Oxygen Atom Function: The Case of Methane Oxidation Mechanism to Synthesis Gas over a Pd Cluster

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Abstract: A dimer model Pd₂ was established to study the adsorption of CHₓ (x = 1–4) and CH₄ dehydrogenation, as well as syngas formation using density functional theory (DFT) at the atomic level. Meanwhile, insight into understanding the role of the oxygen atom on the partial oxidation of methane (POM) was also calculated based on a trimer model of Pd₂O. For the adsorption of CHₓ, results showed that the presence of an oxygen atom was a disadvantage to the adsorption of CHₓ (x = 1–3) species. For CH₄ dissociation, the process of CH₂→CH + H was found to be the rate-limiting step (RSD) on both Pd₂ and Pd₂O. H₂ was formed by the reaction of CH₂ + 2H→CH₂ + H₂. For CO formation, it was primarily formed in the process of CH + O→CHO→CO + H on both the Pd₂ and the Pd₂O catalyst. Thermodynamic and kinetic calculations revealed that formation and maintainance of the oxygen atom on the Pd surface could promote a POM reaction to achieve high H₂ and CO yield and selectivity. Our study provides a helpful understanding of the effect of an adsorbed oxygen atom on a POM reaction with a Pd catalyst.

Keywords: density functional theory; Pd₂; Pd₂O; partial oxidation of methane; reaction mechanism

1. Introduction

Methane (CH₄), the main component of coalbed gas, is directly released to the environment in an amount of around 19 billion cubic meters per year [1]. In the consideration of energy conservation, environmental protection, and rational energy utilization, efficient utilization of methane has become increasingly important [2–7]. Due to the mildly exothermic heat property and suitable production ratio of H₂/CO (syngas) for methanol and Fischer–Tropsch synthesis [8,9], conversions of methane via the partial oxidation of methane (POM) have been proposed in previous studies [10–13].

Metallic palladium (Pd) is one of the most efficient catalysts for CH₄ oxidation, which was outlined both upon experimental and theoretical calculation [14–18]. Liu et al. claimed that Pd/TiO₂ nanoparticles shows good activity for methane oxidation at low temperatures [19]. Li et al. investigated the synthesis gas production from partial oxidation of methane over highly dispersed Pd/SiO₂ catalyst. It was found that the reaction of methane conversion on highly dispersed Pd catalyst was more activity and stability than the other catalysts [20]. However, it is difficult to prepare and research performance small cluster catalyst alone in experiment, but it can be easily solved by density functional theory (DFT). With the further research, Johan et al. investigated methane oxidation on Pd/Al₂O₃ by in situ X-ray absorption fine structure (XAFS) characterization. It was found that methane conversion was increased with the oxidation of Pd, which indicated that PdO was the active phase for methane oxidation [15].
Moreover, Xiong et al. found that Pd and PdO could coexist within a single particle and be mutually transformed at high temperatures by the methods of in situ X-ray diffraction (XRD) and a JEOL 2010 microscope transmission electron microscopy (TEM). A polycrystalline catalyst was formed when Pd and PdO were exposed to methane and oxygen together [21–23].

In addition to the above experiments, methane activation on a Pd bulk surface was also largely investigated using the density functional theory (DFT) method [24–28]. Adsorption and dehydrogenation of CH₄ on Pd (100) and PdO (100) surfaces were studied in previous works that found that the effect of coadsorbed oxygen atoms tends to weaken the adsorbate–substrate interaction. However, the ordered metal surface changes into an amorphous state, identified as being dependent on temperature. Therefore, only obtaining results of the reactions on the surfaces were inadequate.

In recent years, researchers have focused on the effect of methane activation on clusters. Trevor et al. observed methane activation on Pt clusters of 2–24 atoms by using time-of-flight mass spectroscopy; the experiments showed that the most activity-neutral cluster was Pt₂–Pt₅ [29]. The nanocluster had a large surface area and abundant defects, which suggested higher reactivity for the oxidation of methane than that of the bulk surface [17,30–34]. Therefore, an intuitive idea was that the study of the POM mechanism on a Pd cluster would be better matched with the actual reaction process.

In this work, a Pd cluster model of dimer Pd₂ was established to study the reaction mechanisms of POM at the atomic level, while a similar cluster model of trimer Pd₂O was used to investigate the effect of oxygen on methane activation in a Pd system. The adsorption of CHₓ (x = 1–4) and methane dehydrogenation on dimer Pd₂ and trimer Pd₂O were studied by DFT. Subsequently, the formation of hydrogen and carbon monoxide were also identified in detail. Plausible reaction mechanisms and the effect of an oxygen atom on POM were illuminated.

2. Results and Discussion

The structures of the model clusters are shown in Figure 1. In dimer Pd₂, the diatomic distance was 2.545 Å, which was in good agreement with the experiment result of 2.55 Å that Nasresfahani et al. obtained [35]. In trimer Pd₂O, the Pd–Pd bond length was elongated to 2.635 Å. This indicated that, with the adsorption of the oxygen atom, the interaction between two Pd atoms was decreased. CH₄ dehydrogenation and oxidation were considered as necessary processes for POM in order to understand the effect of the oxygen atom that Pd-catalyzed the reaction sufficiently.

![Figure 1. Structures of dimer Pd₂ and trimer Pd₂O (bond unit, Å; turquoise: Pd, red: O).](image)

2.1. Intermediate System in the Reaction

With similar reaction paths, methane dehydrogenation processes are presented as four competitive reaction steps [36–39]: methyl (CH₃), methylene (CH₂), methyldiene (CH), and carbon (C) were generated in an orderly fashion during the cracking. The stable configurations of CH₄–Pd₂(o), CH₃–Pd₂(o), CH₂–Pd₂(o), and CH–Pd₂(o) were obtained by geometry optimization, respectively. The length of the chemical bonds is shown in Figure 2, and the coordination energies are listed in Table 1.
were lower than those of the CH
They also revealed that the interaction between CHx (x = 0–4) and the catalyst was reduced by the introduction of the oxygen atom. Similarly to the process of CH4 dissociation catalyzed by Pd2 and Pd2O, CHx (x = 0–3) dissociation catalyzed by Pd2 and Pd2O were exothermic reactions (Figure 2). For CH3–Pd2, the length of the C–Pd bond was 2.007 Å, while the length increased to 2.235 Å as CH3 was catalyzed by Pd2O. The coordination energy of Pd2 and Pd2O were −2.63 and −2.42 eV, respectively, when CH3 was replaced by CH2. The length of the C–Pd bonds of CH–Pd2 and CH–Pd2O were 1.829 and 1.867 Å, respectively. The coordination energies of CH4–Pd2 and CH4–Pd2O were −5.70 and −4.66 eV, respectively. These results indicated that the coordination energy decreased with the cracking process: CH4 < CH3 < CH2 < CH < C [26,37,38]. They also revealed that the interaction between CHx (x = 0–4) and the catalyst was reduced by the introduction of the oxygen atom.

As shown in Figure 2 and Table 1, CH4 dissociation catalyzed by Pd2 and Pd2O results in an exothermic formation of CH3–Pd2 and CH2–Pd2O systems. In the CH4–Pd2 system, the length of the C–Pd bond was 2.657 Å, while the length decreased to 2.432 Å in CH4–Pd2O [37]. The coordination energy of the two systems was −0.34 and −0.87 eV, respectively. These coordination-energy results, further confirmed that our work was reliable as they were consistent with previous work [38]. Similarly to the process of CH4 dissociation catalyzed by Pd2 and Pd2O, CHx (x = 0–3) dissociation catalyzed by Pd2 and Pd2O were exothermic reactions (Figure 2). For CH3–Pd2, the length of the C–Pd bond was 2.007 Å, while the length increased to 2.235 Å as CH3 was catalyzed by Pd2O. The distance between C and Pd was 1.988 Å in the CH2–Pd2 system, and 2.017 Å in the CH2–Pd2O system, and these lengths were lower than those of the CH3 system. The coordination energies of CH3–Pd2 and CH3–Pd2O were −2.63 and −2.42 eV, respectively. The coordination energy of Pd2 and Pd2O increased to −4.90 and −4.08 eV, respectively, when CH3 was replaced by CH2. The length of the C–Pd bonds of CH–Pd2 and CH–Pd2O were 1.829 and 1.867 Å, respectively. The coordination energies of the CH–Pd2 and CH–Pd2O systems were increased to −5.70 and −4.66 eV, respectively. These results indicated that the coordination energy decreased with the cracking process: CH4 < CH3 < CH2 < CH < C [26,37,38].

To further confirm the effect of the oxygen atom on Pd2, the partial density of states (PDOS) of CHx–Pd2(O) was investigated. In Figure 3a, it is shown that CH4 was hardly activated due to the superwide orbital energy gap of CH4, which was about 8 eV. When CH4 was adsorbed on Pd2O, PDOS peaks were slightly shifted to more negative values than those of the CH4–Pd2 system, indicating the charge transfer from Pd2 to CH4. As shown in Figure 3b,c, when CH3 and CH2 were catalyzed by Pd2O, their peaks shifted to more negative values than those of the CH3/CH2–Pd2 systems. In Figure 3d, we can see that a similar phenomenon was observed in CH.

**Table 1.** Binding energies of CHx (x = 0–4) adsorbates on dimer Pd2 and trimer Pd2O.

| System       | Coordination Energy Pd2 (eV) | Pd2O (eV) |
|--------------|-----------------------------|-----------|
| CH4–Pd2(o)   | −0.32                       | −0.87     |
| CH3–Pd2(o)   | −2.63                       | −2.42     |
| CH2–Pd2(o)   | −4.90                       | −4.08     |
| CH–Pd2(o)    | −5.70                       | −4.66     |
| C–Pd2(o)     | −6.01                       | −5.30     |
Figure 3. Partial density of states (PDOS) of CHx (x = 1–4) before and after being catalyzed by Pd2 and Pd2O. (a–d) CH4, CH3, CH2, and CH, respectively, before and after being catalyzed by Pd2 and Pd2O. Black, red, and blue lines, free CHx and CHx–Pd2(O), respectively. The blue dashed vertical lines indicate the Fermi levels.

2.2. Methane Activation

In order to illuminate the effect of an oxygen atom on CH4 dehydrogenation, the cleavage energy of CH4 on Pd2 and Pd2O was calculated at the same level. In the reaction, CHx with the most stable geometry was chosen as the initial state, and the CHx–1+H with the most stable coadsorbed geometry was chosen as the final state. The transitional reaction states on Pd2 and Pd2O were labeled for TS1–TS4 and TS1’–TS4’, respectively. The configuration of various structures involved in the reaction mechanism associated with the change from CHx–Pd2(O) to CHx–1 + H–Pd2(O) are shown in Figures 4 and 5.
Figure 4. Optimized structure of reactants, intermediates, products, and the transition state of methane activation by Pd$_2$ (turquoise: Pd, gray: C, white: H).

Figure 5. Optimized structure of reactants, intermediates, products, and the transition state of methane activation by Pd$_2$O (turquoise: Pd, gray: C, white: H).

2.2.1. Potential Energy Changes of Methane Activation

An energy barrier and energy changes were generally used to study the reaction mechanism. The energy changes are listed in Tables S1 and S2. The potential energy curves for CH$_4$ dissociation on Pd$_2$ and Pd$_2$O are shown in Figure 6.

Figure 6. Energy profiles of dehydrogenation from CH$_4$ to C: CH$_4$ → CH$_3$ + H → CH$_2$ + 2H → CH + 3H → C + 4H on Pd$_2$ and Pd$_2$O. Black line and red line represent the dissociation of CH$_x$ on Pd$_2$ and Pd$_2$O.
In the process whereby CH$_4$→CH$_3$ + H, the energy barrier (E$_b$) on Pd$_2$ and Pd$_2$O was 0.61 and 1.09 eV, respectively, which was in good agreement with CH$_4$ dissociation over the Pd$_2$ dimer and Pd(111) [40,41]. This indicated that CH$_4$ activation on Pd$_2$O is relatively difficult to achieve compared with that on Pd$_2$ [42,43]. This reaction was an exothermic process (reaction energy (E$_r$) < 0) on Pd$_2$ but an endothermic process (E$_r$ > 0) on Pd$_2$O.

For CH$_3$ + H→CH$_2$ + 2H, E$_b$ on both Pd$_2$ and Pd$_2$O was higher than the first C–H dissociation. E$_b$ was 1.03 and 1.28 eV on Pd$_2$ and Pd$_2$O, respectively. It was shown that the second C–H bond dissociated on Pd$_2$O requires higher energy than that on Pd$_2$ [41,43]. This reaction was an endothermic process (E$_r$ > 0) both on Pd$_2$ and Pd$_2$O. Therefore, the POM experiment required a high reaction temperature, about 800 °C, at the beginning [10].

In terms of CH$_2$ + 2H→CH + 3H, the E$_b$ reached 2.18 eV on Pd$_2$ and 1.71 eV on Pd$_2$O. The largest reaction barriers implied that this step was the rate-determining steps (RDS) in the process of CH$_4$ activation on Pd$_2$ and Pd$_2$O, which was consistent with reported works [26,42].

For the step of CH + 3H→C + 4H, the E$_b$ on Pd$_2$ and Pd$_2$O was 1.58 and 1.33 eV, respectively. The reactions on Pd$_2$ and Pd$_2$O were both endothermic processes (E$_r$ > 0) [26,43]. Above all, compared with the reaction energy barrier and reaction heat details of the steps of CH$_4$ dehydrogenation on Pd$_2$ and Pd$_2$O, it can be seen that, except for CH$_4$ and CH$_3$, the adsorption of the oxygen atom was conducive to CH$_3$ (X = 1,2) dissociation.

### 2.2.2. Thermodynamic and Kinetic Analysis of Methane Activation

Furthermore, the thermodynamics and kinetics of the reaction on the Pd$_2$(O) cluster were studied, as shown in Tables 2 and 3. The activation energy (E$_a$) of CH$_4$→CH$_3$ + H was 0.45 eV on Pd$_2$, but 1.78 eV on Pd$_2$O, indicating that the cleavage of the first C–H bond is easier in the CH$_4$→Pd$_2$ system than that in the CH$_4$–Pd$_2$O system. The corresponding rate constant (κ) values of the two reactions, verified by a conclusion from a previous source, were 1.75 × 10$^{10}$ and 2.09 × 10$^{7}$, respectively. CH$_3$ + H→CH$_2$ + 2H on Pd$_2$(O) had the same trend as the first H atom dissociation.

| Pd$_2$  | E$_a$ (eV) | ΔH$^\ddagger$ (eV) | ΔS$^\ddagger$ (eV) | A (S$^{-1}$) | κ (S$^{-1}$) |
|---------|-----------|---------------------|---------------------|-------------|-------------|
| CH$_4$→CH$_3$ + H | 1.17       | 1.1                | -0.21              | 1.62 × 10$^{12}$ | 4.36 × 10$^5$ |
| CH$_3$ + H→CH$_2$ + 2H | 1.97       | 1.9                | -0.18              | 2.10 × 10$^{12}$ | 9.84 × 10$^0$ |
| CH$_2$ + 2H→CH + 3H | 4.18       | 4.1                | -0.17              | 7.44 × 10$^{12}$ | 7.27 × 10$^{13}$ |
| CH + 3H→C + 4H | 3.01       | 2.93               | -0.15              | 7.04 × 10$^{13}$ | 9.30 × 10$^{-6}$ |

| Pd$_2$O | E$_a$ (eV) | ΔH$^\ddagger$ (eV) | ΔS$^\ddagger$ (eV) | A (S$^{-1}$) | κ (S$^{-1}$) |
|---------|-----------|---------------------|---------------------|-------------|-------------|
| CH$_4$→CH$_3$ + H | 1.92       | 1.85                | -0.32              | 4.07 × 10$^{11}$ | 3.75 × 10$^9$ |
| CH$_3$ + H→CH$_2$ + 2H | 1.94       | 1.87                | -0.42              | 1.11 × 10$^{11}$ | 7.75 × 10$^{-1}$ |
| CH$_2$ + 2H→CH + 3H | 3.47       | 3.4                 | -0.07              | 2.31 × 10$^{12}$ | 4.03 × 10$^{-8}$ |
| CH + 3H→C + 4H | 3.13       | 3.06               | 0.11               | 3.04 × 10$^{12}$ | 3.74 × 10$^{-5}$ |

The E$_a$ of CH$_2$ + 2H→CH + 3H was 3.13 eV on Pd$_2$ and 2.65 eV on Pd$_2$O. The corresponding κ values were 2.17 × 10$^{-6}$ and 6.25 × 10$^{-3}$, respectively. The relatively low E$_a$ and high κ indicated that the cracking process from CH$_2$ to CH on Pd$_2$O could easily occur. In addition, CH$_2$ + 2H→CH + 3H had the highest E$_a$ and the lowest κ compared to the other dehydrogenation reaction on Pd$_2$(O), indicating that CH$_2$→CH was the RDS for CH$_4$ decomposition on Pd$_2$(O).
2.3. Hydrogen Production

The structure of MCH$_2$ + H$_2$ is an important intermediate during hydrogen production [40,44]. Thus, the structures of the corresponding intermediates of Pd$_2$ and Pd$_2$O were calculated. The frequency calculations of transition-state (TS) geometries are shown in Figures 7 and 8. The transition states of the reaction on Pd$_2$ and Pd$_2$O were marked as TS5–TS7 and TS5’–TS7’, respectively. All frequencies of the initial states (IS), intermediate states, and the final state (FS) were positive, which indicates that their structures were stabilized. Intrinsic reaction coordinate (IRC) calculations showed that all optimized transition states correctly connected the relevant reactants and products.

![Figure 7](image1.png)

**Figure 7.** Optimized structure of reactants, intermediates, products, and the transition state of hydrogen generation by Pd$_2$ (turquoise: Pd, gray: C, white: H).

![Figure 8](image2.png)

**Figure 8.** Optimized structure of reactants, intermediates, products, and the transition state of hydrogen generation by Pd$_2$O (turquoise: Pd, gray: C, white: H).

2.3.1. Potential Energy Changes of Hydrogen Generation

The potential energy changes of hydrogen generation were researched to reflect the hydrogen elimination mechanism. As shown in Figure 9, two distinguishable reaction paths were used to describe the formation of H$_2$ on the Pd$_2$ and Pd$_2$O catalysts. The results of potential energy changes are listed in Tables S3 and S4. The energy barrier of the CH$_2$ + 2H → CH$_2$ + H$_2$ reaction was low, as a result of no need for any chemical-bond breakage, similarly to what occurred on Pd$_2$ and Pd$_2$O. From...
Figure 9, we can see that the barrier and overall heat absorption on Pd$_2$ were relatively bigger than those on Pd$_2$O. This illustrated that the presence of oxygen atoms was beneficial to the formation of hydrogen.

![Energy profiles of hydrogen generation](image_url)

**Figure 9.** Energy profiles of hydrogen generation: CH$_2$ + 2H$_2$→CH$_2$ + H$_2$ on Pd$_2$ and Pd$_2$O.

### 2.3.2. Thermodynamic and Kinetic Analysis of Hydrogen Generation

$E_a$ and $\kappa$ were calculated to understand the reaction processes on Pd$_2$(O) in terms of the thermodynamics and kinetics. The relevant data are shown in Tables 4 and 5. The reactions of hydrogen generation included CH$_2$ + 2H→CH$_2$ + 2H$_2$, CH$_2$ + 2H→CH$_2$ + 2HN, and CH$_2$ + 2H→CH$_2$ + H$_2$. The corresponding $E_a$ and $\kappa$ of these reactions on Pd$_2$ were 0.03, 0.68, and 1.11 eV, and 2.44×10$^{12}$, 2.20×10$^9$, and 5.27×10$^6$ s$^{-1}$, respectively. It was seen that hydrogen generation in the presence of an oxygen atom was easier in terms of the thermodynamics of the reaction.

| CH$_2$ + 2H→CH$_2$ + 2H$_2$ | $E_a$ (eV) | $\Delta H^\circ$ (eV) | $\Delta S^\circ$ (eV) | $A$ (S$^{-1}$) | $\kappa$ (S$^{-1}$) |
|-----------------------------|-----------|----------------------|----------------------|--------------|------------------|
| CH$_2$ + 2H→CH$_2$ + 2HN    | 0.48      | 0.09                 | 0.09                 | 5.21×10$^{13}$ | 1.80×10$^{11}$   |
| CH$_2$ + 2HN→CH$_2$ +H$_2$  | 1.08      | –0.08                | –0.08                | 6.57×10$^{12}$ | 5.77×10$^6$      |

### 2.4. Carbon Monoxide Formation

The oxidation of CH$_4$ to CO involves the oxidation process of CH and C. In order to investigate the effect of oxygen atoms on the formation of CO on a Pd catalyst, three possible reaction pathways of
CO formation on Pd$_2$ and Pd$_2$O were studied using DFT calculation \cite{45,46}. The processes were: (1) CH→C + H, C + O→CO; (2) CH + O→CHO→CO + H; and (3) CH + O→COH→CO + H.

2.4.1. Potential Energy Changes of Carbon Monoxide Formation

The geometric optimization structure of reactants, products, intermediates, and transition states in the oxidation process of CH and C are shown in Figure 10. All reactants and products structures were stable due to the positive calculations of frequencies. The transition states of reaction on Pd$_2$ and Pd$_2$O were denoted as TS8–TS13 and TS8’–TS13’, respectively.

![Energy profiles of carbon monoxide formation on Pd$_2$ and Pd$_2$O. Left curve, three reaction paths on Pd$_2$; right curve, three reaction paths on Pd$_2$O.](image)

Three distinguishable reaction paths for the formation of CO on Pd$_2$ are shown in Figure 7, and the corresponding energy is shown in Table S5. In the first reaction path, two processes were involved. The reaction energy barrier ($E_a$) of the CH→C + H and C + O→CO processes was about 1.26 and 0.46 eV, respectively. The next two reactions were followed by a series of reactions. The maximum activation energy barriers in the reactions were CH + O→CHO→CO + H and CH + O→COH→CO + H, whose energy barriers were 0.70 and 0.84 eV for the reaction, respectively. Both reactions were exothermic ($E_r < 0$).

Subsequently, the formation process of carbon monoxide on Pd$_2$O was calculated and the effect of oxygen atoms on the process was discussed. The reaction processes and energies are shown in Table S6. The reactive barrier ($E_r$) in the first reaction path was 0.93 eV for the process of CH→C + H, and 0.39 eV for the process of C + O→CO. The maximum reactive energy barriers of reactions CH + O→CHO→CO + H and CH + O→COH→CO + H were 0.46 and 0.54 eV, respectively.

2.4.2. Thermodynamic and Kinetic Analysis of Carbon Monoxide Formation

Thermodynamic and kinetic data for the reaction on the Pd$_2$ catalyst are listed in Table 6. In the first process, the activation energy ($E_a$) of CH→C + H and C + O→CO was 2.70 and 1.49 eV, respectively. The maximum activation energy ($E_a$) of the second possible pathway of CH + O→COH→CO + H was 1.73 eV. Compared with the above processes, the maximum activation energy ($E_a$) of CH + O→CHO→CO + H was relatively low, at about 1.60 eV. Corresponding rate constants ($\kappa$) were also in good agreement with the trend of their activation energies. The results indicated that the CH + O→CHO→CO + H reaction was the best pathway for the reaction on Pd$_2$, both thermodynamically and kinetically.
where: $E$, $S$, $H$, and $G$ were also obtained by using frequency analysis.

The electron energies ($E_{\text{total energy of free adsorbates}}$).

Binding energies are defined by the following equation:

$$E_{\text{binding}} = E_{\text{adsorbates/clues}} - E_{\text{clues}} - E_{\text{adsorbates}},$$

where: $E_{\text{adsorbates/clues}}$, total energy of adsorbates on Pd$_2$; $E_{\text{clues}}$, total energy of Pd$_2$/Pd$_2$O; $E_{\text{adsorbates}}$, total energy of free adsorbates.

Convergence tolerance in TSs turned out to be the same as in the geometry optimization. Then, the electron energies ($E_{\text{elec}}$) and Mulliken atomic charges of all the structures were calculated. Standard entropy ($S$), enthalpy ($H$), and Gibbs free energy ($G$) were also obtained by using frequency analysis.

### Table 6.
The activation energy ($E_a$), difference enthalpy between the transition state and the initial state ($\Delta H^\circ$), difference entropies between the transition state and the initial state ($\Delta S^\circ$), pre-exponential factor ($A$), rate constant ($\kappa$) for methane activation on Pd$_2$.

| Pd$_2$ | $E_a$ (eV) | $\Delta H^\circ$ (eV) | $\Delta S^\circ$ (eV) | $A$ (S$^{-1}$) | $\kappa$ (S$^{-1}$) |
|-------|----------|----------------|----------------|---------------|---------------|
| CH→C + H | 2.75 | 2.68 | 0.01 | $1.97 \times 10^3$ | $1.95 \times 10^{13}$ |
| C + O→CO | 1.5 | 1.42 | −0.19 | $5.82 \times 10^3$ | $1.81 \times 10^{12}$ |
| CH + O→CHO | 1.6 | 1.53 | 0.03 | $1.87 \times 10^4$ | $2.61 \times 10^{13}$ |
| CHO→CO + H | 0.53 | 0.45 | −0.18 | $4.25 \times 10^4$ | $2.15 \times 10^{12}$ |
| CH + O→COH | 1.64 | 1.56 | −0.11 | $2.19 \times 10^3$ | $4.81 \times 10^{12}$ |
| COH→CO + H | 1.73 | 1.65 | 0.05 | $4.42 \times 10^3$ | $3.31 \times 10^{13}$ |

All thermodynamic and kinetic data for the reaction on Pd$_2$O are listed in Table 7. The minimum activation energy ($E_a$) was found to be about 1.19 eV in CH + O→CHO→CO + H. The corresponding reaction rate ($\kappa$) was 2.68 $\times$ 10$^{13}$ s$^{-1}$. Thus, CH + O→CHO→CO + H was the best pathway of the reaction on Pd$_2$O, both thermodynamically and kinetically.

### Table 7.
The activation energy ($E_a$), difference enthalpy between the transition state and the initial state ($\Delta H^\circ$), difference entropies between the transition state and the initial state ($\Delta S^\circ$), pre-exponential factor ($A$), rate constant ($\kappa$) for methane activation on Pd$_2$O.

| Pd$_2$O | $E_a$ (eV) | $\Delta H^\circ$ (eV) | $\Delta S^\circ$ (eV) | $A$ (S$^{-1}$) | $\kappa$ (S$^{-1}$) |
|-------|----------|----------------|----------------|---------------|---------------|
| CH→C + H | 1.93 | 1.85 | −0.07 | $6.09 \times 10^3$ | $7.59 \times 10^{12}$ |
| C + O→CO | 1.23 | 1.16 | −0.31 | $4.69 \times 10^4$ | $3.98 \times 10^{11}$ |
| CH + O→CHO | 0.58 | 0.51 | −0.11 | $4.28 \times 10^6$ | $4.83 \times 10^{12}$ |
| CHO→CO + H | 1.19 | 1.12 | 0.03 | $5.84 \times 10^5$ | $2.68 \times 10^{13}$ |
| CH + O→COH | 0.62 | 0.54 | −0.15 | $1.75 \times 10^5$ | $3.07 \times 10^{12}$ |
| COH→CO + H | 1.16 | 1.08 | −0.10 | $1.80 \times 10^5$ | $5.32 \times 10^{13}$ |

### 3. Computational Details

All calculations were performed using DFT in generalized gradient approximation (GGA), Perdew Burke, and Ernzerho (PBE) [36]. Exchange correlation was implemented with module DMol3 in Material Studio of Accelrys Inc. The double-numeric quality plus polarization (DNP) functions were applied to all atoms. Considering the calculation cost, all core electrons were represented by DFT semicore pseudopodium functions. The convergence criteria for energy, force, and displacement convergence were constant at 2 $\times$ 10$^{-5}$ hartree, 4 $\times$ 10$^{-3}$ hartree/Å, and 5 $\times$ 10$^{-3}$ Å.

The frequency of all intermediates and transition states was calculated at the same level in order to determine the minimum (no imaginary frequencies) and the first-order saddle point (an imaginary frequency representing the required reaction coordinates). Transition states (TSs) were confirmed by LST/QST (linear synchronous transit and quadratic synchronous transit) method to obtain zero-point-energy (ZPE) corrections. With the aim to define each saddle point linking two desired minima, IRC calculations were used.

Considering the dissociation of methane, we first examined the adsorption direction and energies. Binding energies are defined by the following equation:
The forward or reverse rates of the elementary step within the reaction stayed constant because of the constant enthalpy and entropy differences.

The energy barrier \( (E_b) \) is presented by the difference in the Gibbs free energy between the transition state and initial state. The reaction energy \( (E_r) \) is given by the difference of enthalpy between the final state and initial state.

\[
E_b = G_{TS} - G_{IS},
\]

\[
E_r = H_{FS} - H_{IS},
\]

where \( G_{TS} \) is the Gibbs free energy of transition state; \( G_{IS} \) is the Gibbs free energy of initial state; \( H_{FS} \) and \( H_{IS} \) are the enthalpy of the final and initial state, respectively.

According to the thermodynamics process of transition state theory (TST), the Arrhenius activation energy \( (E_a) \) is given by the following equation:

\[
E_a = RT + \Delta H^\ddagger,
\]

where \( R \) is the gas constant; \( T \) is the reaction temperature; \( \Delta H^\ddagger \) is the change of enthalpy between the transition state and initial state.

By using DFT to study the oxidation of methane, temperature and pressure are taken into account. Therefore, the pre-exponential factor \( A \) and the rate constant of a reaction \( k \) can also be determined according to TST:

\[
A = \frac{k_b T}{h} \exp\left(\frac{\Delta r S_m^\ddagger}{R}\right),
\]

where \( \Delta r S_m^\ddagger \) is the difference of entropy between the transition state and initial state; \( k_b \) is the Boltzmann constant; \( h \) is the Planck constant.

Reaction rate constant \( k \) can be given as the following:

\[
k = \frac{k_b T}{h} \exp\left(\frac{\Delta r G_m^\ddagger}{R}\right) = \frac{k_b T}{h} \exp\left(\frac{\Delta r S_m^\ddagger}{R}\right) \exp\left(\frac{\Delta r H_m^\ddagger}{RT}\right)
\]

4. Conclusions

In summary, CH\(_4\) adsorption and configuration evolution of configurations on Pd\(_2\) and Pd\(_2\)O were studied using DFT calculations. Binding energy \( \text{CH}_x \) (\( x = 1–3 \)), adsorbed on Pd\(_2\), decreased with the oxygen atom adsorption. However, the energy barriers for CH\(_4\) dissociation increased with the presence of the oxygen atom. The reaction of \( \text{CH}_2 \rightarrow \text{CH} + \text{H} \) was the RDS for CH\(_4\) activation on both the catalysts. In syngas synthesis, H\(_2\) was formed by the reaction of \( \text{CH}_2 + 2\text{H} \rightarrow \text{CH}_2 + \text{H}_2 \), and the energy barriers of this reaction were reduced with the presence of the oxygen atom, which indicated that H\(_2\) formation was easier on Pd\(_2\)O than on Pd\(_2\). For CO formation, it was mainly formed in the process of \( \text{CH} + \text{O} \rightarrow \text{CHO} \rightarrow \text{CO} + \text{H} \) on both the Pd\(_2\) and the Pd\(_2\)O catalyst. The addition of oxygen atoms was also beneficial to CO formation, resulting from thermodynamic and kinetic calculations. Thus, forming and maintaining an oxygen atom on the Pd surface could promote a POM reaction to achieve high H\(_2\) and CO selectivity. Our study provides a helpful understanding of the effect of an adsorbed oxygen atom to a POM reaction with a Pd catalyst.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/9/8/666/s1.

Table S1: Gibbs free energies (\( G \)), energy barriers (\( E_b \)), enthalpies (\( H \)), and reaction energies (\( E_r \)) in the process of methane activation by Pd\(_2\). Table S2: Gibbs free energies (\( G \)), energy barriers (\( E_b \)), enthalpies (\( H \)) and reaction energies (\( E_r \)) in the process of methane activation by Pd\(_2\)O. Table S3: Gibbs free energies (\( G \)), energy barriers (\( E_b \)), enthalpies (\( H \)), and reaction energies (\( E_r \)) in the process of hydrogen generation by Pd\(_2\). Table S4: Gibbs free energies (\( G \)), energy barriers (\( E_b \)), enthalpies (\( H \)), and reaction energies (\( E_r \)) in the process of hydrogen generation by Pd\(_2\)O. Table S5: Gibbs free energies (\( G \)), energy barriers (\( E_b \)), enthalpies (\( H \)), and reaction energies (\( E_r \)) in the process of carbon monoxide formation by Pd\(_2\). Table S6: Gibbs free energies (\( G \)), energy barriers (\( E_b \)), enthalpies (\( H \)), and reaction energies (\( E_r \)) in the process of carbon monoxide formation by Pd\(_2\)O.
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