation process.

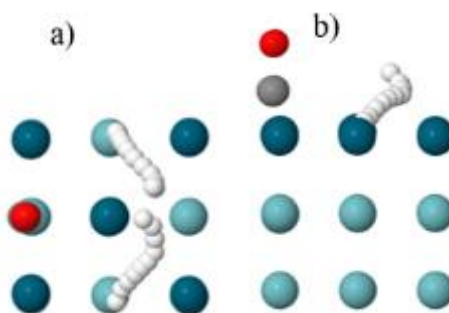


Figure 114. Pathway of H₂ dissociation process on Pd-surface poisoned by CO gas a) top-view and b) side-view.

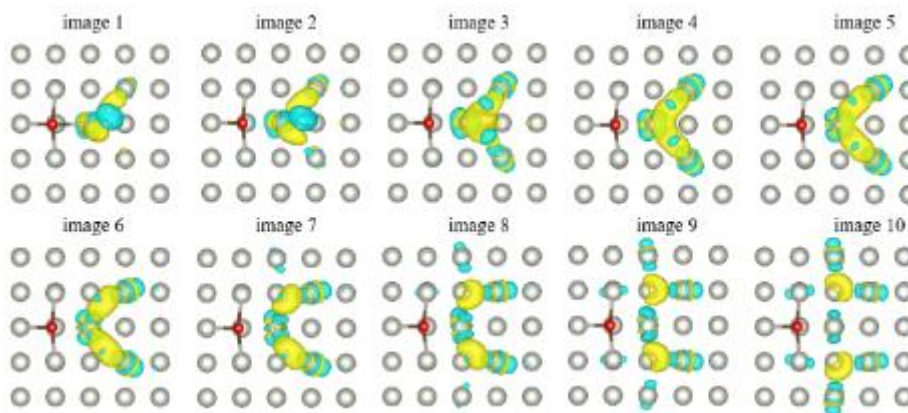


Figure 115. Isosurface of charge density difference for reaction coordinates of H₂ dissociation on Pd-surface poisoned by CO gas “blue: +ve charge, and yellow: -ve charge” (top-view).

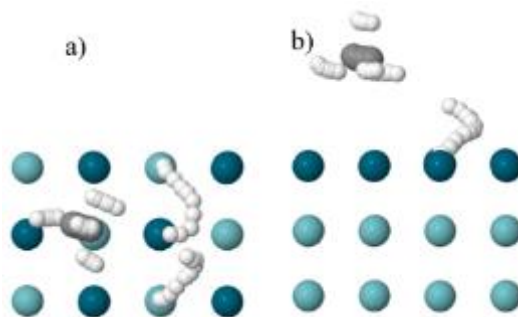


Figure 116. Pathway of H_2 dissociation process on Pd-surface poisoned by CH_4 gas a) top-view and b) side-view.

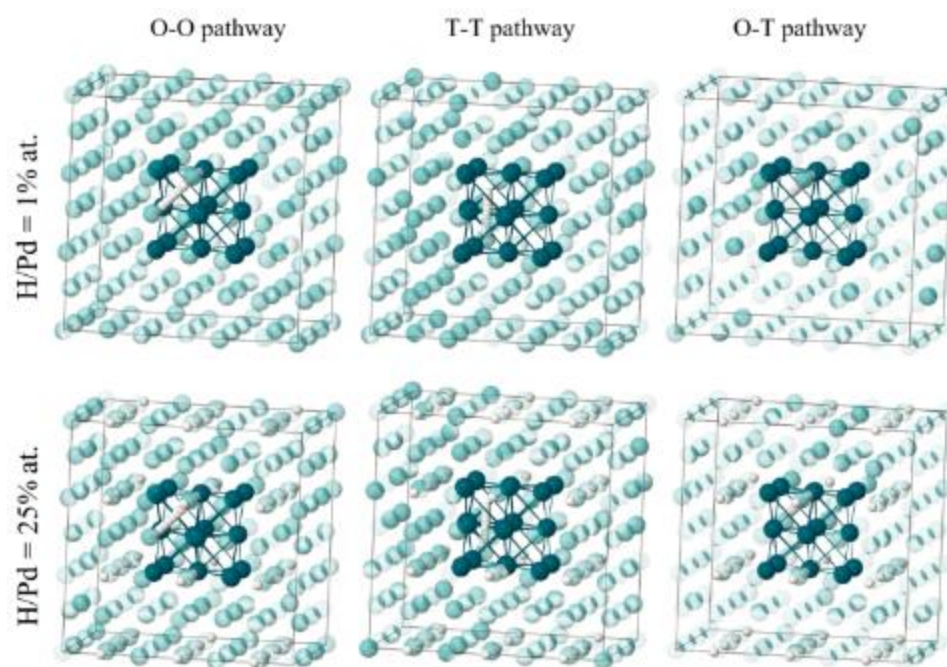


Figure 117. Hydrogen diffusion through various pathways at 1% and 25% at. concentration (3x3x3 cell size).

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