



Density functional study of the chemisorption of C₁, C₂ and C₃ intermediates in propane dissociation on Pt(1 1 1)

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ABSTRACT

DFT–GGA calculations have been used to study the chemisorption of CH_x (x=0–3), C₂H_y (y=3–5) and C₃H_z (z=3–8) on Pt(1 1 1) at the coverage of 1/9 ML. The adsorption energies, favored binding sites and geometric parameters of adsorption configurations are determined. All the carbonaceous species are found to be adsorbed on Pt(1 1 1) with C atoms sp³-hybridized. The geometries of adsorption configurations have been compared with published experimental data to evaluate the reliability of our calculation method. The calculated adsorption energies of C₁ species, ranked in descending order, are as follows, C > CH > CH₂ > CH₃, and the similar trend has been observed with respect to the chemisorption of C₂ species. As for the C₃ species, propylene prefers binding to the surface in the di-σ mode and the adsorption energy is calculated to be –0.93 eV. The stepwise dehydrogenation of propane to propynyl (CCCH₃) is investigated by calculating the change of reaction heat, which suggests that propylidyne (CCH₂CH₃) is the most stable species on Pt(1 1 1). Based on the adsorption energies and Brønsted–Evans–Polanyi (BEP) analysis, propyne is predicted to be the most likely starting point for the C–C scission.

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1. Introduction

In the past three decades, extensive efforts have been devoted to improving a low energy consumption and inexpensive technology to feed the ever-increasing demand for olefins. Propylene plays a key role in petrochemical industry, and it is profitable to produce it from propane [1–3]. Currently, commercial process for propylene synthesis through direct dehydrogenation of propane is available. However, this process suffers from several problems such as coke formation and thermodynamic limitations [4]. Compared to the direct dehydrogenation process, the so-called dehydrogenation oxidation (DHO) is preferred because of the introduction of selective oxidation of H₂.

In 1897, Sabatier discovered that transition metals were good catalysts for the hydrogenation of hydrocarbons, and extensive research was conducted to investigate the mechanism of such reactions. Pt and Pt-based alloys have long been known as important catalysts in heterogeneous catalysis. Pt-based catalyst can be used in many industry processes, including the hydrogenation of olefins, the dehydrogenation and cracking of paraffins, e.g., the conversion of propane to propylene [5–9]. Recently, the chemisorption of hydrocarbons on Pt surface has been extensively studied both theoretically and experimentally [10–13].

The dehydrogenation of propane involves a large number of side reactions including the deep dehydrogenation and hydrogenolysis of propane which lead to numerous fragments ranging from C₁ to C₃ species adsorbed on the catalyst surface. Many experimental studies on hydrocarbon adsorption over transition metals have received a great deal of attention in recent years. At 150 K, the dissociative adsorption of methyl could be identified by reflection–absorption infrared spectrometry (RAIRS) [14]. Moreover, Fuhrmann et al. [15] employed the temperature-programmed XPS and molecular beam techniques to investigate the dissociation of methane and found that methyl was adsorbed on Pt(1 1 1) at 120 K, which was dehydrogenated to CH at 260 K and further dehydrogenated to carbon above 500 K. As for heavier hydrocarbons, Kao and Madix [16] performed both experimental and theoretical studies to verify that propane was physisorbed on the metal surface, and the trapping probability of propane on Pd(1 1 1) was higher than that on Pt(1 1 1). On Pt(6 5 5) and Pt(1 1 0)–(1 × 2), the corrugation of the metal surface played a key role in attracting the propane molecule [17]. At 200 K, the formation of propylene via β-hydride elimination was identified by isotopic labeling TPD experiments [18]. Using RAIRS, Zaera and Chrysostomou proposed that propylene interacted with the Pt(1 1 1) single-crystal surface via two σ metal–carbon covalent bonds, and the rehybridization of C=C double bond of propylene took place at low coverages [1,19]. This propylene adsorption configuration has been confirmed by Tsai et al. [12]. Furthermore, in ultra high vacuum (UHV) conditions, the di-σ binding propylene could be easily dehydrogenated to propylidyne just below the

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room temperature and then to vinylmethylidyne (CCHCH₂) at 450 K [20].

The modern theoretical surface science provides us an opportunity to investigate the chemisorption and surface reaction on the atomic scale, and helps us to understand the catalysis process intuitively. Much theoretical work has been conducted to explore the adsorption and reactions of hydrocarbons in the past decade, especially for the C₁ and C₂ species. Jacob and Goddard [11] performed DFT calculations to investigate the chemisorption of CH_x (x = 1–3) species and found that the adsorption energies of methyl, methylene and methylidyne on the Pt surface were –2.16, –4.13 and –6.35 eV, respectively. Their calculated results were in good agreement with the recent theoretical results [21]. Similar studies have been performed on many other surfaces, such as Ni(1 1 1) [22], Ni(1 0 0) [23], Ru(1 1 2 0) [24], Pd(1 1 1) [25] and Cu(1 1 1) [26], etc. The comparative DFT study on the chemisorption of methyl and ethyl on Pt(1 1 1) [27] suggested that both these two species favor to be adsorbed at the Atop site owing to the strong agostic interactions between C–H bonds and surface Pt. Furthermore, Jacob and Goddard [11] pointed out that the favored adsorption sites of ethylidene (CHCH₃) and ethylidyne (CCH₃) were the Bridge and Fcc sites, respectively. In addition, Valcárcel et al. [28–30] conducted a theoretical study on the adsorption of propylene on Pt(1 1 1). They proposed that propylene preferred to be adsorbed on the surface in the di-σ mode and the adsorption energy was calculated to be –0.90 eV.

In the present study, DFT calculations are employed to investigate the dehydrogenation and C–C cleavage based on the chemisorption of the intermediates on Pt(1 1 1). We focus on the chemisorption of C₃ intermediates, and thus to predict the possible products of the dehydrogenation and cracking of propane from the thermodynamic point of view. The dehydrogenation of the methyl group which is far away from the Pt surface in the C₃ species is not taken into account. The paper is organized as follows. In Section 2, the details of computational methods are described. In Section 3, the adsorption energies, favored adsorption sites, optimized configurations of the hydrocarbon fragments (C₁–C₃) and the changes of reaction heat on Pt(1 1 1) are determined. In Section 4, we conclude by discussing the chemisorption and stability of the hydrocarbons to predict the preferred intermediate in the dehydrogenation process and the starting point for the C–C scission.

2. Computational details

Density functional theory calculations are carried out with the VASP package [31–33] using a plane wave basis set. Calculations are performed using the generalized gradient approximation functional proposed by Perdew et al. [34]. The interactions between valence electrons and ion cores are represented by Blöchl's all-electron-like projector augmented wave method (PAW) [35], which regards the 6s 5d states as the valence configuration for Pt, 2s 2p states for C and 1s state for H. A plane wave energy cut off of 400 eV is used in our calculations to achieve the tight convergence. Brillouin zone sampling is performed using a Monkhorst–Pack grid with respect to the symmetry of the system and the electronic occupancies are determined according to a Methfessel–Paxton scheme [36] with an energy smearing of 0.2 eV.

A four-layer slab with a $p(3 \times 3)$ supercell is used to represent the Pt(1 1 1) surface, achieving the coverage of adsorbates of 1/9 ML. The equilibrium Pt–Pt interatomic distance is calculated to be 2.82 Å. The successive slabs are separated by a vacuum region as thick as 12 Å in order to avoid periodic interactions. The bottom layer of the slab is kept fixed to its crystal lattice position. The first Brillouin zone of the $p(3 \times 3)$ supercell is sampled sufficiently with a $3 \times 3 \times 1$ k-point mesh.

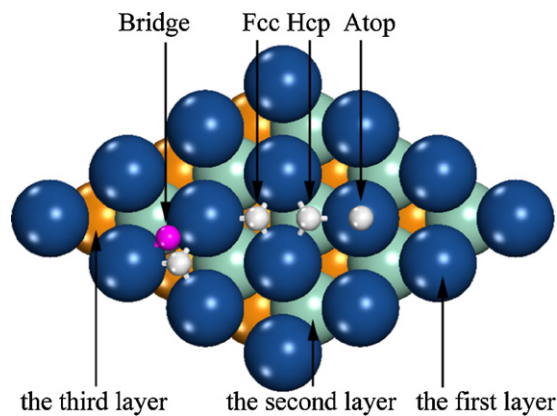


Fig. 1. Schematic representations of geometries of adsorbed H on the Pt(1 1 1) surface. The red ball denotes the initial position of H. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Some preliminary calculations have been performed to evaluate the reliability of our calculation method. The lattice constants of C and Pt are calculated to be 3.58 and 3.98 Å, respectively, and the H–H bond length is found to be 0.75 Å, which are in good agreement with the experimental results. Spin polarization is not considered in the calculation. The binding energy (ΔE_{ads}) of an adsorbate is defined by subtracting the total energy of bare surface and gaseous radical from the total energy of adsorbed adsorbate. The adsorption energy is calculated according to the following expression:

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

where $E_{adsorbate}$ and $E_{surface}$ are DFT total energies of gaseous species and bare surface, respectively. A negative ΔE_{ads} corresponds to an energy gain process.

3. Results and discussion

3.1. H chemisorption on Pt(1 1 1)

H is the main product in the dehydrogenation process of propane, and it is also the least complex atomic species in this study. The Pt(1 1 1) surface exhibits four high-symmetry sites for H adsorption: Atop, Bridge, Fcc and Hcp. Hence, four configurations are employed to study the adsorption of H on Pt(1 1 1), as shown in Fig. 1. The energetically favorable site for H adsorption is the Fcc site, and the adsorption energy is calculated to be –2.73 eV which is consistent with the result obtained by the helium beam diffraction [37]. In our calculations, it is found that H can also be adsorbed at the Atop and hollow sites, but the adsorption energies are lower than that on the Fcc site. The atomic H is relaxed to the adjacent Fcc site even if it is initially placed at the Bridge site. The lengths of Pt–H bonds at the Fcc site are calculated to be 1.87 Å, which is a little larger than the experimental value (1.78 ± 0.8 Å) [38]. This is because the GGA functional tends to underestimate the interatomic forces. The optimized geometric parameters and adsorption energies are in good agreement with the current theoretical results by other groups [27,39]. The shortest H–Pt distance and the height of the H atom above the surface are also listed in Table 1.

3.2. C₁ chemisorption on Pt(1 1 1)

Methyl has one unpaired electron and it can be easily adsorbed on Pt(1 1 1). Similar to H, the adsorption of CH₃ is investigated at the aforementioned four high-symmetry sites. At each site, two orientations of the C–H bonds are considered. After optimization, it is found that CH₃ can only be adsorbed at the Atop and Hcp sites. As

Table 1
Adsorption energies and geometries of H on the Pt(1 1 1) surface.

Site	ΔE_{ads} (eV)	d_{H-Pt} ^a (Å)	$d_{H-surface}$ ^b (Å)
Hcp	−2.66	1.87(3) ^c	0.89
Fcc	−2.73	1.87(3) ^c	0.87
Atop	−2.67	1.56	1.67

^a d_{H-Pt} denotes the shortest H–Pt distance.

^b $d_{H-surface}$ denotes the height of H above the surface.

^c Numbers in parentheses show the amount of the corresponding value.

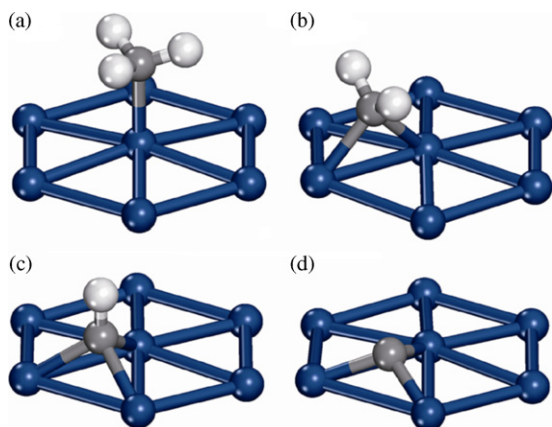


Fig. 2. Schematic representations of the most favorable geometries of C₁ species on the Pt(1 1 1) surface: (a) methyl, (b) methylene, (c) methylidyne, and (d) carbon.

for the two configurations with different orientations of methyl at the Atop site, the adsorption energy difference is less than 0.01 eV which falls within the range of the inherent error of DFT. The optimized configuration of CH₃ at the Atop site is shown in Fig. 2(a), and the adsorption energy is calculated to be −1.99 eV. For the sake of clarity, only seven Pt atoms in the outermost layer are shown. The distance between C and surface is optimized to be 2.27 Å. The underlying Pt atom is displaced out of the surface along the surface normal, and therefore the length of the C–Pt bond is 0.20 Å shorter than $d_{C-surface}$. The CH₃ groups initially placed at the Bridge and Fcc sites are relaxed to the most stable Atop site. This is because CH₃ is a monovalent adsorbate, and it tends to bind with one Pt atom in order to keep the sp³-hybridization. Ford et al. [21] have also found the top site to be preferred by the CH₃ adsorption. Moreover, our calculated adsorption energy and bond lengths are in good agreement with the theoretical studies of Moussounda et al. [10]. The structure parameters are listed in Table 2.

Methylene is a divalent adsorbate. It is reasonable to assume that CH₂ prefers to bind with two Pt atoms. After optimization, the CH₂ groups initially placed at the Atop and hollow sites are relaxed to the Bridge site, which indicates a strong preference of the Bridge site. Interestingly, it is found that the plane with the H–C–H group involved is perpendicular to the Pt–Pt bond at the Bridge site, and this configuration also makes C to preserve the sp³ symmetry, as shown in Fig. 2(b). The adsorption energy is calcu-

Table 2
Adsorption energies and geometries of C₁ atom on the Pt(1 1 1) surface.

Species	Favored site	ΔE_{ads} (eV)	d_{C-Pt} ^a (Å)	$d_{C-surface}$ ^b (Å)	d_{C-H} ^c (Å)
CH ₃	Atop	−1.99	2.07	2.27	1.10(3) ^d
CH ₂	Bridge	−4.06	2.05(2) ^d	1.63	1.10(2) ^d
CH	Fcc	−6.66	2.00(3) ^d	1.18	1.10
C	Fcc	−7.13	1.90(3) ^d	0.80	–

^a d_{C-Pt} denotes the shortest C–Pt distance.

^b $d_{C-surface}$ denotes the height of the C atom above the surface.

^c d_{C-H} denotes the length of the C–H bonds in C₁ species.

^d Numbers in parentheses show the amount of the corresponding value.

lated to be −4.06 eV. For the adsorption at the Bridge site, Kua and Goddard [40] obtained an adsorption energy of 4.52 eV using the cluster approach and Petersen et al. [41] claimed a similar value of 4.61 eV on Pt-(1 × 2). The optimized C–Pt bond length is 2.05 Å, which is a little shorter than that of the methyl group.

Both CH and C favor the Fcc site though the valency of the two species is different. The optimized C–H bond is vertical to the Pt surface at the hollow sites. Compared with CH₃ and CH₂, CH is close to the Pt surface with the $d_{C-surface}$ being 1.18 Å. The adsorption energy is calculated to be −6.66 eV. However, the adsorption energy difference between the configurations located at the Fcc and Hcp sites is only 0.10 eV, which implies that CH diffuses readily between these two sites. Because C has four H atoms missing, it is significantly electrophilic. Hence, C prefers to bind with more Pt atoms to get more electrons. The favored adsorption site is Fcc with a high adsorption energy (−7.13 eV), as shown in Fig. 2(d). The length of the C–Pt bond is calculated to be 1.90 Å, which is shortest among the C₁ species. Paul and Sautet [25] also found that the energetically preferred adsorption site for C on Pd(1 1 1) is the Fcc site, and the adsorption energy is calculated to be −6.40 eV.

3.3. C₂ chemisorption on Pt(1 1 1)

The dehydrogenation of propane is accompanied by the C–C cleavage which generates both C₁ and C₂ species. As the dehydrogenation of the methyl group involved in the C₃ species is not considered, the C₂ species should conceive the methyl group. Thus, the chemisorption of ethyl, ethylidene and ethylidyne is investigated.

Fig. 3(a) shows the adsorption configuration of ethyl on the Pt(1 1 1) surface. Similar to methyl, ethyl prefers to be adsorbed at the Atop site with the CH₃ group positioned over the hollow site. The adsorption energy of ethyl is calculated to be −1.84 eV, 0.15 eV lower than that of methyl. The energy difference is expected to arise from the interaction of methyl group with the methylene group, which weakens the Pt–C bond. The similar phenomenon has been experimentally reported on the H–CH₃ and H–CH₂CH₃ bond energy difference (0.14 eV) [42]. The adsorption energies of the ethyl group with different orientations at the Atop site are very similar (energy difference is less than 0.01 eV), which indicates that the rotation of the adsorbate is feasible. The length of the Pt–C bond is calculated to be 2.10 Å, a little longer than that of methyl. The favorable adsorption configuration of ethyl reported by Jacob and Goddard [11] was in good agreement with our calculated results. The structure parameters are illustrated in Table 3.

The energetically favored site for CHCH₃ is the Bridge site, as shown in Fig. 3(b). By replacing the methyl group with H, the adsorption configuration of ethylidene is almost the same as that of methylene. Upon adsorption, the C–C bond of the ethylidene radical is stretched from 1.46 to 1.50 Å. This is because some electrons are transferred from the metal surface to the electrophilic

Table 3
Adsorption energies and geometries of C₂ species on the Pt(1 1 1) surface.

Species	Favored site	ΔE_{ads} (eV)	d_{C-Pt} ^a (Å)	$d_{C-surface}$ ^b (Å)	d_{C-C} ^c (Å)
Ethyl	Atop	−1.84	2.10	2.32 3.02	1.51
Ethylidene	Bridge	−3.82	2.07(2) ^d	1.69 2.77	1.50
Ethylidyne	Fcc	−5.92	2.02(3) ^d	1.23 2.73	1.49

^a d_{C-Pt} denotes the shortest C–Pt distance.

^b $d_{C-surface}$ denotes the height of the adsorbed C atom above the surface.

^c d_{C-C} denotes the length of the C–C bonds in C₂ species.

^d Numbers in parentheses show the amount of the corresponding value.

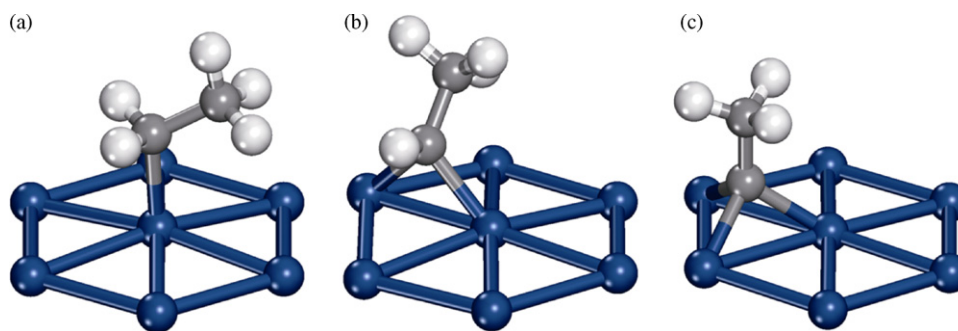


Fig. 3. Schematic representations of geometries of C_2 species on the Pt(111) surface: (a) ethyl, (b) ethylidene, and (c) ethylidyne.

CH group, which weakens the C–C bond. The adsorption energy of ethylidene is calculated to be -3.82 eV, which is 0.24 eV lower than that of methylene but higher than that of ethyl. The length of the Pt–C bond is 2.05 Å, 0.02 Å shorter than that of the methylene group. Both methylene and ethylidene are divalent adsorbates, and the calculated results show that the favored sites for both species are the Bridge site, which was verified by Michaelides and Hu [43].

Ethylidyne has three H atoms missing. As shown in the Fig. 3(c), CCH_3 favors to be adsorbed at the hollow site and forms three covalent C–Pt bonds with the C–C bond vertical to the Pt surface. The calculated parameters are summarized in Table 3. From the table, the energetically favorable site for CCH_3 adsorption is the Fcc site, and the adsorption energy is calculated to be -5.92 eV. Compared with the calculated results of CH, the adsorption energy is lowered by 0.74 eV, but remains 1.90 eV higher than that of ethylidene. This is because ethylidyne is more electrophilic than ethylidene, which enhances the interactions between the adsorbate and metal surface. Ethylidyne is likely to be adsorbed at the Hcp site as well, but the adsorption energy is a little lower (-5.84 eV).

3.4. C_3 chemisorption on Pt(111)

3.4.1. C_3H_8 (propane)

The adsorption of propane is investigated by locating the adsorbate at the Atop, Bridge and hollow sites on Pt(111). After optimization, the propane molecule is repelled by the metal surface, drifting over the surface. The adsorption energies fall within the range of -0.02 to -0.06 eV, which indicates that the nature of the interaction between propane and Pt surface is physisorption. This is because the propane molecule has no unpaired electron, and propane cannot be absorbed by binding with Pt atoms. The structure parameters and adsorption energy are summarized in Table 4. From the table, it is found that the lengths of C–H bonds and C–C bonds are almost the same as those of the isolated propane (C–C: 1.53 Å, C–H: 1.10 – 1.11 Å). Wang [17] investigated the effects of surface step on propane adsorption on Pt(655) through molecular dynamics simulation. It was found that the least efficient zone for propane adsorption was the top of the surface step on the upper terrace, while the most favored zone was near the step edge. Song and Rees [44] claimed that the adsorption heat of propane in silicalite-1 was 0.41 eV and the diffusion barrier was 0.16 eV.

3.4.2. C_3H_7 (1-propyl, 2-propyl)

In our calculations, it is found that the energetically favorable site for 1-propyl is the Atop site. 1-Propyl is relaxed to this site even if the fragment is initially placed at the Bridge or hollow sites. The optimized adsorption configuration of 1-propyl is shown in Fig. 4(b). The adsorption of 1-propyl is similar to the aforementioned monovalent adsorbates. The adsorption energy is calculated to be -1.88 eV, which is a little larger than that of the ethyl group

but lower than that of the methyl group. The optimized C–C bond length is similar to that of propane. As for the adsorption of 2-propyl, it is predicted that the energetically preferred adsorption site is Atop, as shown in Fig. 4(c), and the adsorption energy is calculated to be -1.66 eV which is 0.22 eV lower than that of 1-propyl. The energy difference indicates that the dissociation of C–H bond on methyl group is thermodynamically preferred. This can also be understood by the energy difference between the C–H bonds on the terminal and middle C in propane which is analogous to the adsorption energy difference. It is known that the C–H bond energy in the methylene group is 0.21 eV lower than that in the methyl group.

Table 4

Adsorption energies and geometries of C_3H_x ($x=3$ –8) on the Pt(111) surface.

Species	Favored site	ΔE_{ads} (eV)	d_{C-Pt} ^a (Å)	d_{C-C} ^b (Å)
Propane	–	-0.06	–	$1.53(2)$
1-Propyl	Atop	-1.88	2.10	1.52 1.54
2-Propyl	Atop	-1.66	2.13	$1.52(2)^c$
Propylene	Bridge	-0.93	2.11 2.14	1.50 1.52
1-Propylidene	Bridge	-3.86	$2.07(2)^c$	1.51 1.53
2-Propylidene	Bridge	-3.47	$2.10(2)^c$	$1.51(2)^c$
1-Propenyl	Bridge + Atop ^d	-3.09	2.06 2.08 2.12	1.48 1.52
2-Propenyl	Atop + Bridge ^d	-2.86	2.08 $2.09(2)^c$	1.48 1.51
Propylidyne	Fcc	-3.56	$2.02(3)^c$	1.50 1.54
Propenylidene	Fcc + Atop ^d	-2.26	$1.99(2)^c$ 2.10 2.26	1.42 1.50
Propyne	Bridge + Bridge ^d	-2.09	2.01 2.02 2.26 2.18	1.40 1.50
Propynyl	Fcc + Bridge ^d	-4.63	1.90 2.16 2.17 2.19 2.20	1.34 1.48

^a d_{C-Pt} denotes the shortest C–Pt distance.

^b d_{C-C} denotes the length of the C–C bonds in C_3 species.

^c Numbers in parentheses show the amount of the corresponding value.

^d The site before plus is favored by the C1 group and the site after plus is favored by the C2 group.

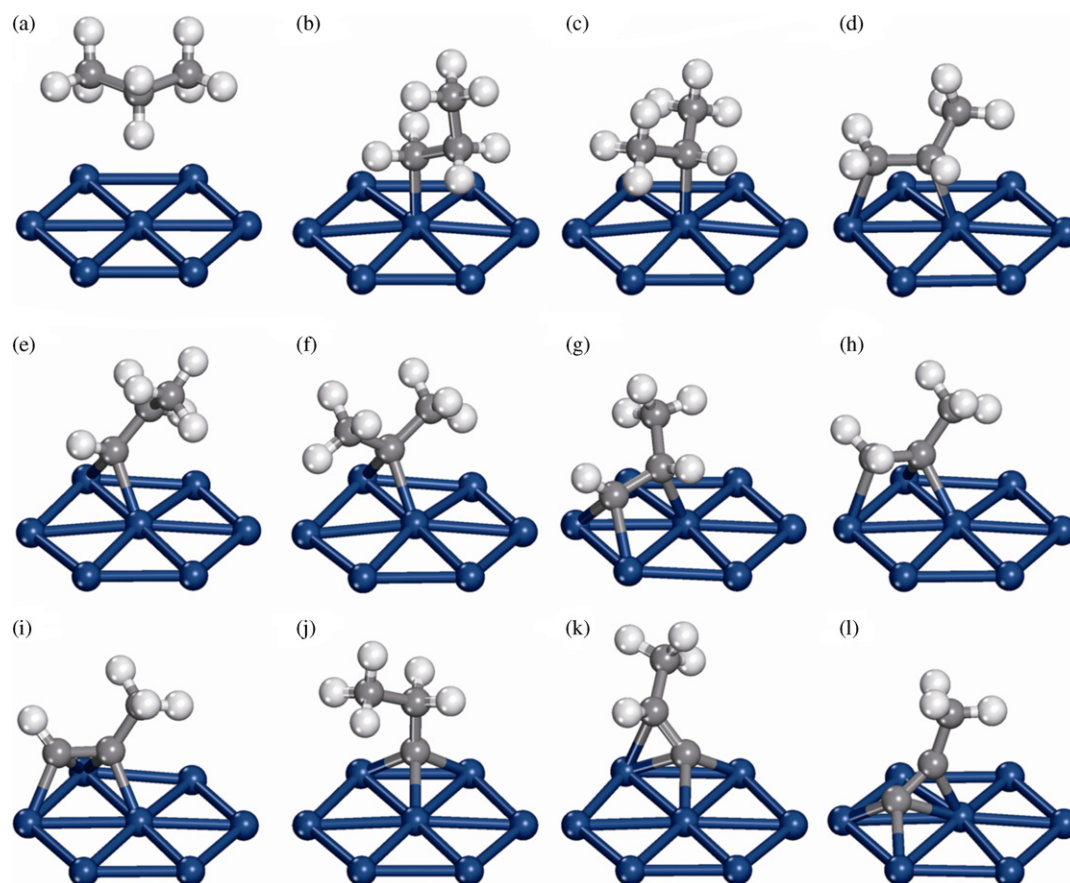


Fig. 4. Schematic representations of the optimized geometries of C_3H_x ($x=3-8$) species on the Pt(111) surface: (a) propane, (b) 1-propyl, (c) 2-propyl, (d) propylene, (e) 1-propylidene, (f) 2-propylidene, (g) 1-propenyl, (h) 2-propenyl, (i) propyne, (j) propylidyne, (k) propenylidene, and (l) propynyl.

3.4.3. C_3H_6 (propylene, 1-propylidene, 2-propylidene)

Propylene is an active intermediate. As propylene has a half-saturated double bond ($C=C$), it can be readily absorbed and decomposed on the Pt(111) surface. The adsorption of propylene is investigated by assigning the propylene molecule at the Atop and Bridge sites (named as π and di- σ adsorption modes, respectively). After optimization, it is found that propylene can be adsorbed stably in both adsorption modes. The energetically favorable site is the Bridge site, and the adsorption energy is calculated to be -0.93 eV which is 0.27 eV higher than that of the π adsorption. The optimized geometry is consistent with the LEED results [45], which revealed that propylene bound to two surface Pt atoms through its unsaturated $C=C$ bond and formed a disordered monolayer. As shown in Fig. 4(d), the $C=C$ bond lies over the Bridge site and forms two covalent $C-Pt$ bonds to share the electronic density with Pt atoms. The calculated structure parameters are listed in Table 4. From the table, it is found that the length of the $C=C$ bond is significantly stretched from 1.36 Å (in gaseous propylene) to 1.50 Å, which is close to the $C-C$ distance of propane. Interestingly, the adsorbed propylene loses its “planarity” as the $C-H$ bonds bend away from the surface plane. The distortion of propylene indicates that the di- σ adsorption mode preserves the sp^3 symmetry of C. The coadsorption of propylene and atomic H is also studied in the same $p(3 \times 3)$ supercell by assigning propylene and atomic H at the Bridge and hollow sites, respectively. The coadsorbed H favors the Fcc site, and the coadsorption energy of these two species is calculated to be -3.60 eV. Compared to the adsorption energy of separated propylene, the coadsorption energy of propylene is lowered by 0.06 eV, which indicates that the adsorption of propylene is weakened by the coadsorbed H. The calculated results are in agreement

with the TPD experiments studied by Zaera and Chrysostomou [1].

To further investigate the chemisorption of propylene on Pt(111), the density of state projected (PDOS) on the C p orbitals of the CH_2 group are given in Fig. 5. The zero energy refers to the Fermi level. By analyzing of PDOSs, it is clear that the $2p$ states in adsorbed propylene shift to low energy region, which indicates that the C atoms interact with the Pt surface to form new covalent bonds. However, Fig. 5 shows little evidence for the preference between the two adsorption configurations. In order to understand the preference of propylene for the di- σ adsorption modes, the charge of C atoms is investigated through Bader charge analysis. This analysis carries out the decomposition of electronic charge density into atomic contributions. Calculations are performed for the two adsorption configurations. The valence charges of all the atoms in propylene are summed up so as to represent the interactions between propylene and Pt surface. For the di- σ and π adsorption, the valence charges are calculated to be 17.90 and 17.81 , respectively, which indicate that the interaction between propylene and Pt surface in the di- σ adsorption is stronger. This is supported by the valence charge density analysis, as shown in Fig. 6. The valence charge density is calculated for the two configurations and plotted perpendicular to the Pt surface with the $C-Pt$ bonds involved. As shown in Fig. 6, the strong $C-Pt$ covalent bonds are formed by sharing electrons in the two configurations. In the di- σ adsorption, the valence charge density between C and Pt surface is larger than that of the π adsorption, indicating a stronger $C-Pt$ bond. Hence, the di- σ adsorption is predicted to be preferred.

As shown in Fig. 4(e), 1-propylidene ($CHCH_2CH_3$) favors the Bridge site with the ethyl group lying over the hollow site on

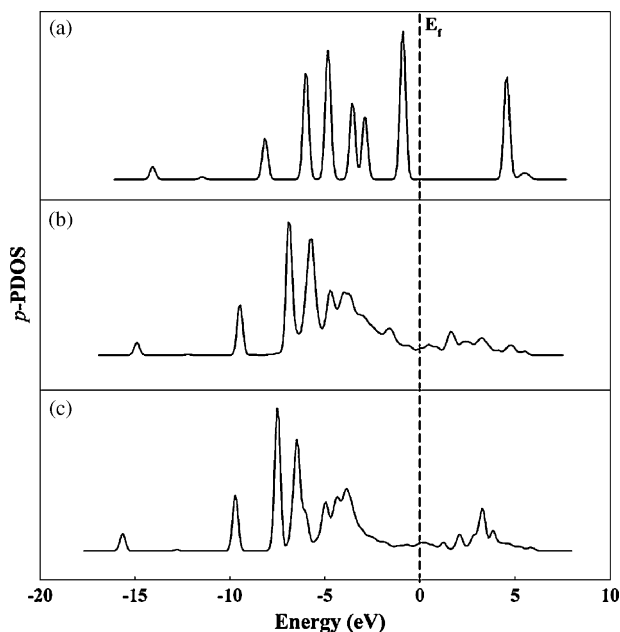


Fig. 5. Density of states projected on the C 2p orbitals of the CH₂ group in propylene. (a) gaseous propylene, (b) propylene adsorbed in the di- σ mode, and (c) propylene adsorbed in the π mode.

Pt(1 1 1). The adsorption energy is calculated to be -3.86 eV, which is lower than those of ethylidene and methylene. The length of C–Pt bond is 2.07 Å, and all the C–C and C–H bonds are almost the same as those in gaseous propane. The adsorption of 2-propylidene (CH₃CCH₃) is similar to 1-propylidene. The calculated results also show that the preferred adsorption site is the Bridge site with the methyl group lying over the hollow site, and the adsorption energy is calculated to be -3.09 eV. The length of C–C bond and Pt–C bond is in good agreement with the results by Valcárcel et al. [29].

3.4.4. C₃H₅ (1-propenyl, 2-propenyl, propylidyne)

Propenyl can be easily generated from the deep dehydrogenation of propylene [20]. As the dehydrogenation of the methyl group in vacuum is not taken into account, C1–C2–CH₃ is employed to represent the C₃H_x ($x=5-8$) intermediates. 1-Propenyl has three H atoms missing, two in the C1 group and one in the C2 group. The favorable adsorption site is the Fcc site, and the adsorption energy is calculated to be -3.09 eV. As shown in Fig. 4(g), the C1 group binds to the surface with two covalent bonds, and the C2 group binds to one Pt atom, which keeps each C atom to be sp³-hybridized. The length of the C1–C2 bond is 1.48 Å, which is shorter than that of propane (1.53 Å). The adsorption of 2-propenyl (CH₂CCH₃) is similar to 1-propenyl, as shown in Fig. 4(h). The C1 group prefers to bind with one Pt atom, while the C2 group prefers two. This is also an evidence that the divalent adsorbates favor the Bridge site and the monovalent adsorbates favor the A_{top} site. The adsorption energy

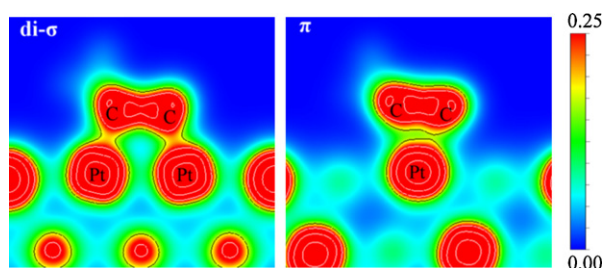


Fig. 6. The valence charge density calculated for different propylene adsorption modes.

is calculated to be -2.86 eV. The optimized bond lengths of the configuration are listed in Table 4.

The LEED [20] analysis indicated that propylidyne favored the Fcc site. The optimized adsorption geometries of propylidyne are similar to those of methylidyne and ethylidyne. As shown in Fig. 4(j), propylidyne is adsorbed at the Fcc site by forming three covalent bonds with Pt atoms with the adsorption energy calculated to be -3.56 eV, and the C–Pt bond lengths are calculated to be 2.02 Å. The adsorption energies of methylidyne, ethylidyne and propylidyne are in the following order, methylidyne > ethylidyne > propylidyne. Hence, it can be deduced that the weakening of the adsorption is attributed to the presence of the saturate hydrocarbon group.

3.4.5. Other hydrocarbons: C₃H₄ (propenylidene, propyne) and C₃H₃ (propynyl)

The configurations of chemisorbed propyne and propenylidene (CCHCH₃) are shown in Fig. 4(i) and (k), respectively. The gaseous propyne binds strongly to the Pt(1 1 1) surface because of the significantly electrophilic C≡C triple bond. Both C1 and C2 groups have two H atoms missing, thus the two groups favor the Bridge sites with the triple bond lying over the Fcc site. The adsorbed propyne loses its linearity in order to keep each C atom to be sp³-hybridized. The bond length of C1–C2 is calculated to be 1.40 Å, which is longer than that in the gaseous propyne but shorter than those in the C₃H_x ($x=5-8$) intermediates. The adsorption energy is calculated to be -2.09 eV. The optimized geometric parameters are in good agreements with the TPD and theoretical results [46,47]. Jacob and Goddard [11] reported that vinylidene (CCH₂) favored to be adsorbed at the Fcc site in order to keep all the C atoms tetrahedral on the Pt(1 1 1) cluster. The configuration of the adsorbed propenylidene is similar to vinylidene by replacing the methyl group with a H atom. After optimization, it is found that the C1 group favors to bind to three Pt atoms, and the C2 group prefers only one Pt atom. The lengths of the C–C and Pt–C bonds are consistent with the results by Valcárcel et al. [29]. The structure parameters and adsorption energies are shown in Table 4.

Propynyl is generated from both propyne and propenylidene by the removal of one H atom. Propynyl favors to be adsorbed at the Fcc site with the C1–C2 bond parallel to the metal surface and the methyl group pointing towards vacuum. The C1 group prefers to bind to three Pt atoms, while the C2 group favors only one, which is similar to the adsorption configuration of propenylidene. The adsorption energy is calculated to be -4.63 eV, and the length of the C1–C2 bond is 1.34 Å which is longer than that of gaseous propyne but shorter than that in the adsorbed propyne.

3.5. Thermodynamic analysis

Dehydrogenation of propane may produce a variety of intermediates. In order to investigate the stability of these species on Pt(1 1 1), we obtain the relative energies of the intermediates with respect to the gas-phase propane and adsorbed H, which are summarized in Fig. 7. It is assumed that any H atoms detached from the hydrocarbons are adsorbed on the surface at a distance far away from the coadsorbed species, which allows us to neglect the coadsorption effects of H. Based on the relative energies of the intermediates, it is possible to calculate the changes of reaction heat for different reactions, and find out the most likely reaction pathway.

It is well known that the activation of C–H bond is strongly endothermic in the gaseous propane, e.g., the experimental C–H bond energies in the methyl group and methylene group are 420 and 401 kJ/mol, respectively. The formation of 1-propyl and 2-propyl from propane is almost thermoneutral with the similar reaction heat calculated to be -0.02 and -0.01 eV, respectively. Hence, it is reasonable to assume that the energy barriers for

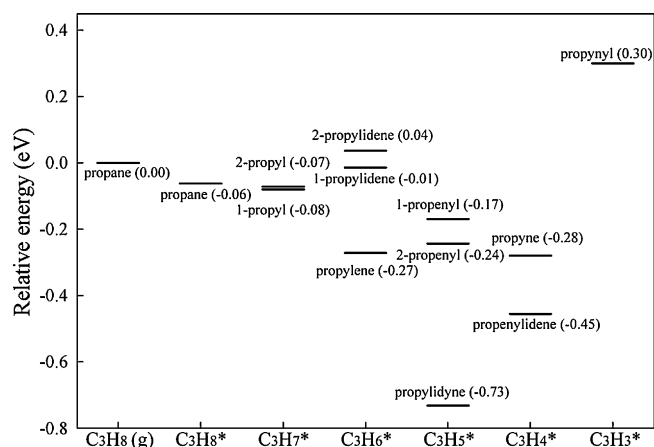


Fig. 7. Energy profile of adsorbed C_3H_x ($x=3-8$) on the Pt(111) surface. The relative energies are obtained using $E_{C_3H_x} = E_{C_3H_x/surface} - (8-x)(E_{H/surface} - E_{surface}) - (E_{C_3H_8(gas)} + E_{surface})$.

the initial activation of propane are close to each other according to the BEP relationship [48,49]. Propylene can be obtained via dehydrogenation, hydrogenation and isomerization. All these three reactions are exothermic, and the most favorable pathway follows the isomerization of 2-propylidene to propylene. The most stable fragment on Pt surface is propylidyne because the dehydrogenation of propane to produce propylidyne releases the maximum amount of heat (-0.73 eV). Propyne is likely to be isomerized to propenylidene and releases 0.17 eV. It is shown in the energy profile that the formation of propynyl from gaseous propane is 0.30 eV endothermic. Moreover, the reaction heat to produce propynyl from propyne is calculated to be 0.58 eV, which is highest among all the dehydrogenation reactions. According to the BEP relationship, the barrier of the formation of propynyl is predicted to be much higher than those of other dehydrogenation reactions. It is reasonable to suggest that propynyl is the most energetically unfavorable intermediates involved in the decomposition of propane. Hence, it can be concluded that the most likely reaction pathway for propane dehydrogenation is propane \rightarrow 1-propyl \rightarrow 1-propylidene \rightarrow propylidyne.

The bond energies of C–C, C=C and C \equiv C are calculated to be -3.95 , -7.59 and -9.87 eV, respectively, indicating that the scission of these bonds is hindered by a large barrier in the gas-phase. However, the C–C bond cleaves readily if the metal atoms form stronger chemical bonds with C atoms [44,45]. In our calculations, it is found that the adsorption is generally enhanced with the proceeding of the stepwise dehydrogenation. It is therefore reasonable to expect that the activation of the C–C bond is related to the number of H atoms in the hydrocarbons. Based on the relative energies of the fragments and reaction heat changes of cracking shown in Table 5, the qualitative approach is performed to investigate the reaction. As the gaseous propane is physisorbed on the Pt(111) surface, the activation energy of the cracking of propane is very close to the C–C bond energy, which indicates that the reaction barrier is quite high. The adsorption energy of propylene is calculated to be -0.93 eV, while the results for the other two C_3H_6 isomers are larger than -3.00 eV. Hence, it is reasonable to assume that the cracking of propylene is unfavorable. In addition, the reaction heat of the cracking of 2-propylidene is 0.34 eV higher than that of 1-propylidene, indicating that the C–C bond breaking of 2-propylidene is energetically preferred. In our calculations, propylidyne is found to be the most thermodynamically favored product in dehydrogenation, while the reaction heat of its cracking is positively 1.09 eV, implying a large barrier according to the BEP relationship. Though the reaction heats of the cracking of propynyl and 2-propylidene are

Table 5

Reaction heat changes for C–C scission of C_3H_x ($x=3-8$) fragments on the Pt(111) surface.

Surface reaction	ΔE_{reac} (eV)
Propane \rightarrow methyl + ethyl	0.18
1-Propyl \rightarrow methylidene + ethyl	0.37
2-Propane \rightarrow methyl + ethylidene	0.28
Propylene \rightarrow methylidene + ethylidene	0.64
1-Propylidene \rightarrow methylidyne + ethyl	-0.23
2-Propylidene \rightarrow methyl + ethylidyne	-0.57
1-Propenyl \rightarrow methylidyne + ethylidene	0.01
2-Propenyl \rightarrow methylidene + ethylidyne	-0.13
Propylidyne \rightarrow C + ethyl	1.09
Propenylidene \rightarrow C + ethylidene	0.91
Propyne \rightarrow methylidyne + ethylidyne	-0.62
Propynyl \rightarrow C + ethylidyne	-0.55

negative, they are not expected to be the likely starting point for the C–C scission because both two species are not favored in the dehydrogenation process. Hence, propyne is suggested to be favorable for cracking owing to strong adsorption and large negative reaction heat.

4. Conclusion

DFT–GGA calculations have been performed to study the chemisorption of CH_x ($x=0-3$), C_2H_y ($y=3-5$) and C_3H_z ($z=3-8$) on Pt(111) at the surface coverage of 0.11 ML. Our calculated results provide a detailed thermodynamic approach to investigate the dehydrogenation and cracking of propane on Pt(111).

1. The atomic H prefers to be adsorbed at the Fcc site, and the adsorption energy is calculated to be -2.73 eV. Calculated adsorption energies of C_1 species are in the following order, $C > CH > CH_2 > CH_3$. CH_3 and CH_2 favor the Atop and Bridge site, respectively, and both CH and C prefer the Fcc sites. This is an evidence that the monovalent and divalent adsorbates favor the Atop and the Bridge sites, respectively, and the trivalent and tetravalent adsorbates prefer the hollow sites. The similar trend has been observed on the adsorption of C_2 species.
2. The chemisorption of C_3H_x ($x=3-7$) is investigated by assigning the adsorbates at all the possible adsorption sites. In general, all the C_3 species favor to be adsorbed at the sites with C atoms kept to be sp^3 -hybridized. The propane molecule is found to be physisorbed on the Pt surface. The optimized adsorption configuration of propylene is characterized as the di- σ mode, and the adsorption energy is calculated to be -0.93 eV which is 0.27 eV higher in energy than that of the π adsorption mode. Our calculated results for adsorption energies and geometries are in good agreement with the recent experimental and theoretical results.
3. In addition, the reaction heat of the dehydrogenation and cracking of propane are calculated. According to the BEP relationship, it is apparent that propylidyne is the most likely product in the dehydrogenation process. The formation of propynyl is predicted to be hindered by a relative high barrier on Pt surface. Combining the analysis of the chemisorption of intermediates and the reaction heat changes of cracking, propyne is suggested to be the most likely starting point for the C–C scission.

Supporting information available

Optimized structures of all the possible adsorption configuration of the aforementioned species are included, as well as the adsorption energies and structure parameters.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.01.017.

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