DFT study of methane catalytic combustion on Pd-based diatomic catalysts

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Abstract. The processes of methane combustion on three Pd-based diatomic catalysts (Pd₂, PdPt and PdNi) are investigated by using density functional theory (DFT) at the B3LYP/6-311++G(d,p)+SDD/B3LYP/6-311G(d,p)+LANL2DZ level. The optimized geometric structures, activation energy (Ea), and reaction rate constant (k) of methane dehydrogenation and oxidation on Pd₂, PdPt and PdNi are compared. The main reaction path for methane combustion on catalyst Pd₂ is CH₄→CH₃→CH₂→CHOH→CHO→CO→CO₂. However, the main reaction paths on catalyst PdPt and PdNi are the same: CH₄→CH₃→CH₂OH→CHOH→CHO→CO→CO₂. The rate-determining steps (RDS) on catalyst Pd₂ and PdPt are the same: CHOH→CHO, while the step of CH₃→CH₂OH is the RDS on PdNi. Further analysis shows that the catalytic activity followed the order of PdPt (k = 1.0639×10⁴ s⁻¹) > Pd₂ (k = 1.7281×10³ s⁻¹) > PdNi (k = 1.9235×10² s⁻¹). Thus, PdPt catalyst exhibits better performance than the other two catalysts in the methane catalytic combustion.

1. Introduction

Energy and environment problems still arouse the huge concern from all nations worldwide. Natural gas is considered one of the ideal clean energy for its abundant reserves, low price, and high thermal efficiency. Nevertheless, the conventional combustion technology requires high temperature, and low energy utilization. It will produce harmful gases (e.g., NOₓ, CO, H₂S). Catalytic combustion, namely efficient combustion on catalyst, is considered the most feasible method of addressing this problem [1]. In the process of catalytic combustion, catalysts are critical to facilitate the combustion process, lowering the reaction temperature, and accelerating complete combustion. Thus, the study on the reaction mechanism of methane on catalysts can be beneficial to select the appropriate catalyst for catalytic combustion and enhance the combustion effect. At present, it is a feasible method to employ computational quantum chemistry to delve into the reaction mechanism at the atomic scale level [2].

Currently, two types of catalysts have been mostly applied for methane combustion, namely noble metal catalysts (Pd, Pt, Rh) [3] and non-noble metal catalysts (Ni, Co, Cu) [4]. Compared with non-noble metal catalysts, noble metal catalysts exhibit high activity at low temperature. To be specific, the most attractive catalytic materials for methane combustion refer to Pd-based catalysts,
demonstrating the higher activity and excellent thermostability of the active phase [5]. However, the limited Pd source and expensive are two major challenges that hinder its large-scale application. Thus, the cost can be significantly lowered using single-atom or diatomic catalysts to up-regulate the utilization rate of metal atoms [6, 7]. For diatomic catalysts, the catalyst performance can be further regulated due to the interaction between two metal atoms [6-9]. Accordingly, studying the mechanism and path of methane dehydrogenation and oxidation processes on diatomic catalysts is of high academic and engineering implication. However, the processes of methane combustion on Pd-based diatomic catalysts, in particular the oxidation reaction path, remain unclear.

In the paper, the catalytic combustion process of methane on catalysts Pd₂, PdPt and PtNi catalysts are systematically studied by using DFT method. At same time, a general comparison between the three catalysts has been presented, based on a combination of thermodynamics and kinetics methods. This work would be helpful to understand the mechanism of methane catalytic combustion process.

2. Calculation methods

The structural towards all reactants, products, intermediates and transition states (TSs) are initially optimized at the B3LYP/6-311G(d, p)+LANL2DZ level. The optimized structures of reactants, products and intermediates are no imaginary frequency, whereas TSs are only one imaginary vibration frequency. All the single point calculations are performed with B3LYP/6-311++G(d, p)+SDD level. Furthermore, the calculations of intrinsic reaction coordinate (IRC) are made to confirm that the optimized TSs correctly connect the relevant reactants and products. All calculations are carried out by the Gaussian 09 program.

According to the transition state theory, the activation energy (Ea) is defined as:

\[ E_a = \Delta H^* + RT \]  \hspace{1cm} (1)

Where \( T \) is reaction temperature, \( R \) is the gas constant, \( \Delta H^* \) is the difference in enthalpies between the transition state and the initial state.

\[ E_r = H^{FS} - H^{IS} \]  \hspace{1cm} (2)

Where \( H^{FS} \) and \( H^{IS} \) is the enthalpy of initial state and final state, separately.

The pre-exponential \( A \) and the reaction rate constant \( k \) are given by:

\[ A = \frac{k_b T}{h} \exp \left( \frac{\Delta S^*}{R} \right) \]  \hspace{1cm} (3)

\[ k = A \exp \left( \frac{-E_a}{RT} \right) = \frac{k_b T}{h} \exp \left( \frac{\Delta S^*}{R} \right) \exp \left( \frac{-\Delta H^*}{RT} \right) \]  \hspace{1cm} (4)

Where \( \Delta S^* \) is the entropy difference between transition state and initial state, \( \exp \) is the natural logarithm, \( k_b \) is the Boltzmann constant and \( h \) is the Planck constant.

As the existing study suggested, methane catalytic combustion can achieve a good conversion rate at a temperature in the range from 573 K to 773 K [10]. Thus, in this study, 673 K is selected as the reaction temperature.

3. Reaction mechanisms

The cleavage of C-H bond and the oxidation of CHₓ are the two major parts in the methane catalytic combustion. Based on existing studies [9-12], the reaction mechanisms are summarized in figure 1.

Figure 1. The possible reaction pathway for methane catalytic combustion process.
4. Results and discussion

4.1. Reaction path of methane catalytic combustion on catalyst Pd

The thermodynamic and kinetic parameters in the process of methane combustion on catalyst Pd are shown in Table 1. As shown in Table 1 and Figure 2, the step of CH₃→CH₂ is more thermodynamically and kinetically positive, with the $E_a$ of 87.61 kJ/mol and $k = 4.2871 \times 10^9$ s⁻¹ in the two transition path of CH₃. And in the three transition path of CH₂, the $E_a$ of CH₂→CHOH is the lowest ($E_a = 96.50$ kJ/mol), coupled with its largest $k$ of $9.1482 \times 10^5$ s⁻¹, thus, CH₂ preferentially reacts with O to form CHOH. According to the comparison between the two paths that form CO₂, the step of CO→CO₂ displayed the lowest $E_a$ of 76.24 kJ/mol and the largest $k$ of $3.5296 \times 10^7$ s⁻¹, which suggests that the reaction is easy to proceed. For these reasons, the main reaction path for methane combustion on catalyst Pd can be concluded as CH₃→CH₂→CHOH→CHO→CO→CO₂.

Table 1. Thermodynamic and kinetic parameters in catalytic combustion process on Pd₂

| Pd₂ | $E_a$ (kJ/mol) | $E_a$ (kJ/mol) | $A$ (s⁻¹) | $k$ (s⁻¹) |
|-----|---------------|---------------|-----------|-----------|
| CH₄→CH₃ | 7.4380 | 21.7319 | 1.0387×10¹³ | 2.1369×10¹³ |
| CH₃→CH₂ | 33.8374 | 87.6110 | 2.7038×10¹³ | 4.2871×10⁶ |
| CH₂→CH | 125.8533 | 182.2524 | 5.6614×10¹⁴ | 4.0517×10⁴ |
| CH→C | 130.8133 | 177.2061 | 5.3379×10¹³ | 9.7660×10³ |
| C→CO | -500.1761 | 8.3366 | 1.6130×10¹³ | 3.6357×10⁻¹² |
| CH→CHO | -261.6731 | 76.1638 | 6.1171×10¹³ | 7.5022×10⁷ |
| CH₂→CHOH | -243.5519 | 96.5035 | 2.8271×10¹³ | 9.1482×10⁶ |
| CH₃→CHOH | -125.3282 | 121.9446 | 1.9143×10¹³ | 6.5679×10⁸ |
| C→CHO | -222.2039 | 62.7317 | 4.9180×10¹³ | 6.6519×10⁸ |
| CH→CHOH | -107.3856 | 92.0376 | 1.8154×10¹³ | 1.3050×10⁶ |
| CH₂→CHOH | -25.4096 | 100.9432 | 1.7387×10¹³ | 2.5447×10⁶ |
| CHO→CO | -47.9049 | 36.0383 | 3.3932×10¹³ | 5.4143×10⁻¹⁰ |
| CHO→COH | -25.9032 | 145.3641 | 3.3098×10¹³ | 1.7281×10⁸ |
| CH₂OH→CHOH | 46.9229 | 85.4370 | 3.5628×10¹³ | 8.3312×10⁶ |
| CO→CO₂ | -108.1653 | 76.2452 | 2.9201×10¹³ | 3.5296×10⁷ |
| CO→COOH | 104.1903 | 138.6822 | 3.2452×10¹³ | 5.5925×10⁵ |
| COOH→CO₂ | -33.6852 | 85.7915 | 2.9174×10¹³ | 6.4031×10⁶ |

The optimized structures of reactant, intermediate, product, TS and the imaginary frequency value of TS in the rate-determining step (RDS) of methane catalytic combustion on catalyst Pd₂ are illustrated in Figure 3. Along the main reaction path on Pd₂, the step of CHOH→CHO has the highest $E_a$ of 145.36 kJ/mol and the smallest $k$ of $1.7281 \times 10^5$ s⁻¹, which means that the step is difficult to react. Accordingly, the RDS of methane catalytic combustion on catalyst Pd₂ is CHOH→CHO.

Figure 2. Reaction path of methane catalytic combustion on catalyst Pd₂. (Red solid line arrows is the main reaction path; Black dotted line arrows are possible reaction paths.)

Figure 3. Optimized geometric structures of reactant, intermediate and TS in the RDS of methane catalytic combustion on catalyst Pd₂.

(bond unit: Å, frequency: cm⁻¹)
4.2. Reaction path of methane catalytic combustion on catalyst PdPt

The thermodynamic and kinetic parameters in the process of methane combustion on catalyst PdPt are shown in table 2. As shown in table 2 and figure 4, the step of CH3→CH3OH (EA = 28.06 kJ/mol, k = 1.4035×1011 s⁻¹) is more thermodynamically and kinetically favorable in the two transition path of CH3. In the two transition path of CO2, the step of CO→CO2 with a lowest EA of 90.06 kJ/mol and a largest k of 9.8015×107 s⁻¹, indicating that CO preferentially reacts with O to form CO2. Thus, the main reaction path on catalyst PdPt is CH3→CH3→CH3OH→CHOH→CHO→CO→CO2.

Table 2. Thermodynamic and kinetic parameters in catalytic combustion process on PdPt

| PdPt   | EA (kJ/mol) | E_a (kJ/mol) | A (s⁻¹) | k (s⁻¹) |
|--------|-------------|--------------|---------|---------|
| CH3→CH3 | 37.0064     | 78.7368      | 4.3601×10¹² | 3.3763×10⁶ |
| CH3→CH2 | 18.7671     | 140.6749     | 2.0289×10¹³ | 2.4489×10² |
| CH2→CH  | 54.3610     | 106.1417     | 5.3741×10¹³ | 3.1063×10⁵ |
| CH→C   | 113.6605    | 165.2759     | 3.6697×10¹³ | 5.4571×10⁰ |
| C→CO   | -343.8880   | 22.9948      | 4.5218×10¹³ | 7.4234×10¹¹ |
| CH→CHO  | -191.2519   | 185.9779     | 2.8099×10¹³ | 1.0334×10⁻¹ |
| CH2→CHOH| -12.3845    | 186.1066     | 1.2073×10¹⁴ | 4.3390×10⁻¹ |
| CH3→CH2OH| -10.9195   | 28.0646      | 2.1155×10¹³ | 1.4035×10¹¹ |
| C→CHO  | -122.4087   | 179.8527     | 5.6322×10¹² | 6.1894×10⁻¹ |
| CH→CHOH | -13.0225    | 127.0932     | 1.9819×10¹³ | 2.7096×10⁻³ |
| CH2→CHOH | 107.6901    | 175.1110     | 1.9810×10¹³ | 5.0800×10⁻¹ |
| CHO→CO | -70.5682    | 67.4891      | 5.2445×10¹³ | 3.0313×10⁸ |
| CHO→CHO | -28.7912    | 122.9029     | 3.6801×10¹³ | 1.0639×10⁴ |
| CH3OH→CHOH| -25.0867   | 15.5016      | 4.4628×10¹³ | 2.7956×10⁻¹² |
| CO→CO2 | 8.1233      | 90.0553      | 9.5680×10¹² | 9.8015×10⁻⁵ |
| CO→COOH | 128.4158    | 251.2137     | 1.9368×10¹³ | 6.1584×10⁷ |
| COOH→CO2| -25.7509    | 130.3436     | 3.3900×10¹⁰ | 2.5927×10⁻³ |

The optimized structures of reactant, intermediate, product, TS and the imaginary frequency value of TS in the RDS of methane catalytic combustion on catalyst PdPt are shown in figure 5. Along the main reaction path of methane catalytic combustion on PdPt, the EA of CHOH→CHO is the highest (EA = 122.90 kJ/mol), coupled with its smallest k of 1.0639×10⁴ s⁻¹, which means that the step is difficult to react. Thus, the RDS of methane catalytic combustion on catalyst PdPt is CHOH→CHO.

4.3. Reaction path of methane catalytic combustion on catalyst PdNi

The thermodynamic and kinetic parameters for the process of methane combustion on catalyst PdNi are shown in table 3. As shown in table 3 and figure 6, in the two transition path of CH3, the step of CH3→CH3OH with the EA of 154.80 kJ/mol and the k of 1.9235×10¹⁰ s⁻¹, is more thermodynamically and kinetically favorable. Compare the two paths that form CO2, the step of CO→CO2 with a lowest
higher catalytic activity than that of catalysts Pd
\(1.0639 \times 10^7\) s\(^{-1}\), which means that CO preferentially reacts with O to form CO\(_2\). Thus, it can be concluded that the main reaction path on catalyst PdNi is as follows:
\[
\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2\text{OH} \rightarrow \text{CHOH} \rightarrow \text{CHO} \rightarrow \text{CO} \rightarrow \text{CO}_2.
\]

The optimized structures of reactant, intermediate, product, TS and the imaginary frequency value of TS in the RDS of methane catalytic combustion on catalyst PdNi are shown in figure 7. Along the main reaction path on PdNi, the \(E_a\) of CH\(_3\)→CH\(_2\)OH is highest (\(E_a = 154.80\) kJ/mol) and coupled with its smallest \(k\) of 1.9235×10\(^7\) s\(^{-1}\), indicating that the step is difficult to react. Accordingly, the RDS on catalyst PdNi refers to the step of CH\(_3\)→CH\(_2\)OH.

The \(E_a\) of 78.94 kJ/mol and a larger \(k\) of 2.1294×10\(^7\) s\(^{-1}\), which means that CO preferentially reacts with O to form CO\(_2\). Thus, it can be concluded that the main reaction path on catalyst PdNi is as follows:
\[
\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2\text{OH} \rightarrow \text{CHOH} \rightarrow \text{CHO} \rightarrow \text{CO} \rightarrow \text{CO}_2.
\]

\begin{table}  
\centering  
\begin{tabular}{|c|c|c|c|c|}  
\hline  
\text{Reactant} & \text{Intermediate} & \text{Product} & \text{TS} & \text{Imaginary Frequency Value} \\
\hline  
\text{CH}_4 & \text{CH}_3 & \text{CH}_2\text{OH} & \text{CHOH} & \text{CHO} \\
\hline  
\text{CO} & \text{COOH} & \text{CO}_2 & \text{CO}_2 & \text{CO}_2 \\
\hline  
\end{tabular}  
\caption{Thermodynamic and kinetic parameters in catalytic combustion process on PdNi}  
\end{table}

\begin{figure}[h]  
\centering  
\includegraphics[width=\textwidth]{reaction_path.png}  
\caption{Reaction path of methane catalytic combustion on catalyst PdNi. (Red solid line arrows is the main reaction path; Black dotted line arrows are possible reaction paths.)}  
\end{figure}

\begin{figure}[h]  
\centering  
\includegraphics[width=\textwidth]{optimized_structures.png}  
\caption{Optimized geometric structures of reactant, intermediate and TS in the RDS of methane catalytic combustion on catalyst PdNi. (bond unit: Å, frequency: cm\(^{-1}\))}  
\end{figure}

Compared the \(E_a\) and \(k\) in the RDS for methane catalytic combustion on catalysts Pd\(_2\), PdPt and PdNi, the \(E_a\) of three catalysts is in the order of PdNi (\(E_a = 154.80\) kJ/mol) > Pd\(_2\) (\(E_a = 154.36\) kJ/mol) > PdPt (\(E_a = 122.90\) kJ/mol), while the trend of the reaction rate constant follows the order of PdPt (\(k = 1.0639 \times 10^7\) s\(^{-1}\)) > Pd\(_2\) (\(k = 1.7281 \times 10^7\) s\(^{-1}\)) > PdNi (\(k = 1.9235 \times 10^7\) s\(^{-1}\)). Thus, the catalyst PdPt shows higher catalytic activity than that of catalysts Pd\(_2\) and PdNi.
5. Conclusions
In brief, the methane catalytic combustion processes on Pd-based diatomic catalysts (Pd$_2$, PdPt and PdNi) are investigated, and their catalytic abilities are further analyzed by DFT computations. The results obtained in this study lead to the following conclusions:

1. The main reaction path of methane combustion on catalyst Pd$_2$ is as follows: $\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2 \rightarrow \text{CHOH} \rightarrow \text{CHO} \rightarrow \text{CO} \rightarrow \text{CO}_2$, while the main reaction path on catalyst PdPt is $\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2 \text{OH} \rightarrow \text{CHOH} \rightarrow \text{CHO} \rightarrow \text{CO} \rightarrow \text{CO}_2$, which is identical to that on PdNi.

2. The rate-determining step on catalysts Pd$_2$ and PdPt is the step of $\text{CHOH} \rightarrow \text{CHO}$, and the rate-determining step on catalyst PdNi refers to the step of $\text{CH}_4 \rightarrow \text{CH}_2 \text{OH}$.

3. The catalytic activity follows the order of PdPt ($k = 1.0639 \times 10^4 \text{ s}^{-1}$) > Pd$_2$ ($k = 1.7281 \times 10^2 \text{ s}^{-1}$) > PdNi ($k = 1.9235 \times 10^2 \text{ s}^{-1}$). Thus, the diatomic catalyst PdPt shows better performance than the other two catalysts in the methane catalytic combustion process.

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