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Research Article

Theoretical Study of Methane Dissociation on Pt(111) Surface Using Density Functional Theory (DFT) Calculations

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Abstract

In this work, methane (CH_4) dissociation on Pt(111) surface dissociation was studied based on density functional theory (DFT) calculations to evaluate the nature of adsorption and to calculate the rate constant. The most stable configurations for H and CH_3 were tested on the surface of Pt(111), and the results displayed that H tends to be adsorbed at the fcc site while CH_3 tends to be adsorbed at the top site. The energy of barrier and rate constant of reaction were calculated and found to be (2.28 eV) and (3.21007E−08 s^{-1}) respectively. In addition, the adsorption energy for the reactant and products to investigate the nature of adsorption of the reactant and products on Pt(111) surface either physisorption or chemisorption. The results showed that the kind of adsorption of CH_4 adsorbed on the surface of Pt(111) at top site is physisorption, while CH_3 and H species adsorption on the Pt(111) surface is chemisorption.

Keywords: Methane dissociation; Pt(111) Surface; DFT; Density Functional Theory; reforming

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1. Introduction

CH_4, one of the most dominant natural gas components, has been widely utilized in synthesis of chemicals such as synthesis gas and alcohol [1], production of hydrogen and energy [2]. Recently, CH_4 dissociation on the surface of transition metal has drawn considerable attention either from theoretical [3–6] or experimental [7–9] studies. Generally, it is assumed that CH_4 dissociation on the transition metal surface step is the rate-limiting step for numerous of these heterogeneous reactions [10].

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DFT calculations have been widely investigated for the dissociation of CH_4 on group VIII surfaces. The common suitable metals for dehydrogenation reactions are Cu, Pt, Pd, and Ni [11–20]. Aykan Akça [21] investigated the surface of pure Cu(111) and the role of doping with Pd on the dissociation of CH_4. He studied the sequent dehydrogenation reaction of CH_4 on both the surface of pure Cu(111) and PdCu(111) using DFT calculations. The results displayed H atom and CH_x (x = 0–4) species are adsorbed more strongly on the Cu(111) than on Pd-doped Cu(111) surface, and the surface of Pd-doped Cu(111) is higher active than the surface of Cu(111) [21]. Sudipta Roy studied a series of surface and subsurface Ni-Pt bimetallic surfaces using DFT calculations. It was found that acti-

vation energy barriers reduced when Ni was added to Pt(111), whereas addition of Pt to Ni(111) surface led to a linear increase in barrier [22]. Nave *et al.* [23] used DFT calculations to examine methane dissociation on five metal surfaces which are Pt(100), Pt(111), Pt(110)-(1×2), Ni(100) and Ni(111). For all five metals, the lower energy route for dissociation is on a top site, and the barriers are large, 0.66–1.12 eV. Also, they stated on the Pt surfaces, there is a strong preference to bond the methyl fragment on the top site, whereas on the surface of Ni it prefers to bond on the bridge or hollow sites. For the dissociation of CH_4 on the Pt (h k l) surface, Petersen *et al*. [24] investigated the CH_4 dissociation adsorption intermediates presented CHx where x is from 0 to 3, on Pt (110) $p(1 \times 2)$ using DFT calculations. They stated the top site is favorably occupied by CH_3, while CH_2, CH, C are at the bridge, 3-fold fcc site and 4-fold sites respectively. Zhang *et al*. [25] studied CH_4 dissociation on Pt(h k l) surfaces. They investigated the adsorption sites which are favorable and stable configurations of CHx, where x is from 0 to 4 and H species on the surfaces of Pt with (100), (110), and (111) orientations. Over Pt(111), they found that the most stable configuration is an adsorption on the top site. For CH_3, only one stable structure can be obtained over the top site where the initial structures at the hcp, fcc, and bridge sites are chosen to be on the top site. Three stable structures for H are found which are the top, fcc and hcp sites where the initial structure is changed from the bridge site to the fcc site. Among these structures, it is found that H prefers to be adsorbed at the fcc site.

Newly, theoretical calculations have become a potent research tool for comprehension the chemical reactions either at atomic or at molecular level. Particularly, DFT calculations can predict the precise reaction barriers, energetic and geometries [26]. Few theoretical studies focused on dissociation of CH_4 on Pt(111) [25,27,28]. Also, for all we know, there is no researcher interested in estimating the reaction rate constant for dissociation of CH_4 on Pt(111) based on DFT calculations. In this work, CH_4 dissociation on the surface of Pt(111) was studied to estimate the rate constant based on DFT calculations. Also, the most stable configurations for H and CH_3 were investigated on the surface of Pt(111), various adsorption sites on Pt(111) surface can be considered to be top, bridge, fcc and hcp sites. The total energy and barrier energy of the initial, transition and final states also were calculated. In addition, the adsorption energy for the reactant and products were found to know the nature of adsorption of the reactant and products on Pt(111) surface: either physisorption or chemisorption.

2. Computational Methods and Model

DFT periodic calculations were carried out using the Vienna ab initio simulation package (VASP) [29,30]. The Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) was utilized for the correlation and exchange energy. A cutoff energy of 400 eV was employed for the plane wave basis set. The meshes of k-points were set to 4×4×1 for Pt(111) surface to model the Brillouin zone. Because Pt is a paramagnetic element, spin polarization can be neglected [25]. For optimizing the structure and the energy calculation, the convergence criteria were set to 1×10^{-6} eV/atom for the tolerance of SCF. Transition states (TS) was located using the climbing-image nudged elastic band (CI_NEB) method by taking 5 images to search the minimum energy path and to estimate the activation energy of the reactions where the NEB is used to provide the initial guess of the transition state. Then using the structure of that image with the highest potential energy as an input structure to specify the precise location of the transition state via dimer method.

The surface of Pt(111) was simulated via a periodic slab with four atomic layers and a full relaxation of the upper two layers and fix of the bottom two layers as shown in Figure 1. In this work, the supper cell with p(2×2) was chosen in the calculation to represent the coverage of pre-adsorbed CH_4 atom. The vacuum space which separates the slabs in the perpendicular direction to the surface was set to 18.3 Å. The adsorption sites of Pt(111) surface are top, bridge, hcp and fcc.

The energy of adsorption is described as in Equation (1):

$$E_{ads} = E_{(adsorbate/surface)} - E_{surface} - E_{adsorbate} \quad (1)$$

where, $E_{(adsorbate/surface)}$ is the total adsorbate energy on the slab model, $E_{surface}$ is the total ener-

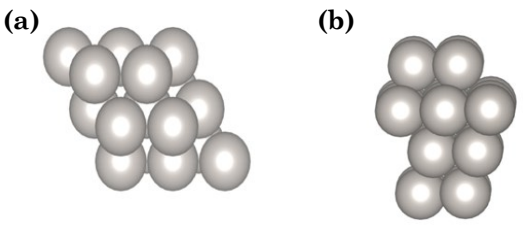

Figure 1. (a) Top and (b) side view of Pt(111) slab model.

gy of the clean surface of Pt(111), and $E_{adsorbate}$ is the total energy of species isolated (free adsorbate).

3. Results and Discussion

3.1 Single Adsorption of CH_4, CH_3 and H on Pt (111) Surface

It is important to be aware of the discrete bonding natures of distinct adsorbed species on the Pt(111) surface before examining the CH_4 dissociation mechanism on Pt(111) surface. Therefore, we examined the most stable configurations of CH_3 and H on the surface of Pt(111) to obtain the most stable structures of co-adsorbed ($H-CH_3$) on the surface of Pt(111) as a final state.

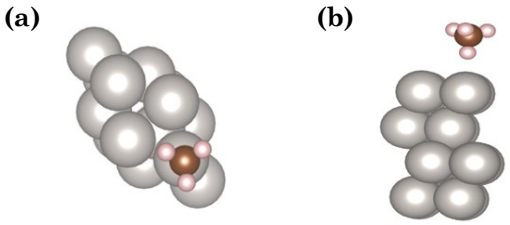

Figure 2. (a) Top view and (b) side view of CH_4 at top site on the surface of Pt(111).

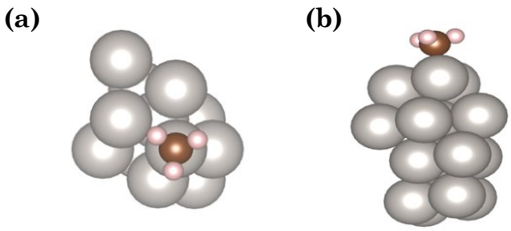

Figure 3. (a) Top view and (b) side view of CH_3 on surface of Pt(111).

3.1.1 CH_4 adsorbed on Pt(111) surface

In general, the CH_4 adsorption on the surfaces of transition metal is categorized as a physical adsorption which emerges from the van der Waals force. The stable structures observed for initial state of CH_4 are at the top, bridge, hcp and fcc sites, respectively [25].

For initial state, we assume that the adsorption on the top site is the most stable configuration, building on Zhang *et al.* results [25], as displayed in Figure 2. For the CH_4 adsorption energy, it was found to be (13.63 kJ.mol^{-1}) while Zhang *et al.* [25] acquired an energy of adsorption of 3.8 kJ.mol^{-1} on the top site. Dianat *et al.* [31] evaluated an energy adsorption of 7.7 kJ.mol^{-1} for CH_4 adsorption upon the surface of Pt(111) utilizing DFT slab calculations. This small magnitude confirms that the adsorption of CH_4 on Pt(111) is physisorption.

3.1.2 CH_3 adsorbed on Pt(111) surface

The initial structures of CH_3 on the hcp, fcc, and bridge sites are selected on the top site, so one stable configuration can be acquired at the top site as can be seen from the Figure 3. The

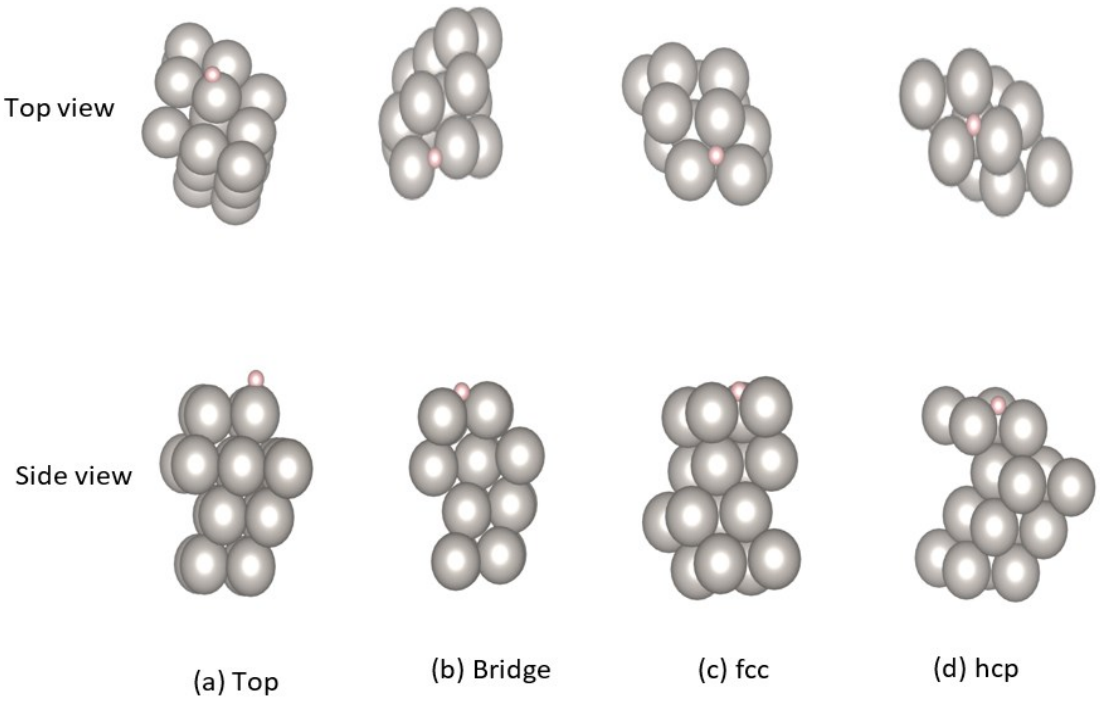

Figure 4. Top and side views of H on the surface of Pt(111) at different sites.

energy of adsorption for CH_3 over the top site is −2.7 eV (−262 kJ.mol^{-1}). The length of C−Pt bond is 2.077 Å, and lengths of all C−H bonds are 1.097 Å which is consistent with the Zhang *et al*. [25].

3.1.3 H adsorbed on Pt(111) surface

For an H atom, four stable structures are found which are at the top, bridge, fcc and hcp sites as shown in Figure 4. The most stable configuration for adsorption H was found at the fcc site where the energy of adsorption is −3.727 eV (−363.7 kJ.mol^{-1}). The lengths of H−Pt bonds are 1.55, 1.76, 1.87, and 1.869 Å, respectively. These results are similar to the Zhang *et al*. results [25] except they obtained three stable configurations instead of four where the initial structure is changed from the bridge site to the fcc site in their work while in our work the hydrogen exists in bridge site on Pt(111) surface as displayed in Figure 4.

3.2 CH_4 Dissociation on Pt(111) Surface

For the dissociation of CH_4 step into H and CH_3, the initially adsorbed CH_4 on the top site was chosen as an initial state, and the most stable co-adsorbed arrangement of CH_3 (on top site) and H (on fcc site) was selected to be the final state. The transition state structure for dissociation of CH_4 on Pt(111) surfaces was obtained from NEB and dimer calculations as shown in Figure 5.

In this study, the total energies of the CH_4 dissociation step on the surfaces of Pt(111) and energy barriers were calculated. Figure 6 depicts the energy profile of CH_4 dissociation on Pt(111) showing the energy change of the dissociation of CH_4 from CH_4 to CH_3 and H. It can be seen from this figure that the dissociation of CH_4 into CH_3−H on Pt(111) surface requires to overcome an energy barrier of 2.28 eV (220.15 kJ.mol^{-1}), while barrier for the backward reaction is 2.1 eV (202.61 kJ.mol^{-1}). The length bonds for C−H at transition state and C−H at the initial state were 2.05646 Å and 1.0394 Å, respectively.

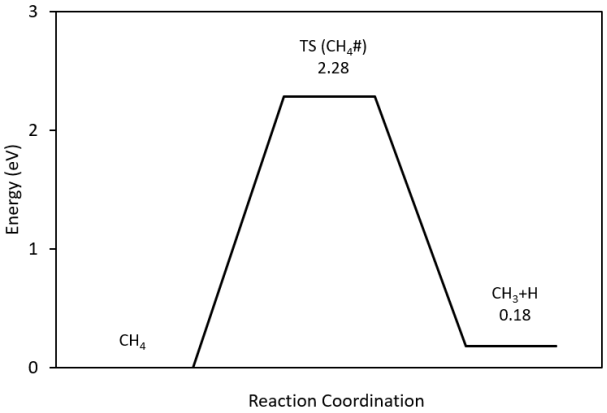

Figure 6. The energy profile scheme of CH_4 dissociation to CH_3 and H on the surface of Pt(111).

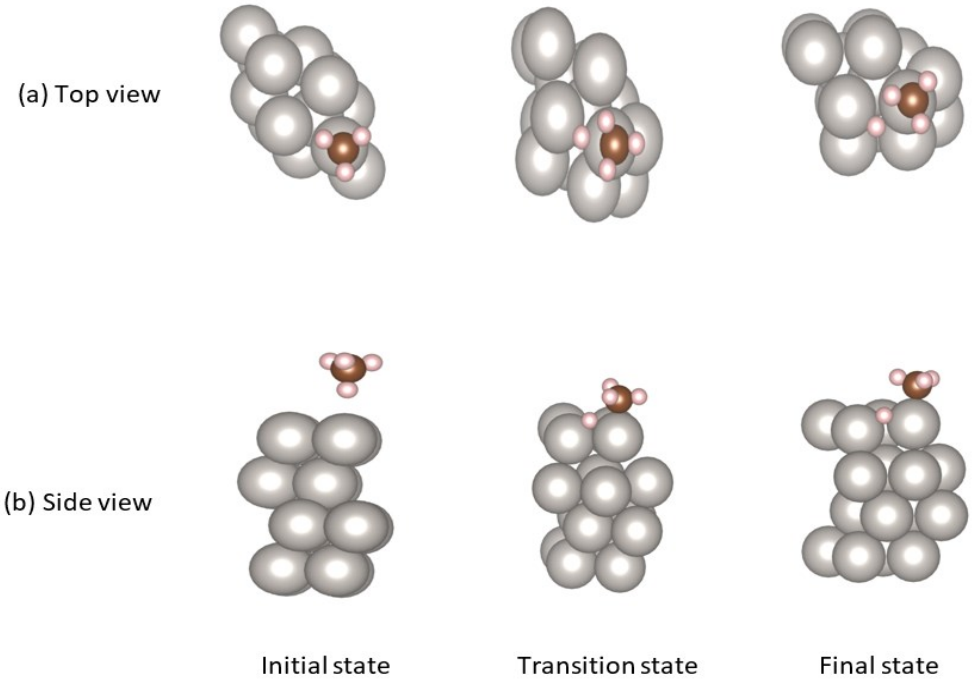

Figure 5. (a) Top view and (b) side view of CH_4 dissociation on Pt(111) surface for different states.

The reaction equation of CH_4 dissociation can be described as in Equation (2).

$$CH_4 \rightleftharpoons CH_4^{\#} \rightarrow CH_3 + H \quad (2)$$

To estimate the reaction rate constant, the rate constant can be calculated from Equation (3).

$$K_{TST} = \frac{K_B T}{h} \frac{q^{\#}_{CH_4}}{q_{CH_4}} \left(\frac{\Delta E}{RT} \right) = \frac{K_B T}{h} \frac{q^{\#}_{trans(3)} q^{\#}_{rot(3)} q^{\#}_{vib(8)}}{q_{trans(3)} q_{rot(3)} q_{vib(9)}} \left(\frac{\Delta E}{RT} \right) \quad (3)$$

Table 1. CH_4 dissociation calculations.

Initial State Calculations	
For Isolated CH_4 (free adsorption)	$E_{\text{tot CH4 isolated}}$ = −0.23901976E+02 eV
For Initial state of CH_4 on Pt (111)	$E_{\text{tot (CH4 adsorbed on Pt)}}$ = −0.11654393E+03 eV Adsorption energy = −13.63 kJ/mol
For vibrational calculations	Vibrational modes are: 3096.3 cm^{-1} 3063.8 cm^{-1} 2973.9 cm^{-1} 2803.8 cm^{-1} 1496.7 cm^{-1} 1494.4 cm^{-1} 1296.5 cm^{-1} 1289.9 cm^{-1} 1276.2 cm^{-1}
Transition State Calculations	
For transition state of CH_4 on Pt (111)	E_{TS} =−0.11426214E+03 eV
For vibrational calculations	Vibrational modes are: 3044.8 cm^{-1} 3010.4 cm^{-1} 2811.1 cm^{-1} 1381.3 cm^{-1} 1219.9 cm^{-1} 1110.2 cm^{-1} 958.5 cm^{-1} 857.9 cm^{-1} 730.6 cm^{-1}
Final State Calculations	
For isolated CH_3 (free adsorption)	$E_{\text{tot CH3 isolated}}$ = −0.17459030E+02 eV
For CH_3 Adsorbed on Pt (111)	$E_{\text{tot (CH3 adsorbed at top site)}}$ = −0.11267099E+03 eV Adsorption energy: E = −2.71 eV = −262 kJ/mol
For isolated H (free adsorption)	$E_{\text{tot H isolated}}$ = −0.91627852E-01 eV
For H adsorbed on Pt (111)	The total energies on different sites: E_T = −0.96319473E+02 eV E_B = −0.96317967E+02 eV E_{fcc} = −0.96361804E+02 eV E_{hcp} = −0.96311756E+02 eV Adsorption energies E_T = −3.769eV = −359.6 kJ/mol E_B = −3.725 eV = −359.4 kJ/mol E_{fcc} = −3.727 eV = −363.7 kJ/mol E_{hcp} = −3.719 eV = −358.8 kJ/mol
H–CH_3 co-adsorbed on Pt(111)	$E_{(CH3top\text{-}Hfcc)}$ = −0.11636206E+03 eV

where, K_{TST} is the rate constant of the reaction, K_B denotes Boltzmann's constant, T is the temperature, and h refers to Planck's constant. q_{trans}, q_{rot}, and q_{vib} are the translational, rotational, and vibrational partition functions of CH_4 over Pt(111) surface as a reactant. # denotes transition state partition functions. (ΔE) is the minimum energy at which reaction can occur (barrier energy). We can cancel the translational partition functions since both the transition and initial species are same. Since CH_4 is a nonlinear molecule, there are 3 modes of rotational partition functions. For a nonlinear molecule, the number of vibrational modes is equal to 3N-6, so there are 9 modes of vibrational partition functions for CH_4 molecule. From above equation, the K_{TST} was found to be (3.21007E−08 s^{-1}). All results are summarized in Table 1.

4. Conclusion

The dissociation of CH_4 on Pt(111) surface was tested using DFT calculations. From the results, one can conclude that the kind of adsorption of CH_4 adsorbed at the top site of a Pt(111) surface is physisorption, while H and CH_3 species adsorption on Pt(111) surface is chemisorption. On a Pt(111) surface, H tends to be adsorbed on the fcc site while CH_3 tends to be adsorbed at the top site. The minimum pathway of CH_4 dissociation of Pt(111) surface was achieved using Neb calculation as a first guess and then specifying the transition state location using a dimer method. Both barrier energy and reaction rate constant were calculated and found to be (2.28 eV) and (3.21007E−08 s^{-1}) respectively.

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CRediT Author Statement

Author Contributions: Zahraa Al-Auda: Writing, Formal analysis, Software; Keith Hohn: Review and Editing. All authors have read and agreed to the published version of the manuscript. All authors have read and agreed to the published version of the manuscript.

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