

Incident angle dependence of H₂ adsorption on a defective Pt(111) surface: first-principles calculation

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The effects of the incident angle on molecular hydrogen (H₂) dissociative adsorption on a defective platinum (Pt) surface are determined using density functional theory method. The potential energy is calculated as functions of the H₂ interatomic distance r and H₂ center of mass distance Z from the surface for different incident angles and approach sites. The potential energy surface for each incident angle and approach site is obtained by plotting the potential energy as functions of r and Z. Based on the potential energy surfaces, H₂ dissociative adsorption occurs for all the incident angles and approach sites considered, with one hydrogen (H) atom residing closer to the Pt surface than the other H atom. The activation barriers for H₂ approaching the top and hexagonal close packed sites are much lower than those obtained for H₂ approaching the vacant site. In general, the desorption energy is found to decrease as the incident angle of H₂ is increased.

INTRODUCTION

Over the past decades, the harmful effects on the environment brought about by burning fossil fuels have given rise to a growing scientific interest in the development of alternative energies. Today, great efforts are being devoted to investigating

and developing hydrogen fuel cells that are capable of generating electrical energy with water and heat as the only byproducts. The fuel cell operates by catalysis wherein the component electrons and protons of hydrogen are separated by a catalyst at the anode and the electrons are forced to travel through an external circuit creating an electrical current. Although platinum is a rare and expensive metal, it is widely used as catalyst due to its efficiency in accelerating chemical reactions in fuel cells. Moreover, it is durable and can withstand the harsh acidic environment of the fuel cell. A detailed investigation on the interaction between hydrogen and platinum can contribute to the design of more efficient hydrogen fuel cells and hydrogen storage systems. Thus, several studies on the interaction of hydrogen with metals, particularly hydrogen adsorption on platinum have been performed (Abanador et al. 2013, Arboleda et al. 2006a,b, Arboleda et al. 2007, Arboleda and Kasai 2008a,b, Badescu et al. 2002, Crespos et al. 2004, Gee et al. 2000, Gudmundsdottir et al. 2013, Kallen and Wahnstrom 2002, Koido et al. 2011, Ludwig et al. 2006, Luntz et al. 1990, McCormack et al. 2005, Nobuhara et al. 2000, Nobuhara et al. 2001, Nobuhara et al. 2002a,b, Nobuhara et al. 2004, Olsen et al. 1999, Olsen et al. 2002, Olsen et al. 2004a,b, Pijper et al. 2000, Pijper et al. 2001, Pijper et al. 2002a,b, Poelsema et al. 2010, Poelsema et al. 2011, Ras et al. 2013, Roman et al. 2006, Tsuda and Kasai 2006, Vincent et al. 2004, Watson et al. 2001, Xu et al. 1999).

In a previous study, density functional theory (DFT)-based calculations on a defective Pt(111) surface revealed hydrogen to

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Submitted: September 19, 2013

Revised: January 27, 2014

Accepted: January 29, 2014

Published: March 22, 2014

Editor-in-charge: Manuel P. Soriaga

KEYWORDS

density functional theory, dissociative adsorption, potential energy surface, hydrogen fuel cell, hydrogen storage

Table 1. Summary of DFT-based results for H₂ dissociative adsorption on a defective Pt(111) surface.

Approach Site	Incident Angle θ (°)	Activation Barrier (eV)	Desorption Energy (eV)	Interatomic Distance r (Å)	H2 CM Distance Z (Å)	Upper H atom		Lower H atom	
						h (Å)	d (Å)	h (Å)	d (Å)
Top	0	0*	1.2*	n/a	n/a	n/a	n/a	n/a	n/a
	15	0	0.9644	2.14	1.25	1.527	4.101	0.973	3.432
	30	0.0957	0.8927	1.74	1.25	1.685	4.768	0.815	3.325
	55	0.723	0.185	1.94	0.75	1.545	4.285	-0.045	3.173
HCP	0	0.15*	n/a	n/a	n/a	n/a	n/a	n/a	n/a
	15	0.171	1.126	2.54	1.25	1.579	4.091	0.921	1.638
	30	0.0957	0.9067	3.14	0.75	1.535	4.126	-0.035	1.407
	55	0.163	0.3483	0.94	1	1.385	2.041	0.615	1.502
Vacant	0	0.862*	2.1551*	3.94*	1*	1*	1.97*	1*	1.97*
	15	0.932	1.672	2.74	0	0.355	1.323	-0.355	-1.323
	30	1.116	1.465	2.74	0	0.685	1.186	-0.685	-1.186
	55	0.998	1.594	2.34	-0.5	0.484	1.385	-1.458	0.043

*results of previous studies (Arboleda et al. 2007, Arboleda et al. 2008)

H: height from the Pt surface

D: distance from the center of vacant site

e1		e2	
h (Å)	d (Å)	h (Å)	d (Å)
1	2.1354	1	-2.1354

be preferably adsorbed on the bridge sites at the step edges of a vacancy and to be expected to have a migration barrier above 30 meV (Roman et al. 2006). In another study, it was found that the vacant sites enhance the surface reactivity by lowering the activation barriers for H₂ dissociative adsorption (Arboleda et al. 2007, Arboleda and Kasai 2008a,b). It has also been shown that incident H₂ initially in a nonparallel (e.g., perpendicular) orientation tends to reorient itself towards a parallel orientation where it is easier for H₂ to be adsorbed (Arboleda and Kasai 2008a,b).

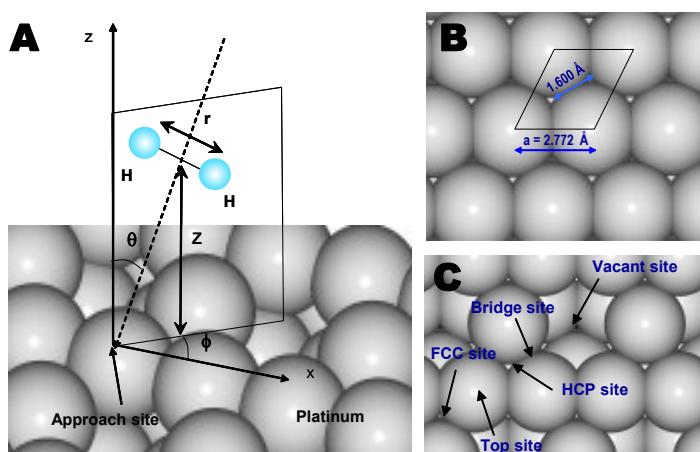


Figure 1. A, The H₂ orientation where r is the interatomic distance, Z is the H₂ CM distance from the surface, ϕ is the azimuthal angle, and θ is the incident angle. B, The ideal Pt(111) surface showing the unit cell used with a lattice constant of 2.772 Å; and C, the Pt surface with vacancies.

In an experimental study (Luntz et al. 1990), molecular beam techniques were utilized to measure the dissociative chemisorption probability at zero surface coverage for deuterium (D₂) and H₂ on Pt(111) as a function of initial energy, angle of incidence, surface temperature, isotopic mass and nozzle temperature. A similar study was done by Koido et al. (2011) using molecular dynamics. Both studies showed the following trend: the dissociation probability increases with the initial translational energy and decreases with increasing angle of incidence.

In a preliminary study (Natividad et al. 2009), we performed total energy DFT-based calculations to investigate the effects of the incident angle on H₂ dissociative adsorption on a defective Pt(111) surface. The potential energy was calculated as functions of the H₂ interatomic distance r and H₂ center of mass (CM) distance Z from the surface for incident angles 15°, 30° and 55° approaching the top and hexagonal close packed (HCP) sites. We obtained the potential energy plots as functions of Z for different values of r. Based on the plots, it was observed that as the incident angle increases, the desorption energy decreases.

Here, we consider another approach site, the vacant site, to investigate its effect on the adsorption of H₂ at different incident angles. We calculate the potential energy as functions of r and Z for incident angles 15°, 30° and 55° with H₂ approaching the said site. From the calculated values of the potential energy for the top and HCP sites (obtained from our preliminary study (Natividad et al. 2009)) and the vacant site as approach sites, we obtain the potential energy surface (PES) contour plots and de-

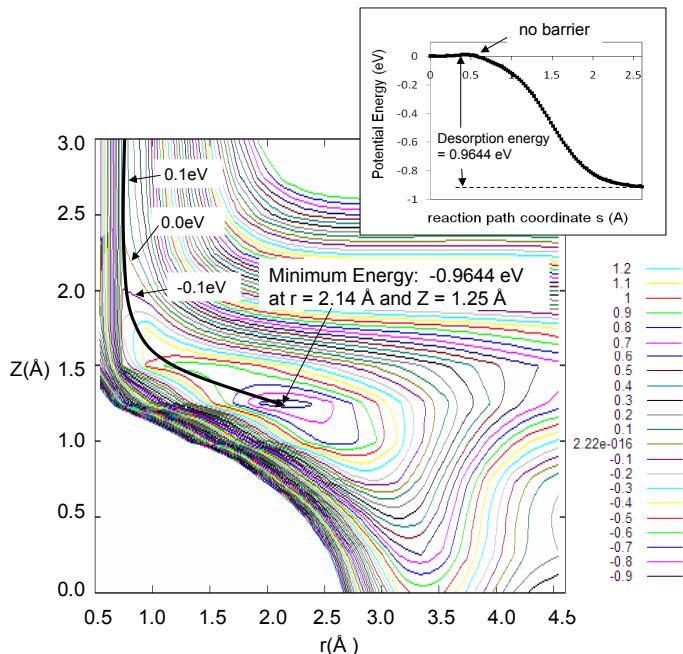


Figure 2. PES contour plot as functions of the H_2 interatomic distance r and H_2 CM distance from the surface for incident angle $\theta = 15^\circ$ and top site as the approach site. The contour spacing is 0.1eV. The thick solid line traces the reaction path (path of minimum potential) for H_2 adsorption. The inset shows the potential energy plot along this path as a function of the reaction path coordinate s . The origin of the reaction path corresponds to $Z = 3.0 \text{ \AA}$.

determine the reaction path (path of least potential) for H_2 adsorption on a defective Pt(111) surface. The potential energy curves along the reaction path are obtained by plotting the potential energy as functions of the reaction path coordinate s . From these curves, the barrier height and the desorption energy are determined.

COMPUTATIONAL METHOD

DFT-based calculations of the total energy are performed using the Dacapo software. The total energy was computed in a super cell geometry using plane waves and pseudopotentials. The generalized gradient approximation (GGA) was used for the exchange correlation energy (Perdew et al. 1992). The metal surface is represented by periodically repeated slabs consisting of three substrate layers, separated by a vacuum layer equivalent to six atomic layers. The first substrate layer contains three Pt atoms, while each of the next two layers contains four Pt atoms. A surface with an ordered arrangement of vacancy defects is created by removing one atom in four at the first layer. This was done for simplification and computational practicality. The shortest distance between two Pt atoms is 2.772 Å and the slab thickness is 4.527 Å. The bare Coulomb potential is used for hydrogen, while the ultrasoft pseudopotential scheme (Vanderbilt 1990) is used to represent the ion cores of the metal atoms. For this system, a cutoff energy of 30 Ry is applied to limit the plane wave basis set. The surface Brillouin zone is sam-

pled using 16 special k-points, with 8 points in the irreducible wedge, via the special point sampling technique of Monkhorst and Pack (1976). Convergence of the numerical results is checked with respect to the slab thickness, the kinetic energy cutoff and the k-point set in each calculation.

The potential energy is calculated as functions of the H_2 interatomic distance r and the H_2 CM distance Z from the surface for different incident angles and approach sites. The Pt lattice is kept frozen as H_2 approached the surface. Figure 1 shows the model used for the hydrogen orientation and the Pt(111) surface. The approach sites considered are the top site, the HCP site and the vacant site. For each approach site, the angle of incidence θ is varied and for each θ , r and Z are varied. The incident angles considered for each approach site are 15° , 30° and 55° . The H_2 interatomic distance r is varied from 0.54 Å to 4.54 Å with an interval of 0.2 Å while the H_2 CM distance Z from the surface is varied from 3.0 Å to 0.0 Å with a 1.0-Å interval for the top and HCP sites as approach sites and from 3.0 Å to -3.0 Å for H_2 approaching the vacant site. The azimuthal angle ϕ and the angle made by the H_2 bond axis with the line of approach are kept constant at 30° and 90° , respectively. PES contour plots for different incident angles and approach sites are generated by plotting the potential energy as functions of r and Z .

RESULTS AND DISCUSSIONS

To determine the dependence of H_2 adsorption on the orientation of H_2 as it approaches the Pt surface, we calculated the potential energy as functions of r and Z for different incident angles and approach sites. Table 1 summarizes the results of the DFT-based calculations. We also obtained the PESs as functions of Z and r and the potential energy curves along the reaction paths as functions of the reaction path coordinate s . The zero reference energy for the plots was chosen to correspond to the total energy of the H_2 -Pt system when H_2 is sufficiently far from the surface (i.e., $Z = 3.0 \text{ \AA}$ and $r = 0.74 \text{ \AA}$).

Figure 2 shows the PES for the angle of incidence $\theta = 15^\circ$ and the top site as the approach site. The thick solid line represents the reaction path (i.e., the path of least potential) for H_2 adsorption. The inset shows the potential energy curve along this path as a function of the reaction path coordinate s . The origin of the reaction path corresponds to $Z = 3.0 \text{ \AA}$ and $r = 0.74 \text{ \AA}$. It can be seen from the figure that there is no energy barrier to be overcome by H_2 in the adsorption process. The minimum energy is found to be -0.9644 eV occurring at $r = 2.14 \text{ \AA}$ and $Z = 1.25 \text{ \AA}$. At these values of r and Z , the lower H atom is 0.973 Å (refer to Table 1) from the Pt surface while the upper H atom is 1.527 Å from the surface (Fig. 3). These suggest that dissociation of H_2 occurs and both H atoms are adsorbed with one atom residing closer to the Pt surface than the other. It was reported in another study (Roman et al. 2006) that the strongest adsorption for an H atom on such a defective Pt(111) surface occurs at points e1 and e2 (Fig. 4), with the former slightly preferred over the other. Point e1 is 2.1354 Å from the center of the vacant site to the

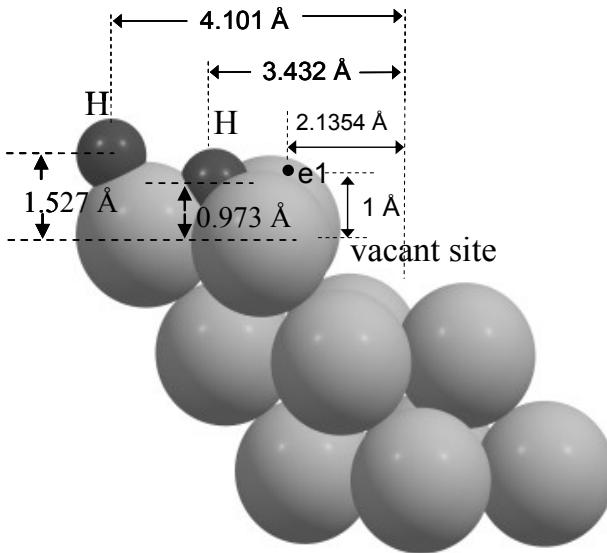


Figure 3. Locations of the adsorbed H atoms on the Pt(111) surface for incident angle $\theta = 15^\circ$ and top site as the approach site.

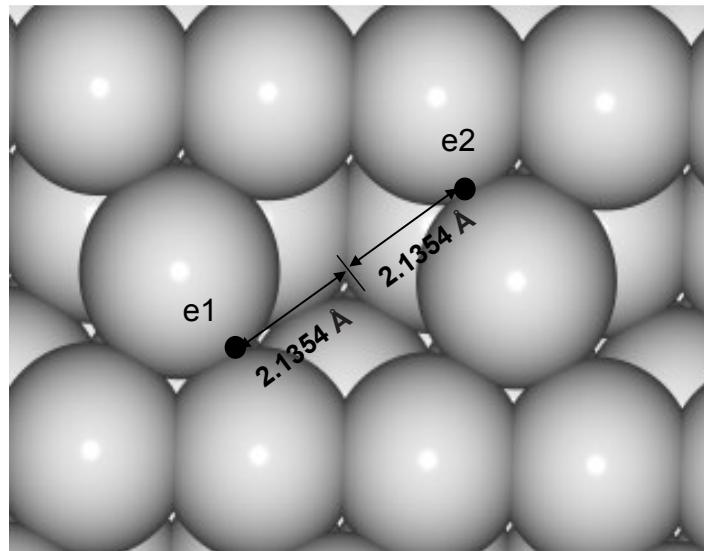


Figure 4. Locations of the strongest (e1) and second strongest H atom adsorption (e2) on defective Pt(111) surface.

bridge sites of the first-layer Pt atoms adjacent to the (100) vacancy step edges, while e2 is 2.1354 Å to that of the (111) vacancy step edges. Both are located 1.0 Å above the surface. The height of the adsorbed lower H atom from the Pt surface in this study almost coincides with that of e1. Its distance from the center of the vacant site (3.432 Å), however, is larger than that of e1. This shift is probably due to the attraction of the lower H atom to the upper H atom.

The corresponding PES contour plot for incident angle $\theta = 30^\circ$ and the top site as the approach site is shown in Fig. 5. An activation barrier of 0.0957 eV is observed for this case. The calculated minimum energy is -0.7972 eV at $r = 1.74$ Å and $Z = 1.25$ Å. The height of the lower H atom from the Pt surface is 0.815 Å while that of the upper H atom is 1.685 Å. Here, dissociative adsorption also occurs with the lower H atom residing closer to the Pt surface. The height of the lower H atom is slightly shorter than that of e1 and, as in the previous case, its distance from the center of the vacant site (3.325 Å) is larger than e1.

Figure 6 shows the PES for the incident angle $\theta = 55^\circ$ and the top site as the approach site. The activation barrier is found to be 0.723 eV and the minimum energy is 0.538 eV at $r = 1.94$ Å and $Z = 0.75$ Å. It can be observed from the potential energy curve (see inset of Fig. 4) that the minimum at $s = 3.16$ Å is a local minimum since there is a lower minimum next to it (at $s = 4.08$ Å). At the local minimum, the adsorbed H atoms are said to be in a metastable, or weakly stable, state since they are susceptible to fall into the lower energy state by overcoming the barrier, or tunneling through it. The distances of the adsorbed upper and lower H atoms from the Pt surface are 1.545 Å and -0.045 Å, respectively, and their distances from the center of the vacant site are 4.285 Å and 3.173 Å, respectively. The height of the

lower H atom is much lower than that of e1 due to the larger incident angle and, as in the previous cases, its distance from the vacant site is larger than that of e1 due to the attraction of the lower H atom to the upper H atom.

The activation barrier for the case wherein the incident angle $\theta = 15^\circ$ and HCP site as the approach site is found to be 0.171 eV and the minimum energy is -0.955 eV at $r = 2.54$ Å and $Z = 1.25$ Å (refer to Table 1). The lower hydrogen atom is 0.921 Å from the Pt surface, while the upper H atom is 1.579 Å from the Pt surface. These suggest that dissociation of H_2 occurs and both H atoms are adsorbed with the lower atom residing closer to the Pt surface. The distance of the lower H atom from the center of the vacant site is 1.638 Å. Its height almost coincides with that of e1, but its distance from the center of the vacant site is shorter than that of e1. This shift is probably due to the attraction of the lower H atom to the vacant site.

For the incident angle $\theta = 30^\circ$ and HCP site as the approach site, the activation barrier is found to be 0.0957 eV (see Table 1). The minimum energy is -0.8111 eV occurring at $r = 3.14$ Å and $Z = 0.75$ Å. The distance of the lower H atom from the Pt surface is -0.035 Å, while that of the upper H atom is 1.535 Å. This implies that H_2 is dissociated into its component atoms and both are adsorbed with the lower H atom residing farther into the subsurface of the metal substrate. The height of the lower atom is much lower than that of e1 and, as in the previous case for this approach site, its distance from the center of the vacant site (1.407 Å) is shorter than that of e1.

An activation barrier of 0.163 eV is observed for the incident angle $\theta = 55^\circ$ and HCP site as the approach site. The minimum energy is -0.1853 eV occurring at $r = 0.94$ Å and $Z = 1.0$ Å

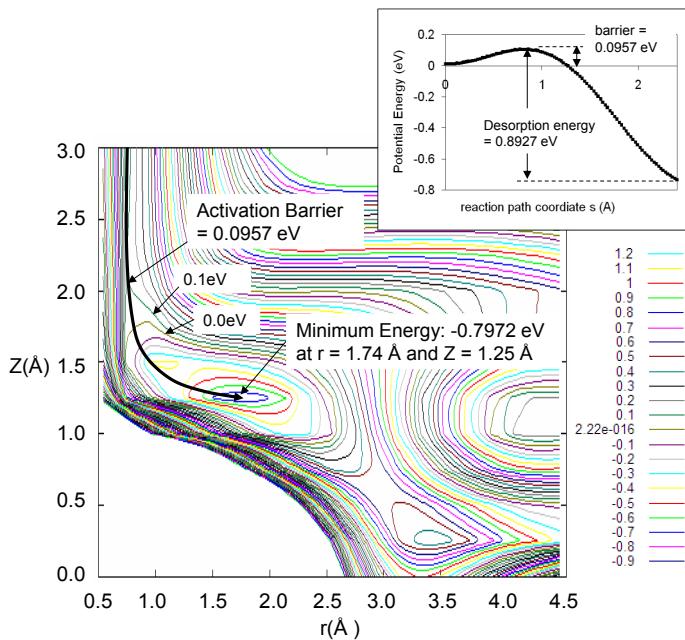


Figure 5. PES contour plot as functions of the H₂ interatomic distance *r* and H₂ CM distance from the surface for incident angle $\theta = 30^\circ$ and top site as the approach site. The contour spacing is 0.1eV. The thick solid line traces the reaction path (path of minimum potential) for H₂ adsorption. The inset shows the potential energy plot along this path as a function of the reaction path coordinate *s*.

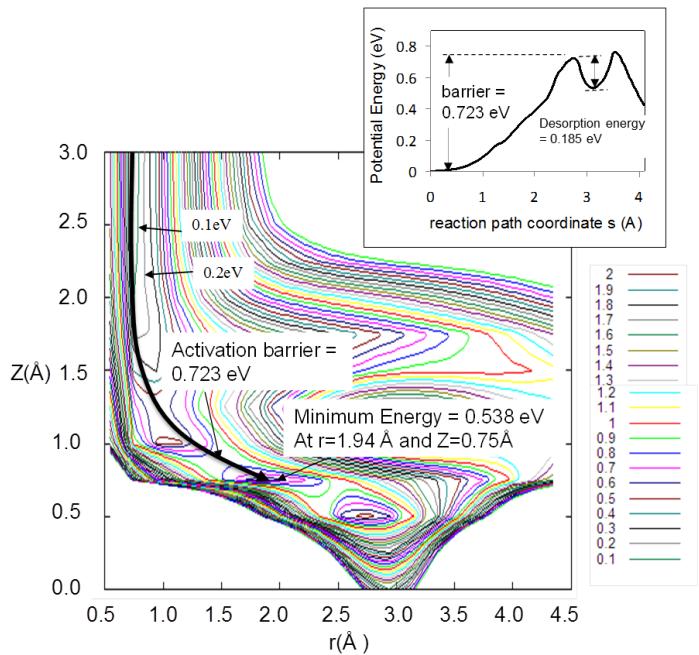


Figure 6. PES contour plot as functions of the H₂ interatomic distance *r* and H₂ CM distance from the surface for incident angle $\theta = 55^\circ$ and top site as the approach site. The contour spacing is 0.1eV. The thick solid line traces the reaction path (path of minimum potential) for H₂ adsorption. The inset shows the potential energy plot along this path as a function of the reaction path coordinate *s*.

(see Table 1). The distances of the upper and lower adsorbed H atoms from the Pt surface are 1.385 Å and 0.615 Å, respectively, and their distances from the center of the vacant site are 2.041 Å and 1.502 Å, respectively. Here, the distance of the lower H atom from the center of the vacant site and its distance from the surface are also lower than those of e1.

For the configuration wherein the incident angle $\theta = 15^\circ$ and the vacant site is the approach site, the activation barrier is found to be 0.932 eV and the minimum energy is -0.741 eV occurring at *r* = 2.74 Å and *Z* = 0.0 Å (see Table 1). Dissociative adsorption occurs with one H atom residing 0.355 Å below the Pt surface and the other atom residing 0.355 Å above it. The distance of both adsorbed H atoms from the vacant site (1.323 Å) and their distances from the Pt surface are shorter than those of e1 and e2. This is probably due to the attraction of the adsorbed H atoms to the vacant site.

The activation barrier for incident angle $\theta = 30^\circ$ and the vacant site as the approach site is 1.116 eV and the minimum energy is -0.349 eV at *r* = 2.74 Å and *Z* = 0.0 Å (refer to Table 1). The height of one adsorbed H atom from the Pt surface is 0.685 Å while the other H atom is 0.685 Å below it. The distance of the H atoms from the vacant site is 1.186 Å. As in the previous case for this approach site, the distance of both adsorbed H atoms from the vacant site and their distances from the Pt surface are shorter than those of e1 and e2.

For the incident angle $\theta = 55^\circ$ and the vacant site as the approach site, the activation barrier is found to be 0.9984 eV and the minimum energy is -0.597 eV at *r* = 2.34 Å and *Z* = -0.5 Å (see Table 1). At these values of *r* and *Z* from the surface, the height of the upper H atom from the Pt surface is 0.484 Å, while the lower H atom is 1.458 Å below it. The distance of the upper H atom from the vacant site is 1.385 Å, while that of the lower H atom is 0.043 Å. As in the previous cases for this approach site, the distance of both adsorbed H atoms from the vacant site and their distances from the Pt surface are shorter than those of e1 and e2.

Figure 7 shows the potential energy as a function of the reaction path coordinate *s* for the different configurations. It can be observed from these plots that the height of the activation barrier is much lower (even zero for the top site) for H₂ approaching the top and HCP sites as compared to those obtained for H₂ approaching the vacant site. This suggests that dissociative adsorption is favorable for H₂ approaching the top and HCP sites and unfavorable for H₂ approaching the vacant site.

It was shown in previous studies (Arboleda et al. 2007, Arboleda and Kasai 2008a,b) that, for the H₂ bond axis parallel to the surface, the barrier is lowest (almost zero for the ideal surface and zero for the defective surface) when the CM of H₂ is directly above the top site while the H atoms are directed towards the HCP and face centered cubic (FCC) hollow sites. This

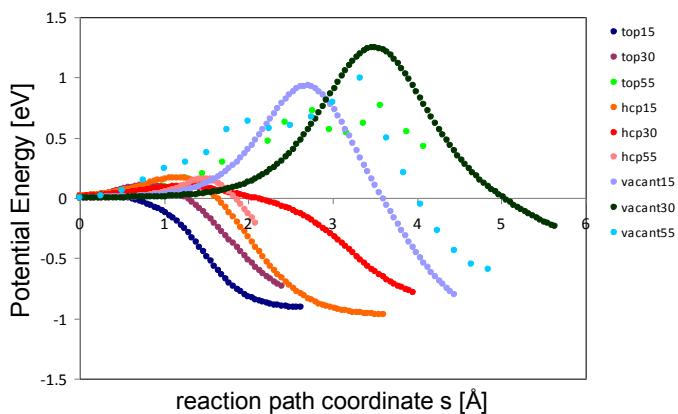


Figure 7. Potential energy as a function of the reaction path coordinate s for the different configurations.

orientation of H_2 is the same as in this study when the incident angle $\theta = 0^\circ$ and the top site is the approach site. In this work, the activation barrier is zero for H_2 approaching the top site at $\theta = 15^\circ$. This result confirms that, for small incident angles, the Pt atom located on the top site significantly aids H_2 dissociative adsorption on the $\text{Pt}(111)$ surface. For the case where the approach site is the vacant site, the activation barriers are much higher than those of the other two configurations. This is due to the absence of a Pt atom at the approach site.

From the potential energy curves (Fig. 7) and Table 1, it is clear that the desorption energy, in general, decreases as the angle of incidence of H_2 increases. This suggests that at large incident angles, the adsorbed H atoms become unstable since they can be easily detached from the surface. Thus, for hydrogen fuel cells and hydrogen storage systems, H_2 adsorption at large incident angles is undesirable. However, it may be beneficial to other surface reactions such as hydrogen abstraction (i.e., the removal of an adsorbed hydrogen by another H atom) from a metal surface. If an H atom is allowed to approach the surface at a large angle, it may react with an adsorbed H atom to form H_2 and, since its adsorption energy at that incident angle is small, its initial kinetic may be enough for the molecule to desorb.

CONCLUSIONS

Based on the calculations and the PESs, H_2 adsorption and dissociation are found to depend on the angle of incidence and the approach site. Dissociative adsorption of H_2 on the Pt surface is observed for all the incident angles and approach sites considered. In each case, both H atoms are adsorbed with one H atom residing closer to the Pt surface than the other H atom. The height of the adsorbed lower H atom almost coincides with that of e1 for $\theta = 15^\circ$ for the top and HCP sites as approach sites. The distance from the center of the vacant site of the lower H atom, however, is farther than e1 for H_2 approaching the top site and shorter than e1 for H_2 approaching the HCP site. For the case wherein the vacant site is the approach site, the distances of the

adsorbed H atoms from the surface and their distances from the vacant site are much shorter than those of e1 and e2. The activation barriers for H_2 approaching the top and HCP sites are much lower than those obtained for H_2 approaching the vacant site. The highest desorption energy occurs at $\theta = 15^\circ$ for each approach site. In general, the desorption energy decreases as the angle of incidence of H_2 increases.

ACKNOWLEDGMENTS

The calculations presented here were carried out using the computer facilities of the High Performance Computing Laboratory of De La Salle University, Manila, Philippines.

CONFLICTS OF INTEREST

None.

REFERENCES:

- Abanador PM, Villagracia ARC, Arboleda NB, David MY, First principle investigation of atomic hydrogen adsorption on Pd-doped MgB_2 . *Phil Sci Letts* 2013; 6:176-181.
- Arboleda NB, Kasai H, Nakanishi H, Dino WA, Quantum dynamics study on the interaction of H_2 on a $\text{Pt}(111)$ surface. *Thin Solid Films* 2006; 509:227-229.
- Arboleda NB, Tsuda M, Kasai H. A quantum dynamics study on the H^+ transmission in a Pt-Nafion interface. *e-J Surf Sci Nanotech* 2006; 4:640-643.
- Arboleda NB, Kasai H, Dino WA, Nakanishi H. Potential energy of H_2 dissociation and sticking on $\text{Pt}(111)$ surface: a first principles calculation. *Jpn J Appl Phys* 2007; 46:4233-4237.
- Arboleda NB, Kasai H. First principles investigations on fuel cell reactions: H_2 - $\text{Pt}(111)$ interactions. *e-J Surf Sci Nanotech* 2008a; 6:134-137.
- Arboleda NB, Kasai H. Potential Energy Surfaces for H_2 Dissociative adsorption on $\text{Pt}(111)$ surface - effects of vacancies. *Surf Interface Anal* 2008b; 40:1103-1107.
- Badescu SC, Salo P, Ala-Nissila T, Ying SC, Jacobi K, Wang Y, Bedurftig K, Ertl G. Energetics and Vibrational States for Hydrogen on $\text{Pt}(111)$. *Phys Rev Lett* 2002; 88:136101-136104.
- Crespos C, Collins MA, Pijper E, Kroes GJ. Application of the modified Shepard interpolation method to the determination of the potential energy surface for a molecule-surface reaction: $\text{H}_2+\text{Pt}(111)$. *J Chem Phys* 2004; 120:2392-2404.
- Gee AT, Hayden BE, Mormiche C, Nunney TS. The role of steps in the dynamics of hydrogen dissociation on $\text{Pt}(533)$. *J Chem Phys* 2000; 112:7660-7668.
- Gudmundsdottir S, Skulason E, Weststrate K-J, Juurlink L, Jonsson H. Hydrogen adsorption and desorption at the $\text{Pt}(110)-(1\times 2)$ surface: experimental and theoretical study. *Phys Chem Chem Phys* 2013; 15:6323-6332.
- Kallen G, Wahnstrom G, Quantum treatment of H adsorbed on a $\text{Pt}(111)$ surface. *Phys Rev B* 2002; 65:033406-033409.

- Kido T, Tomarikawa K, Yonemura S, Tokumasu T. Molecular dynamics study of the effects of translational energy and incident angle on dissociation probability of hydrogen/deuterium molecules on Pt(111). *J Appl Phys* 2011; 110: 024301-024308.
- Ludwig J, Vlachos DG, van Duin ACT, Goddard III WA. Dynamics of the dissociation of hydrogen on stepped platinum surfaces using the ReaxFF reactive force field. *J Phys Chem B* 2006; 110:4274-4282.
- Luntz AC, Brown JK, Williams MD. Molecular beam studies of H₂ and D₂ dissociative chemisorption on Pt(111). *J Chem Phys* 1990; 93:5240-5246.
- McCormack DA, Olsen RA, Baerends EJ. Mechanisms of H₂ dissociative adsorption on the Pt(211) stepped surface. *J Chem Phys* 2005; 122:194708-194724.
- Monkhorst HJ, Pack JD. Special points for Brillouin-zone integrations. *Phys Rev B* 1976; 13:5188-5192.
- Natividad MT, Arboleda NB, Kasai H. Angle of incidence effects on H₂ dissociation and adsorption on defective Pt (111) surface: an ab-initio study, Proceedings of the Osaka University-De La Salle University Academic Research and Workshops, De La Salle University, 2009.
- Nobuhara K, Nakanishi H, Kasai H, Okiji A. Interactions of atomic hydrogen with Cu(111), Pt(111) and Pd(111). *J Appl Phys* 2000; 88:6897-6901.
- Nobuhara K, Nakanishi H, Kasai H, Okiji A. Behavior of H atom in adsorption states on metal surfaces-localization and delocalization. *Surf Sci* 2001; 493:271-277.
- Nobuhara K, Nakanishi H, Kasai H, Okiji A. Quantum mechanical behavior of an H atom on Cu(111) and Pt(111). *J Appl Phys* 2002a; 91:1855-1859.
- Nobuhara K, Kasai H, Nakanishi H, Okiji A. Vibrational properties of an H atom adsorbed on Pt(111). *Surf Sci* 2002b; 507:82-86.
- Nobuhara K, Kasai H, Dino WA, Nakanishi H. H₂ dissociative adsorption on Mg, Ti, Ni, Pd and La surfaces. *Surf Sci* 2004; 566-568:703-707.
- Olsen RA, Kroes GJ, Baerends EJ. Atomic and molecular hydrogen interacting with Pt(111). *J Chem Phys* 1999; 111:11155-11163.
- Olsen RA, Busnengo HF, Salin A, Somers MF, Kroes GJ, Baerends EJ. Constructing accurate potential energy surfaces for a diatomic molecule interacting with a solid surface: H₂+Pt(111) and H₂+Cu(100). *J Chem Phys* 2002; 116:3841-3855.
- Olsen RA, McCormack DA, Baerends EJ. How molecular trapping enhances the reactivity of rough surfaces. *Surf Sci* 2004a; 571:L325-L330.
- Olsen RA, Badescu SC, Ying SC, Baerends EJ. Adsorption and diffusion on a stepped surface: atomic hydrogen on Pt (211). *J Chem Phys* 2004a; 120:11852-11863.
- Perdew JP, Chevary JA, Vosko SH, Jackson KA, Pederson MR, Singh DJ, Fiolhais C. Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Phy. Rev B* 1992; 46:6671-6687.
- Pijper E, Kroes GJ, Olsen RA, Baerends EJ. The effect of corrugation on the quantum dynamics of dissociative and diffractive scattering of H₂ from Pt(111). *J Chem Phys* 2000; 113:8300-8312.
- Pijper E, Somers MF, Kroes GJ, Olsen RA, Baerends EJ, Busnengo HF, Salin A, Lemoine D. Six-dimensional quantum dynamics of scattering of (v=0, j=0) H₂ from Pt (111): comparison to experiment and to classical dynamics results. *Chem Phys Lett* 2001; 347:277-284.
- Pijper E, Kroes GJ, Olsen RA, Baerends EJ. Dissociative and diffractive scattering of H₂ from Pt(111): a four dimensional quantum dynamics study. *J Chem Phys* 2002a; 116:9435-9448.
- Pijper E, Kroes GJ, Olsen RA, Baerends EJ. Reactive and diffractive scattering of H₂ from Pt(111) studied using a six-dimensional wave packet method. *J Chem Phys* 2002b; 117:5885-5898.
- Poelsema B, Lenz K, Comsa G. The dissociative adsorption of hydrogen on defect-'free' Pt(111). *J Phys: Condens Matter* 2010; 22:304006.
- Poelsema B, Lenz K, Comsa G. The dissociative adsorption of hydrogen on Pt(111): Actuation and acceleration by atomic defects. *J Chem Phys* 2011; 134:074703-074712.
- Ras EJ, Louwense MJ, Mittelmeijer-Hazeleger MC, Rothenberg G. Predicting adsorption on metals: simple yet effective descriptors for surface catalysis. *Phys Chem Chem Phys* 2013; 15:4436-4443.
- Roman TA, Nakanishi H, Dino WA, Kasai H. Hydrogen atom quantum migration on platinum. *e-J Surf Sci Nanotech* 2006; 4:619-623.
- Tsuda M, Kasai H. H₂ Dissociative Adsorption on strained/CO-precovered Pt. *Jpn J App Phys* 2006; 45:L1219-L1221.
- Vanderbilt D. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Phys Rev B* 1990; 41:7892-7895.
- Vincent JK, Olsen RA, Kroes GJ, Baerends EJ. Dissociative chemisorption of H₂ on Pt(111): isotope effect and effects of the rotational distribution and energy dispersion. *Surf Sci* 2004; 573:433-445.
- Watson GW, Willock DJ, Wells RPK, Hutchings GJ. A comparison of the adsorption and diffusion of hydrogen on the {111} surfaces of Ni, Pd, and Pt from density functional theory calculations. *J Phys Chem B* 2001; 105:4889-4894.
- Xu X, Wu DY, Ren B, Xian H, Tian Z-Q. On-top adsorption of hydrogen at platinum electrodes: a quantum-chemical study. *Chem Phys Lett* 1999; 311:193-201.