

A DFT Study of Hydrogen Adsorption on Metallic Platinum: Associative or Dissociative Adsorption

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In this study, molecular and atomic adsorption energies and the total density of states (DOS) of hydrogen at the on-top, bridge, and hollow positions of face-centered cubic (FCC) (100) and (111) surfaces of metallic platinum were investigated by density functional theory (DFT) calculations. The results of DOS showed that there was a higher interaction between hydrogen molecules and the FCC (111) surface than the FCC (100) surface of metallic platinum. Also, the intensity of the antibonding orbital of the bridge position was higher than that of the other two positions on the FCC (100) surface, which shows that the hydrogen molecule in the bridge position was ready to be dissociated into hydrogen atoms. In addition, the intensities of the antibonding orbital of hollow and bridge positions were higher than that of the on-top position on the FCC (111) surface, indicating that the hydrogen molecule in hollow and bridge positions was dissociated into hydrogen atoms. The results showed that a comparison between the activation energy barrier (ΔE_{ads}), calculated by the Lennard-Jones potential, and molecular adsorption energy could determine whether the hydrogen molecule was dissociated on the surface. Accordingly, if the activation energy barrier (ΔE_{ads}) is higher than the molecular adsorption energy, the probability that the hydrogen molecule will dissociate on the surface is very low.

Keywords: DFT calculations, FCC surfaces, Hydrogen, Molecular adsorption, Platinum

INTRODUCTION

Platinum is a common catalyst for catalytic hydrogenation reactions; thus, it is important to study how hydrogen is adsorbed on the surface of platinum to understand surface catalytic reactions [1]. Hydrogen molecules are adsorbed on the surface of platinum catalyst and undergo a dissociative chemisorption process [2-4]. Understanding the absorption behavior of hydrogen on the surface of the catalyst improves our knowledge of suitable catalysts for the hydrogenation process [5-6]. The hydrogen may be molecularly or atomically chemisorbed or molecularly physisorbed. In cases when hydrogen is molecularly chemisorbed on platinum, the antibonding σ^* orbital of the hydrogen molecule is filled by electrons from the platinum surface. Then, chemisorbed hydrogen

molecules will dissociate on the platinum surface. Christine *et al.* examined the hydrogen adsorption on the face-centered cubic (FCC) (111) surface of platinum by measuring LEED (low-energy electron scattering) and thermal absorption spectroscopy [7]. They showed that hydrogen can be adsorbed molecularly and atomically on the surface of metallic platinum. Although other studies have shown that hydrogen may not always dissociate on platinum surfaces, the exact cause of this has not yet been determined [7-9].

Computational studies on the surface of the catalysts using density functional theory (DFT) are powerful tools to provide useful information at the atomic level on the ability of certain metallic surfaces to act as catalysts for specific chemical reactions [4,10]. Mendes and Giorado investigated the adsorption of hydrogen on platinum-modified clusters with fullerenes using extensive computational theory [11]. Hu *et al.* used DFT calculations to investigate how hydrogen interacted with the various compounds of platinum-gold

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bimetallic nanoparticles [12]. They studied systems containing platinum and gold atoms and showed that the adsorption energy and geometry of most suitable adsorption sites depended on the distribution of metal atoms. Groot *et al.* examined catalytic activity in stepped surfaces and edge sites on platinum [13]. They found that the location of atoms varied from stepped to edge positions, making it difficult to accurately predict the synthetic reaction. Aguilera *et al.* examined the surface shape of platinum nanoparticles on adsorbed hydrogen uptake [14]. Using standard DFT calculations, they showed that hydrogen was more likely to be adsorbed on the FCC (100) than the FCC (111) surface of the metallic phase of platinum. Despite an extensive body of research on hydrogen adsorption on metallic platinum surfaces, there is no explanation for the simultaneous existence of atomic and molecular species of hydrogen on the surface of platinum catalysts.

In this study, the adsorption behavior of hydrogen on two low-index surfaces, *i.e.*, FCC (100) and (111), of the metallic phase of platinum was investigated by DFT simulations. To investigate the simultaneous presence of atomic and molecular species of hydrogen on the platinum surface, its molecular (associative) and atomic (dissociative) adsorptions were investigated. Some trends were identified in the energetic and electronic effects of the associative and dissociative hydrogen adsorption, from which some predictions could be made concerning the hydrogen evolution under the hollow, bridge, and on-top positions on different low-index surfaces.

COMPUTATIONAL Details

DFT simulations for atomic and molecular adsorption of hydrogen on (100) and (111) surfaces of the metallic phase of platinum were done using a three-metal-layer slab model within the slab model approximation. Three different positions (*i.e.*, on-top, hollow, and bridge) at a 0.25 monolayer (ML) coverage using p (2 × 2) unit cells were studied on the FCC structure of metallic platinum (Fig. 1). The geometry of the metallic platinum atoms was optimized with a lattice constant of 3.9239 Å [15]. During the geometry optimization, all platinum atoms were allowed to relax, except those in the bottom layer of the slab model.

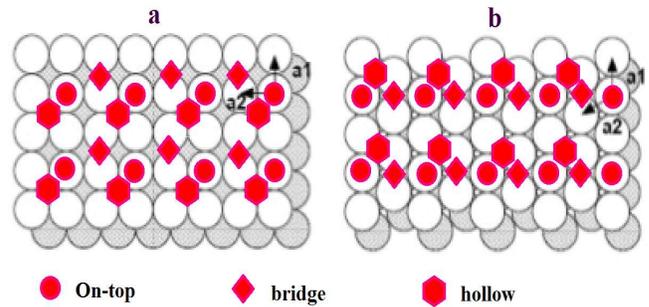


Fig. 1. Adsorption positions on (a) FCC (100) and (b) FCC (111) surfaces at the 0.25 ML coverage of p (2 × 2) arrangement.

Quantum ESPRESSO package with a double-zeta plus polarization (DZ) basis set and the iterative solution of the Kohn-Sham equations were used to evaluate hydrogen adsorption on post-tension (Pt) surfaces using DFT calculations [16]. The localization radii of the basis functions were determined with an energy shift of 0.01 eV and using pseudo-potentials from the Quantum-ESPRESSO library. A standard DFT super-cell approach with the RevPBE-D3 (BJ) form of the generalized-gradient approximation (GGA) functional was performed. Spin polarization was included in the calculations, and the Fermi level smearing of 0.2 eV was used to account for fractional occupancies. The energy of hydrogen adsorption was calculated as follows [17]:

$$E_{\text{ads}} = E_{\text{H/Pt slab}} - E_{\text{Pt slab}} - E_{\text{H}} \quad (1)$$

where $E_{\text{H/Pt slab}}$ is the energy of a slab model of the chemisorbed hydrogen atoms or molecules on the platinum surface, $E_{\text{Pt slab}}$ is the energy of the uncovered surface, and E_{H} is the energy of free hydrogen atoms or molecules in the gas phase. The Lennard-Jones potential (V_{LJ}) is an easy model that describes the fundamental features of interactions between atoms and molecules. Based on this model, two interacting particles repel each other at very close distances, attract each other at a moderate distance, and do not interact at infinite distances. The Lennard-Jones potential for hydrogen adsorption, which is the intermolecular potential between hydrogen atoms or molecules and surface platinum atoms, was calculated using the following equation [18]:

$$V_{LJ} = \varepsilon \left[\left(\frac{r_m}{r} \right)^{12} - 2 \left(\frac{r_m}{r} \right)^6 \right] \quad (2)$$

where ε is the calculated adsorption energy, r is the distance between the hydrogen atom (or molecule) and surface platinum atoms, and r_m is the interaction between hydrogen atoms or molecules and surface platinum atoms when the physical or chemical adsorption is done. In the present work, the dissociative or associative adsorption of hydrogen on platinum surfaces was determined based on a comparison between the activation energy barrier (ΔE_{ads}), calculated by the Lennard-Jones potential, and molecular adsorption energy. Based on this method, if the activation energy barrier (ΔE_{ads}) is higher than the molecular adsorption energy, it is

highly unlikely that the hydrogen molecule will dissociate on the surface.

RESULTS AND DISCUSSION

Molecular Adsorption of Hydrogen

To evaluate the adsorption of hydrogen molecules, molecular and atomic adsorption energies of hydrogen were calculated by DFT calculations. In the first step, the molecular adsorption of hydrogen was considered. Figure 2 shows the adsorbed hydrogen molecules at the 0.25 ML coverage using a p (2 × 2) unit cell for on-top, hollow, and bridge positions on the FCC (100) surface of platinum. Table 1 lists the adsorption energies of the hydrogen molecule (E_{ads}), the distance between the hydrogen atoms in

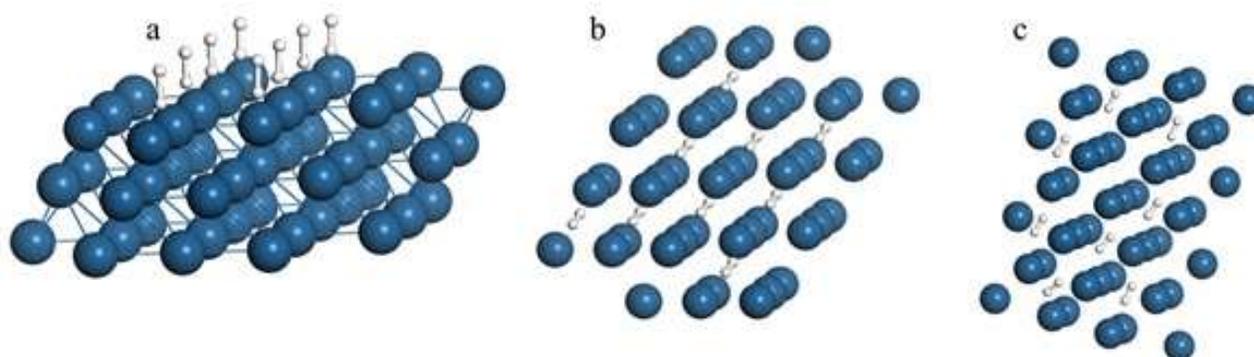


Fig. 2. Hydrogen molecules adsorbed on the FCC (100) surface of platinum at the 0.25 ML coverage in three positions: (a) on-top adsorption mode (2 × 2), (b) bridge adsorption mode (2 × 2), (c) hollow adsorption mode (2 × 2).

Table 1. The Adsorption of Hydrogen Molecule on FCC (100) and FCC (111) Surfaces of Pt at the 0.25 ML Coverage

FCC surface	Position	E_{ads} (kJ mol ⁻¹)	$d_{\text{H}_2}^{\text{a}}$ (Å)	$\Delta d_{\text{H}_2}^{\text{b}}$ (Å)	$Z_{\text{H}_2}^{\text{c}}$ (Å)
(100)	on top	-22.2	0.752	0.010	2.533
	bridge	-25.3	0.755	0.015	2.531
	hollow	-28.7	0.757	0.017	2.530
(111)	on top	-12.7	0.747	0.005	2.536
	bridge	-15.2	0.749	0.007	2.534
	hollow	-19.4	0.751	0.009	2.532

Note: ^a = the distance between the hydrogen atoms in the molecule adsorbed on the surface; ^b = the difference in the bond length in the adsorbed molecule relative to the gaseous state; ^c = the distance between the hydrogen molecule and the surface.

the adsorbed hydrogen molecule on the surface (d_{H_2}), the difference between the lengths of the bonds in the hydrogen molecule in the gas phase and the adsorbed phase (Δd_{H_2}), and the distance between the hydrogen molecule and the surface of platinum (Z_{H_2}) on the (100) and (111) surfaces at the 0.25 ML coverage in three different positions.

Table 1 shows that the adsorption energies of the hydrogen molecule in the on-top, bridge, and hollow positions on the FCC (100) surface of Pt were equal to $-22.2 \text{ kJ mol}^{-1}$, $-25.3 \text{ kJ mol}^{-1}$, and $-28.7 \text{ kJ mol}^{-1}$, respectively. Also, the adsorption energies of the hydrogen molecule in the on-top, bridge, and hollow positions on the FCC (111) surface of Pt were equal to $-12.7 \text{ kJ mol}^{-1}$, $-15.2 \text{ kJ mol}^{-1}$, and $-19.4 \text{ kJ mol}^{-1}$, respectively, which are lower than those of the FCC (100) surface. These results show that the number of coordinates influenced the adsorption energy, a finding which is consistent with those of previous studies [7-8,19]. In this work, calculated adsorption energies were used as ε in Eq. (2) to calculate the potential energies of molecular adsorption. Higher adsorption energies in the FCC (100) surface were associated with higher surface free energy in the FCC (100) surface, as reported in previous works [3,19-21]. In addition, the adsorption energy for the hollow position in both FCC (100) and (111) surfaces was higher than that in the other two considered positions. It should be noted that the number of coordinates was one in the on-top position, two in the bridge position, and three in the hollow position. Therefore, it was expected that the adsorption of hydrogen molecules had higher adsorption energy in the hollow position.

Table 1 shows that the distance between the hydrogen atoms in the molecule adsorbed on the surface (d_{H_2} (Å)) at the on-top, bridge, and hollow positions on the FCC (100) surface of Pt was equal to 0.752 Å , 0.755 Å , and 0.757 Å , respectively. Also, the calculated d_{H_2} (Å) at the on-top, bridge, and hollow positions on the FCC (111) surface of Pt was equal to 0.747 Å , 0.749 Å , and 0.751 Å , respectively. When these distances were compared with the distance between the hydrogen atoms in the gas phase (0.742 Å), the difference in the bond length in the adsorbed molecule and the gas-phase molecule (Δd_{H_2} (Å)) on the FCC (100) surface of Pt was equal to 0.010 Å , 0.015 Å , and 0.017 Å at the on-top, bridge, and hollow positions, respectively. The calculated Δd_{H_2} for the on-top, bridge, and hollow positions

on the FCC (111) surface of Pt was equal to 0.005 Å , 0.007 Å , and 0.009 Å , respectively. The higher surface free energy of the FCC (100) caused the hydrogen atoms to be more adsorbed on the platinum surface, resulting in a higher distance between the FCC (100) and the adjacent atom in the hydrogen molecule.

Furthermore, Table 1 shows that the distance of the hydrogen molecule to the surface (Z_{H_2} (Å)) on the FCC (100) surface of Pt was equal to 2.533 Å , 2.531 Å , and 2.530 Å at the on-top, bridge, and hollow positions, respectively. Also, the calculated Z_{H_2} (Å) for the on-top, bridge, and hollow positions on the FCC (111) surface of Pt was equal to 2.536 Å , 2.534 Å , and 2.532 Å , respectively, which were higher than those of the FCC (100) surface due to its higher surface free energy compared to that of the FCC (111) surface. These calculated distances were then used as r_m in Eq. (2) to calculate the potential energies of molecular adsorption.

Atomic Adsorption of the Hydrogen

In this stage, a single-layer of hydrogen atoms was located on the surface at the on-top, bridge, and hollow positions of the FCC (100) and (111) surfaces of the platinum crystal at the 0.25 ML coverage using a p (2×2) unit cell. The calculated results are presented in Table 2.

The adsorption energies of the hydrogen atoms (E_{ads}) at the on-top, bridge and hollow positions on the FCC (100) surface of Pt were equal to -302 kJ mol^{-1} , -351 kJ mol^{-1} , and -373 kJ mol^{-1} , respectively. Also, the calculated atomic E_{ads} at the on-top, bridge, and hollow positions on the FCC (111) surface was equal to -265 kJ mol^{-1} , -336 kJ mol^{-1} , and -349 kJ mol^{-1} , respectively, which were lower than those of the FCC (100) surface. These results showed that the number of coordinates influenced the adsorption energy. This finding is consistent with the data from the previous studies [9, 22-23].

Then, the calculated adsorption energies were used as ε in Eq. (2) to calculate the potential energies of chemical adsorption of hydrogen atoms. The calculated distance of hydrogen atoms from the surface (Z_H) at the on-top, bridge, and hollow positions was equal to 1.86 Å , 1.84 Å , and 1.84 Å , respectively, for the FCC (100) surface and 1.91 Å , 1.88 Å , and 1.87 Å , respectively, for the FCC (111) surface. These calculated distances were then used as r_m in Eq. (2) to

Table 2. The Adsorption of Hydrogen Atom on the FCC (100) and (111) Surfaces of Pt at the 0.25 ML

FCC surface	Position	E_{ads} (kJ mol ⁻¹)	Z_{H}^{a} (Å)	ΔH_{ads} (kJ mol ⁻¹)	ΔE_{ads} (kJ mol ⁻¹)	$\Delta H_{\text{ads}}^{\text{total}}$ (kJ mol ⁻¹)
(100)	on top	-302	1.86	-168	38.3	-152
	bridge	-351	1.84	-266	25.1	-266
	hollow	-373	1.81	-310	29.7	-309
(111)	on top	-265	1.91	-94	29.9	-77
	bridge	-336	1.88	-236	12.5	-239
	hollow	-349	1.87	-262	13.1	-268

Note: ^a = the distance between the hydrogen atom and the surface.

calculate the potential energies of the chemical adsorption of hydrogen.

The enthalpy of chemical adsorption of hydrogen (ΔH_{ads}) on the platinum surface was obtained by Eq. (3) and is listed in Table 2 [2]:

$$\Delta H_{\text{ads}} = 2E_{\text{chem}} - E_{\text{diss}} \quad (3)$$

where E_{chem} , is the adsorption energy of hydrogen atoms on the surface and E_{diss} is the dissociation energy of the hydrogen molecule (-436 kJ mol⁻¹). The experimental result for ΔH_{ads} of hydrogen on platinum at the 0.25 ML coverage was less than that calculated in this study because the activation energy (ΔE_{ads}) is not considered in Eq. (3) [24-25]. Thus, the actual ΔH_{ads} of hydrogen on the metallic platinum surface had to be calculated by considering the activation energy (ΔE_{ads}) and physical adsorption energy according to Eq. (4) [3]:

$$\Delta H_{\text{ads}}^{\text{total}} = 2E_{\text{chem}} + E_{\text{phys}} - E_{\text{diss}} - \Delta E_{\text{ads}} \quad (4)$$

The activated energy (ΔE_{ads}) was calculated using the Lennard-Jones potential energy function (Eq. (2)) for physical and chemical adsorption of hydrogen on the FCC (100) and FCC (111) surfaces at the on-top, bridge, and hollow positions (Figs. 3 and 4).

The physical adsorption r_{m} is the distance between the physically adsorbed hydrogen molecule and the surface (Z_{H_2}), and the chemical adsorption r_{m} is the distance between

the chemically adsorbed hydrogen atoms and the surface (Z_{H}). The weakly adsorbed hydrogen molecule can be desorbed or dissociated into chemisorption hydrogen atoms if the physical adsorption overcomes the activation energy barrier (ΔE_{ads}). Activation energy barrier (ΔE_{ads}) is determined by a comparison of the molecular and atomic adsorption [26]. The calculated activation energy barriers (ΔE_{ads}) on the FCC (100) and FCC (111) surfaces at the on-top, bridge, and hollow positions are listed in Table 2. The activation energy barrier (ΔE_{ads}) of hydrogen adsorption was 38.3 kJ mol⁻¹, 25.1 kJ mol⁻¹, and 29.7 kJ mol⁻¹ for the FCC (100) surface and 29.9 kJ mol⁻¹, 12.5 kJ mol⁻¹, and 13.1 kJ mol⁻¹ for the FCC (111) surface at the on-top, bridge, and hollow positions, respectively. The actual ΔH_{ads} of hydrogen on the metallic platinum surface was calculated for different positions on the FCC (100) and (111) surfaces using the activation energy (ΔE_{ads}) and physical adsorption energy according to Eq. (4), and the results are listed in Table 2. Some of the calculated data were still higher than the experimental results, which can be attributed to errors in DFT calculations and the difference between the FCC (100) and (111) surfaces and the real metallic platinum surfaces.

Hydrogen Adsorption on Metallic Pt: Dissociation or Association

The experimental studies of the surface adsorption of hydrogen show two different types of hydrogen adsorption (*i.e.*, molecular and atomic adsorption) on the metallic platinum surface [7-8]. The reason for the simultaneous presence of atomic and molecular species on the surface of

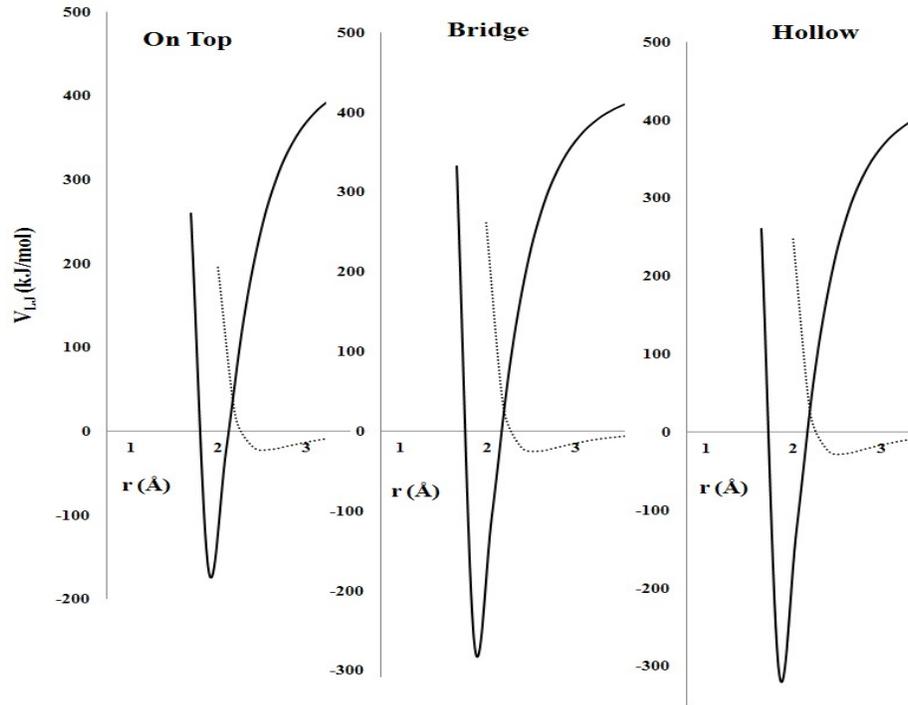


Fig. 3. Physical (fold line) and chemical adsorption pathways (solid line) of hydrogen on the FCC (100) surface of Pt.

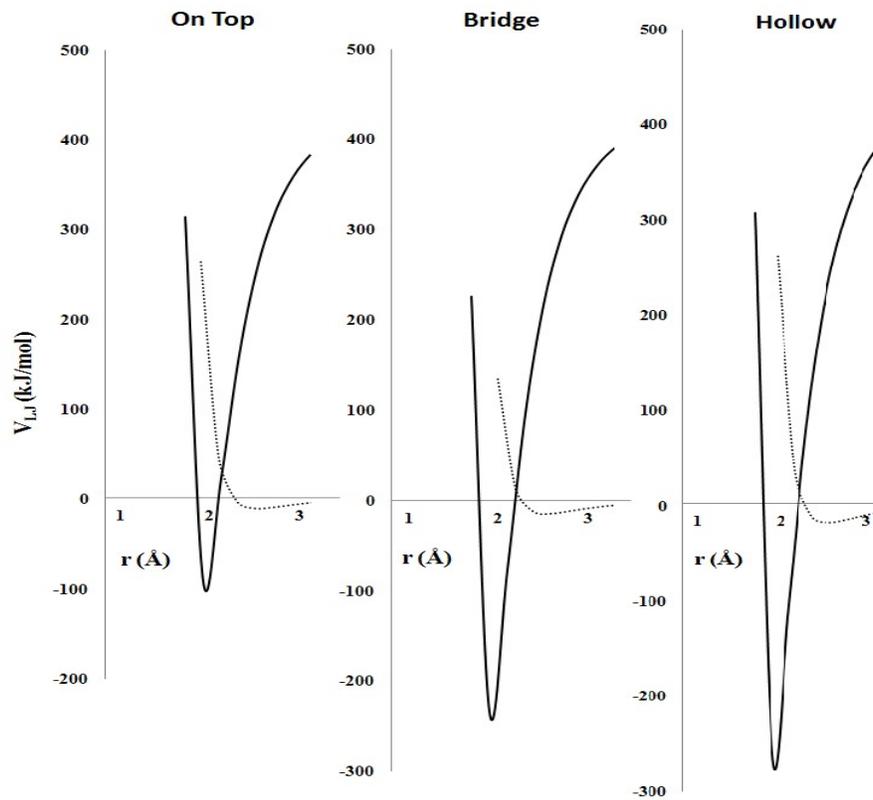


Fig. 4. Physical (fold line) and chemical adsorption pathways (solid line) of hydrogen on the FCC (111) surface of Pt.

metal platinum is not well known, but various reasons, such as spatial constraints on the surface of metal platinum for hydrogen dissociation, have been suggested to account for this phenomenon.

The total density of states (DOS) of the FCC (100) and FCC (111) surfaces of metallic platinum and molecular hydrogen adsorption on these two surfaces at the on-top, bridge, and hollow positions are shown in Fig. 5, which shows that the electron density of the FCC (100) surface of metallic platinum was higher than that of the FCC (111) surface.

The DOS of gaseous hydrogen molecules in previous studies shows a sharp peak at about -9 eV, which corresponds to the σ bonding state between the two hydrogen atoms [8, 21,27]. The interaction between adsorbed hydrogen electrons and the electrons on the Pt surface gives rise to bonding and antibonding states. Firstly, σ bonding interaction due to the overlap of filled σ orbitals on the hydrogen molecule with the metal orbitals at -15.2 eV (Fig. 5) leads to electron density transfer from the hydrogen molecule to the metal center [8,21]. Secondly, the antibonding orbital (σ^*) reduces the hydrogen bond strength at -13.1 eV (Fig. 5) [8]. The

interactions between the adsorbed hydrogen molecule and the FCC (100) and FCC (111) platinum metallic surfaces are shown in Fig. 5.

The detail of the molecular orbital picture of Hydrogen adsorbed on the FCC (111) and FCC (110) surfaces of the Pt was analyzed using the crystal orbital Hamilton population (COHP) method (Fig. 6). The COHP calculations enabled us to localize the total energy change to the immediate vicinity of the perturbation. Since the COHP analysis was carried out on the energy scale, negative energies (COHP contributions) indicated bonding interactions while positive energies (COHP contributions) indicated antibonding interactions. Figure 6 shows that the bonding region near the H band at -15.2 eV was stabilized whereas the antibonding region near the H band at -13.1 eV was destabilized. As shown in Figs. 5 and 6, increased interaction between the hydrogen molecule and the metal surface led to a decrease in the intensity of the bonding peak and an increase in the intensity of the antibonding peak. Finally, when sufficient electron density was transferred from the bonding to antibonding orbitals, the hydrogen molecule decomposed into its atoms. As shown in Fig. 5, the intensity of the molecular hydrogen orbitals on the

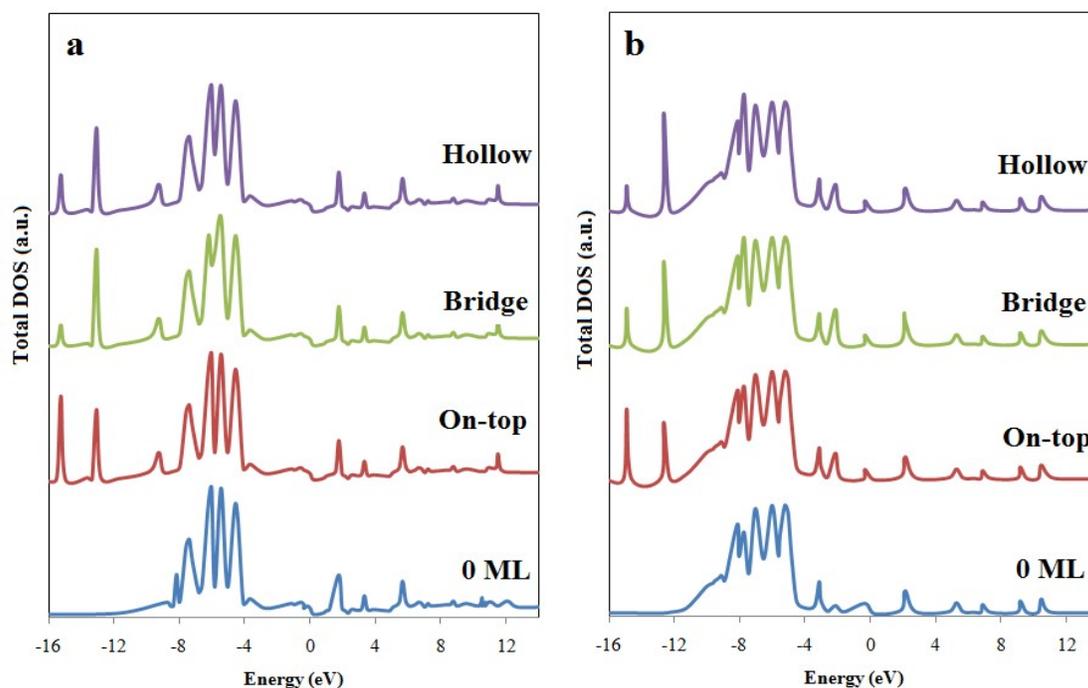


Fig. 5. The DOS projected on the hydrogen molecule and the surface of Pt metal states: (a) FCC (100) and (b) FCC (111).

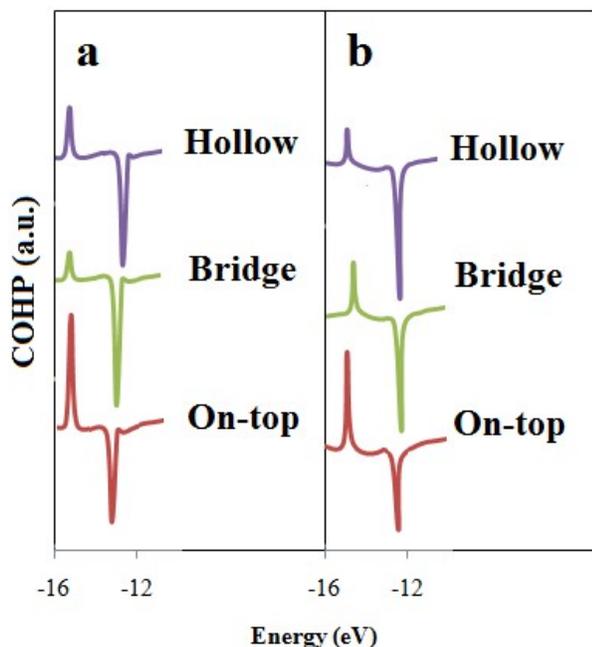


Fig. 6. COHP projected on the hydrogen molecule and the surface of Pt metal states: (a) FCC (100) and (b) FCC (111).

FCC (111) surface increased, which indicates a higher interaction between hydrogen molecules and the metallic surface due to the higher planar density of the FCC (111) surface. As can be seen in Fig. 5, the intensity of the antibonding orbital (σ^*) for the bridge position was higher than that of the other two positions on the FCC (100) surface, showing that the hydrogen molecule at the bridge position dissociated into hydrogen atoms. In addition, Fig. 5 shows that the intensities of antibonding orbital (σ^*) for hollow and bridge positions were higher than that of the on-top position on the FCC (111) surface, indicating that the hydrogen molecule in hollow and bridge positions dissociated into hydrogen atoms. However, the hydrogen adsorbed on the on-top position may have been molecularly adsorbed. Also, the intensity of the antibonding orbital (σ^*) for the bridge position was higher than that of the other two positions on the FCC (100) surface, showing that the hydrogen molecule in this position dissociated into hydrogen atoms. The results showed the symmetric dissociation of the hydrogen molecule into two atoms on two adjacent atoms of platinum at the

bridge position. In addition, the intensities of the antibonding orbital (σ^*) for hollow and bridge positions were higher than the on-top position on the FCC (111) surface, indicating that the hydrogen molecule in hollow and bridge positions dissociated into hydrogen atoms.

As shown in Figs. 3 and 4 and Table 2, the activation energy barrier (ΔE_{ads}) for hydrogen adsorption on the metallic platinum surface depended on the FCC surface and position. The results showed that a comparison between the activation energy barrier (ΔE_{ads}), calculated from the Lennard-Jones potential function, and molecular adsorption energy can help determine whether the hydrogen molecule is dissociated on the surface. If the activation energy barrier (ΔE_{ads}) is higher than the molecular adsorption energy, the probability that the hydrogen molecule will dissociate on the surface is very low. The value of the activation energy barrier (ΔE_{ads}) for hydrogen adsorption at the on-top, bridge, and hollow positions on the FCC (100) surface was found to be 38.3 kJ mol⁻¹, 25.1 kJ mol⁻¹, and 29.7 kJ mol⁻¹, respectively. When these values were compared with the heat of physical adsorption (Table 1), it became clear that only in the bridge position, the heat of physical adsorption was higher than the activation energy barrier. Thus, it can be stated that for this position, the physical adsorption provided the energy needed to overcome the activation energy barrier (ΔE_{ads}). Therefore, it was expected that the hydrogen molecule dissociated at the bridge position on the FCC (100) surface of platinum but the hydrogen be adsorbed in the molecular form at the other two positions (*i.e.*, hollow and on-top). In addition, the activation energy barrier of hydrogen adsorption at the on-top, bridge, and hollow positions on the FCC (111) surface was 29.9 kJ mol⁻¹, 12.5 kJ mol⁻¹, and 13.1 kJ mol⁻¹, respectively. When these activation barrier energies were compared with the released energy due to physical adsorption at the on-top, bridge, and hollow positions on the FCC (111) surface of the platinum surface, it became clear that only in the on-top position, the heat of physical adsorption was lower than the activation energy barrier. Accordingly, it was expected that the hydrogen molecule dissociated on the other two positions (*i.e.*, hollow and bridge) for the FCC (111) surface. These results were fully consistent with the DOS results and can justify the physical and chemical adsorption on the platinum surface.

CONCLUSIONS

DFT simulations for atomic and molecular adsorption of hydrogen at the on-top, bridge, and hollow positions of FCC (100) and (111) surfaces of platinum metallic phase were performed using a three-metal-layer slab model within the slab model approximation. The geometries of the FCC surfaces of platinum and hydrogen adsorption energies were calculated with the generalized-gradient approximation (GGA) using the RevPBE-D3 (BJ) functional. The total DOS showed that the interaction between hydrogen molecules and metallic surfaces on the FCC (111) surface was higher than that on the FCC (100) surface. Also, the results of DOS showed that the intensity of the antibonding orbital for the bridge position was higher than that of the other two positions (*i.e.*, hollow and on-top) on the FCC (100) surface, which indicates that the hydrogen molecule in the bridge position dissociated into hydrogen atoms. In addition, the intensity of the antibonding orbital for hollow and bridge positions was higher than that of the on-top position on the FCC (111) surface, indicating that the hydrogen molecule in hollow and bridge positions dissociated into hydrogen atoms and that the hydrogen adsorbed on the on-top position may have been molecularly adsorbed.

The Lennard-Jones potential for atomic and molecular adsorptions demonstrated that a comparison between the activation energy barrier (ΔE_{ads}) and molecular adsorption energy can be used to determine whether the hydrogen molecule is dissociated on the surface. If the activation energy barrier (ΔE_{ads}) is higher than the molecular adsorption energy, it is highly unlikely that the hydrogen molecule will dissociate on the surface. Furthermore, the results showed that in the bridge position on the FCC (100) surface and bridge and hollow positions on the FCC (111) surface, the physical adsorption provided the energy needed to overcome the activation energy barrier (ΔE_{ads}). Therefore, it was expected that the hydrogen molecule dissociated in bridge and hollow positions on the FCC surfaces of platinum.

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