Highly Dispersed Pd Species Supported on CeO$_2$ Catalyst for Lean Methane Combustion: The Effect of the Occurrence State of Surface Pd Species on the Catalytic Activity

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Abstract: The correlation between the occurrence state of surface Pd species of Pd/CeO$_2$ for lean CH$_4$ combustion is investigated. Herein, by using a reduction-deposition method, we have synthesized a highly active 0.5% PdO/CeO$_2$-RE catalyst, in which the Pd nanoparticles are evenly dispersed on the CeO$_2$ nanorods CeO$_2$-R. Based on comprehensive characterization, we have revealed that the uniformly dispersed Pd nanoparticles with a particle size distribution of 2.3 ± 0.6 nm are responsible for the generation of PdO and Pd$_x$Ce$_{1-x}$O$_2$-$\delta$ phase with –Pd$^{2+}$–O$^{2-}$–Ce$^{4+}$– linkage, which can easily provide oxygen vacancies and facilitate the transfer of reactive oxygen species between the CeO$_2$-R and Pd species. As a consequence, the remarkable catalytic activity of 0.5% Pd/CeO$_2$-RE is related to the high concentration of PdO species on the surface of the catalyst and the synergistic interaction between the Pd species and the CeO$_2$ nanorod.

Keywords: Pd$_x$Ce$_{1-x}$O$_2$-$\delta$ phase; occurrence state; metal-support interaction; CH$_4$ oxidation

1. Introduction

Natural gas, which contains 85% methane, has an extensive range of applications because of its abundant reserves, environmental friendliness and safety [1–3]. For example, natural gas as a vehicle fuel has the advantages of high calorific value, low exhaust pollution and cost-effectiveness. It has been popularized and applied all over the world. Nevertheless, methane is now considered to be more responsible for global warming than carbon dioxide, as it causes 20 times more greenhouse effect than carbon dioxide. Catalytic oxidation is a typical gas-solid catalytic reaction. It has become one of the most effective means to abate low concentration methane by opting for an appropriate catalyst to reduce the activation energy of the reaction and make it a flameless reaction at a lower ignition temperature of 250–350 °C [4].

For noble metal catalysts, supported Pd catalysts have attracted more concern owing to their pronounced catalytic activity for methane oxidation [5–7]. By comparison to the inert and non-reducible support, such as alumina, CeO$_2$, not only has higher oxygen storage capacity, but can also greatly increase the rate of redox reaction rate, becoming a suitable carrier candidate for Pd-based catalyst [8–11].

The distinct crystal surfaces exposed to support preferentially affect the catalytic activity, since most heterogeneous catalytic reactions happen on the surface of the catalyst. In recent years, more and more attention has been paid to the rod CeO$_2$ occupied by (110) and (100) facets since it has the lowest oxygen vacancy formation energy as well as the strongest reducibility among different morphology CeO$_2$ support [12–15]. Nolan et al. [16] calculated the vacancy formation energy of CeO$_2$ applying DFT corrected for on-site Coulomb interactions DFT+U; they found the vacancy formation energy of the crystal face was ranked
in the order of (110) < (100) < (111). In 2005, Li et al. [17] observed that CeO$_2$ nanorod exposed (100)/(100) planes had higher reactivity, which was responsible for higher catalytic performance in carbon monoxide oxidation. Recently, Lu et al. [18] found that CeO$_2$-R exposed with (110) and (100) facets had lower oxygen vacancy formation energy and higher surface oxygen mobility. Moreover, the interactions between surface Pd species and CeO$_2$ had been extensively investigated. They concluded that Pd species on CeO$_2$-R and CeO$_2$ nanocubes mainly formed Pd$_x$Ce$_{1-x}$O$_{2-δ}$ phase with a –Pd$^{2+}$–O$^2$–Ce$^{4+}$– bond, while PdO$_x$ phase was primarily distributed on the surface of CeO$_2$ octahedrons. The formation of Pd$_x$Ce$_{1-x}$O$_{2-δ}$ phase was accompanied by the formation of more oxygen vacancies.

For supported Pd catalysts, the relationship between the occurrence state of Pd species and catalytic activity of lean methane oxidation is rarely reported. Guo et al. [19] researched the influence of the chemical state of Pd species on the catalytic performance for methane oxidation on Pd/CeO$_2$, they associated the superior activity of methane oxidation with a high level of PdO and adsorbed oxygen, while Pd$_x$Ce$_{1-x}$O$_{2-δ}$ acts as a transition layer, more Pd$_x$Ce$_{1-x}$O$_{2-δ}$ will hinder the diffusion of lattice oxygen. Therefore, in order to clarify the structure-activity relationship between surface Pd species occurrence state and catalytic activity of CH$_4$ lean oxidation, herein, a variety of Pd/CeO$_2$ catalysts with different Pd loading (0.3%, 0.5%, 1.0%) were prepared via reduction-deposition and impregnation. Based on comprehensive characterization, we reveal that the excellent catalytic activity is not only associated with the proportion of surface PdO species, but also closely bound to the oxygen vacancy and defect provided by Pd$_x$Ce$_{1-x}$O$_{2-δ}$ phase. Excess PdO species will prevent lattice oxygen migration from bulk CeO$_2$ to surface Pd species.

2. Results and Discussion

2.1. Structural Properties and Morphologies of Samples

Figure 1 presents the XRD results of CeO$_2$-R and Pd/CeO$_2$ catalysts. The diffraction peaks assigned to cubic fluorite CeO$_2$ crystal phase are observed in all the samples. Except for CeO$_2$, there is no new diffraction peak related to Pd or PdO$_x$ species in the XRD pattern, owing to the low loading amount and high dispersion of Pd species. However, another possible reason may be that the Pd nanoparticles on the surface enter into CeO$_2$ lattice to form Pd$_x$Ce$_{1-x}$O$_{2-δ}$ solid solution since the ionic radius of Pd$^{2+}$ (0.97 Å) is smaller than that of Ce$^{4+}$ (1.14 Å) [7,20]. In addition, both CeO$_2$-R and Pd/CeO$_2$ catalysts have similar grain size, indicating that the loading of Pd does not significantly change the grain size of CeO$_2$-R. Figure S1 shows the nitrogen adsorption/desorption isotherm of the sample, by which the pore structure parameters can be measured. The mesopore structures in all samples can be evidenced by the typical IV adsorption isotherm with an H3-type hysteresis loop at relative pressures between 0.8 and 1.0. As shown in Table 1, the specific surface area of CeO$_2$-R is 52.8 m$^2$/g. When the Pd species are loaded, the specific surface area decreases obviously, which is mainly due to the pore blockage of CeO$_2$-R by active Pd species. The specific surface area of 0.5% PdO/CeO$_2$-RE is comparable to that of 1% PdO/CeO$_2$-RE, indicating that there may be a dispersion threshold on the surface of CeO$_2$-R and higher Pd loading has a negligible effect on the dispersion.

| Samples         | Pd Loading $^a$ (wt%) | Specific Surface Area $^b$ (m$^2$/g) | Pd Dispersion $^c$ (%) | Grain Size $^d$ (nm) |
|-----------------|-----------------------|--------------------------------------|------------------------|----------------------|
| CeO$_2$-R       | -                     | 52.8                                 | -                      | 12.0                 |
| 0.3% PdO/CeO$_2$-RE | 0.31                   | 35.3                                 | 31.4                   | 11.9                 |
| 0.5% PdO/CeO$_2$-RE | 0.47                   | 30.2                                 | 33.2                   | 12.0                 |
| 1% PdO/CeO$_2$-RE | 0.89                   | 29.4                                 | 29.1                   | 12.0                 |
| 0.5% PdO/CeO$_2$-IM | 0.48                   | 27.9                                 | 30.2                   | 12.1                 |

$^a$ Detected by ICP-AES. $^b$ Measured by N$_2$ adsorption-desorption isotherm. $^c$ Measured by CO chemical adsorption. $^d$ Calculated by the Scherrer equation from the diffraction peak of (111).
The TEM and HRTEM images of CeO$_2$-R are presented in Figure 2. The CeO$_2$-R performs a narrow diameter range of 9.8–12.5 nm and a length distribution between 60 and 200 nm, which has high crystallinity. It can be observed from Figure 2b that the lattice fringe with the spacings of 0.19 and 0.27 nm are assigned to the corresponding (1 1 0) and (1 0 0) crystal faces of CeO$_2$-R.

As is illustrated in Figure 3, after reduction treatment with sodium cyanoborohydride, the surfaces of the three samples are all coated by Pd nanoparticles, indicating that loading Pd has no effect on the original morphology of CeO$_2$-R. Interestingly, in the case of 0.5% Pd/CeO$_2$-RE, it can be observed that a core-shell unit is successfully assembled and Pd nano grain with a particle size distribution of 2.3 ± 0.6 nm are homogeneously scattered on the surface of CeO$_2$-R, the result indicates that the intimate contact occurs between Pd nanoparticles and CeO$_2$-R. When the loading of Pd increases to 1.0%, the Pd nanoparticles obviously aggregate and grow up, the distribution of Pd nanoparticles is 6.9 ± 2.1 nm, as summarized in Figure 3i.

**Figure 1.** XRD pattern of CeO$_2$-R and Pd/CeO$_2$ catalysts.

**Figure 2.** TEM (a), HR-TEM (b) images of CeO$_2$-R.

| Samples  | Pd Loading a (wt%) | Specific Surface Area b (m$^2$/g) | Pd Dispersion c (%) | Grain Size d (nm) |
|----------|--------------------|-----------------------------------|--------------------|-------------------|
| CeO$_2$-R | 0.00               | 52.8                               | 12.0               | 200 nm            |
| 0.3% PdO/CeO$_2$-RE | 0.31               | 35.3                               | 31.4               | 11.9              |
| 0.5% PdO/CeO$_2$-IM  | 0.48               | 27.9                               | 30.2               | 12.1              |
| 0.5% PdO/CeO$_2$-RE  | 0.47               | 30.2                               | 33.2               | 12.0              |
| 1% PdO/CeO$_2$-RE    | 0.89               | 29.4                               | 29.1               | 12.0              |

* a Detected by ICP-AES. b Measured by N$_2$ adsorption-desorption isotherm. c Measured by CO chemical adsorption. d Calculated by the Scherrer equation from the diffraction peak of (111).
between Pd nanoparticles and CeO$_2$-R. When the loading of Pd increases to 1.0%, the Pd nanoparticles obviously aggregate and grow up, the distribution of Pd nanoparticles is $6.9 \pm 2.1$ nm, as summarized in Figure 3i.

Figure 3. TEM, HRTEM images and Pd particle size distributions of (a–c) 0.3% Pd/CeO$_2$-RE, (d–f) 0.5% Pd/CeO$_2$-RE and (g–i) 1% Pd/CeO$_2$-RE.

Figure 4 depicts the TEM and HRTEM pictures of 0.3% PdO/CeO$_2$-RE, 0.5% PdO/CeO$_2$-RE, 1% PdO/CeO$_2$-RE and 0.5% PdO/CeO$_2$-IM catalysts calcinated at 400 °C. As presented in Figure 4a,b, no PdO nanoparticles are observed over 0.3% PdO/CeO$_2$-RE and 0.5% PdO/CeO$_2$-RE. Notably, when subjected to calcination treatment, the PdO nanoparticles either disperse evenly on the surface or form Pd$_x$Ce$_{1-x}$O$_{2-\delta}$ phase with the –Pd$^{2+}$–O$^{2-}$–Ce$^{4+}$– linkages. Nevertheless, it can be seen that the PdO nanoparticles exist on the surface of 1% PdO/CeO$_2$-RE (Figure 4c,d); its lattice fringe spacing is 0.3 nm, which corresponds to the PdO (1 0 0) plane. Additionally, Figure 4e,f shows that the Pd nanoparticles selectively exposed on (1 1 1) plane are attached on the surface of 0.5% PdO/CeO$_2$-IM. The results reveal that the Pd species prepared by impregnation methods are partially entered into the CeO$_2$ matrix, while the Pd species synthesized by the reduction-deposition method are primarily dispersed on the surface of CeO$_2$, which can readily form PdO or incorporate into the lattice of CeO$_2$ after the calcination.
Figure 4. TEM and HRTEM images of (a) 0.3% PdO/CeO$_2$-RE, (b) 0.5% PdO/CeO$_2$-RE, (c,d) 1% PdO/CeO$_2$-RE and (e,f) 0.5% PdO/CeO$_2$-IM.

2.2. Chemical and Electronic States

The XPS experiments are conducted to provide deep insight into the surface species composition and chemical states on Pd/CeO$_2$. Figure 5 shows the XPS spectra of Pd 3d, Ce 3d and O 1s for the as-synthesized samples. As presented in Figure 5a, catalysts prepared by the reduction-deposition method all manifest two Pd 3d$_{5/2}$ peaks at around 337.1 and 338.2 eV, respectively. The peak centered at 337.1 eV can be assigned to PdO species on the surface of PdO/CeO$_2$ catalysts. The peaks that appeared at 338.2 eV can be attributed to Pd$_x$Ce$_{1-x}$O$_{2-\delta}$ phase, which can be explained by the strong metal-support interaction promoting the incorporation of Pd ion into the CeO$_2$ lattice to transform Pd$_x$Ce$_{1-x}$O$_{2-\delta}$ phase [21–25]. In the case of 0.5% PdO/CeO$_2$-IM, there is another peak that arose at 336.2 eV, which corresponds to Pd$^0$. This finding coincides with the result of the TEM observation. The above results indicate that various occurrence states of Pd species exist on the surface of as-prepared samples.

The Ce 3d XPS spectra of as-prepared samples are shown in Figure 5b, which can be deconvoluted into 8 groups. The doublets labelled as (u,”, v”) are the characteristic peaks of Ce$^{3+}$, and the doublets denoted as (u, v), (u’, v’) and (u”, v”) are assigned to Ce$^{4+}$. The content of Ce$^{3+}$ on the surface can be calculated by the area ratio of Ce$^{3+}$/ (Ce$^{3+}$ + Ce$^{4+}$), it can be summarized from Table 2 that the content of Ce$^{3+}$ increases after Pd loading, which may be linked to the strong interaction between Pd species and CeO$_2$, according to the previous literature [25–27], the appearance of Ce$^{3+}$ is associated with the oxygen...
vacancy on the surface of CeO$_2$, 0.3% PdO/CeO$_2$-RE has the highest concentration of Ce$^{3+}$ (0.25), followed by 0.5% PdO/CeO$_2$-RE (0.24), 0.5% PdO/CeO$_2$-IM (0.19) and 0.3% PdO/CeO$_2$-RE (0.18).

| Sample          | Surface Pd Species Content (%) | Ce$^{3+}$/Ce$^{4+}$ (%) | O$_{ads}$/O$_{ads}$(%) | Pd Atomic (%) | TOF a ($\times 10^3$ s$^{-1}$) | $E_a$ (kJ/mol) |
|-----------------|-------------------------------|-------------------------|------------------------|---------------|--------------------------------|----------------|
| CeO$_2$-R      | 55.28                         | -                       | 0.16                   | 0.41          | 0.12                           | 22.3           |
| PdO/CeO$_2$-RE | 44.72                         | -                       | 0.25                   | 0.49          | 0.36                           | 25.5           |
| PdO/CeO$_2$-IM | 27.34                         | -                       | 0.24                   | 0.47          | 0.36                           | 61.6           |
| 0.5% PdO/CeO$_2$-RE | 18.66                   | -                       | 0.24                   | 0.43          | 1.34                           | 9.6            |
| 1% PdO/CeO$_2$-IM | 12.76                  | -                       | 0.19                   | 0.45          | 0.30                           | 10.5           |

a TOF values are calculated based on the conversion of methane at 360 °C.

To further study the oxygen vacancy on the sample surface, the O 1s XPS spectra are also studied. It is generally believed that the oxygen vacancy is usually associated with the ratio (O$_{ads}$/O$_{bulk}$) of the surface chemisorbed oxygen (O$_{ads}$) and the lattice oxygen (O$_{bulk}$) located in the bulk CeO$_2$ [28–30]. As shown in Figure 5c, the ratios are as follows: 0.3% PdO/CeO$_2$-RE > 0.5% PdO/CeO$_2$-IM > 0.5% PdO/CeO$_2$-IM > 1% PdO/CeO$_2$-RE. Combined with the Ce 3d XPS spectra, it can be speculated that the more oxygen vacancies are generated, the higher the content of Ce$^{3+}$ on the catalyst surface.

2.3. Redox Ability

The H$_2$-TPR test allows us to further explore the reducibility of surface Pd species, and the results are presented in Figure 6 and Table S1. The TPR profile of CeO$_2$-R shows that the peaks at 420 °C and 571 °C correspond to the reduction of surface adsorbed oxygen and lattice oxygen species of the CeO$_2$ support, while the peak at a high temperature (T > 700 °C) is generally ascribed to the reduction of interior lattice oxygen of bulk CeO$_2$. Clearly, for Pd/CeO$_2$ samples prepared by the reduction method, the reduction peak shifted toward low temperature (T < 200 °C), indicating that the presence of Pd species greatly enhances the reduction ability of CeO$_2$. 

Figure 5. Pd 3d (a), Ce 3d (b) and O 1s (c) XPS spectra of the as-synthesized samples.

Table 2. Chemical and structural data of CeO$_2$-R and Pd/CeO$_2$ catalysts.
In the H$_2$-TPR profile of 1% PdO/CeO$_2$-RE, there is a reduction peak before 200 °C, corresponding to the reduction of PdO species, and the H$_2$ consumption is 106 µmol/g, which is significantly higher than the theoretical value (91.5 µmol/g) calculated from the actual Pd content (0.89%). The remaining hydrogen consumption is due to the hydrogen spillover effect between Pd and CeO$_2$-R, which also reflects the strong metal support interaction [31]. For the 0.3% PdO/CeO$_2$-RE and 0.5% PdO/CeO$_2$-RE, the reduction peaks of PdO shift to 140 °C and 151 °C, and the H$_2$ consumption is 19 µmol/g and 24 µmol/g, respectively, indicating that there are more PdO species in 0.5% PdO/CeO$_2$-RE. However, the reduction peak at 252 °C can be considered to be the co-reduction peak of Pd species and lattice oxygen in Pd$_x$Ce$_{1-x}$O$_2$-$\delta$ phase. However, unlike the catalyst prepared via the reduction-deposition method, 0.5% PdO/CeO$_2$-IM has a negative peak before 100 °C, which is associated with the decomposition of Pd hydride phase. The appearance of Pd species on the surface is also evidenced by the above XPS results. Similarly, the high-temperature peaks around 790 °C of all the Pd/CeO$_2$ catalysts correspond to the reduction of bulk CeO$_2$ hardly coupling with Pd species. Combined with the above analysis, highly dispersed Pd species loaded on the surface of CeO$_2$ can significantly enhance the oxygen mobility of the carrier, so as to boost the catalytic oxidation of CH$_4$.

2.4. Catalytic CH$_4$ Oxidation

Figure 7a depicts the light-off curves of CeO$_2$-R and Pd/CeO$_2$ catalysts for methane oxidation. The order of catalytic activity is as follows: 0.5% PdO/CeO$_2$-RE > 0.3% PdO/CeO$_2$-RE > 0.5% PdO/CeO$_2$-IM > 1% PdO/CeO$_2$-RE > CeO$_2$-R, according to the results of methane conversion. Of all the catalysts, CeO$_2$-R presents the worst catalytic activity with a complete methane conversion temperature as high as 650 °C. The incorporation of Pd substantially promoted the oxidation of methane. Obviously, the catalytic activity of Pd/CeO$_2$ catalysts varies with the change of composition, and this discrepancy is preliminarily ascribed to the change of surface Pd species occurrence state. Although 0.5% PdO/CeO$_2$-RE and 0.5% PdO/CeO$_2$-IM both have the same Pd loading, 0.5% PdO/CeO$_2$-RE exhibits superior catalytic activity, in which the temperature of 90% methane conversion ($T_{90}$) is 50 °C lower than that of 0.5% PdO/CeO$_2$-IM. Meanwhile, the reaction rates, turnover frequency (TOF) and apparent activation energy ($E_a$) of Pd/CeO$_2$ are shown in Table 2. The $E_a$ can be calculated by the linear correlation between the ln $r$ and 1/$T$ as can be seen in Figure 7b. Among the four catalysts, the 0.5% PdO/CeO$_2$-RE catalyst exhibits the highest TOF and the lowest $E_a$, which is conducive to the rapid oxidation of methane.
Despite the controversy, PdO is generally considered as the main active phase in CH₄ oxidation, uniformly dispersed on the surface of CeO₂-R, assembling an analogous CeO₂@Pd core-shell structure due to the close Ce-Pd contact. After calcination, Pd is transformed into PdO without causing serious aggregation, in addition, some of Pd species and CeO₂ form a PdₓCe₁₋ₓO₂₋δ phase due to the strong interaction, which can be shown by the above characterization.

As shown in XPS, there are three main occurrence states of surface Pd species: Pd⁰, Pd²⁺ and Pd⁵⁺ (2 < δ ≤ 4) in the form of PdₓCe₁₋ₓO₂₋δ phase. It has been long recognized that the reaction rate of methane oxidation is closely related to the breaking of C-H bonds. Despite the controversy, PdO is generally considered as the main active phase in CH₄ oxidation, which occurs through the Marsvan–Krevelen reaction mechanism [32–34]. The concentration of PdO species on the surface is proportional to Pd loading. The proportion of PdO species on the surface of 1% PdO/CeO₂-RE is 81.34% and is higher than that of 0.5% PdO/CeO₂-RE (72.66%) and 0.3% PdO/CeO₂-RE (55.28%). Nevertheless, its catalytic activity is not optimal, and the main factor is that the higher the Pd loading, the more serious agglomeration of the PdO nanoparticles, which inhibits the replenishment and diffusion of oxygen from the bulk CeO₂. Associated with TEM results, it is found that both 0.5% Pd/CeO₂-RE and 0.5% PdO/CeO₂-RE (the latter calcined at 400 °C) have uniform distributions of surface Pd species.

For CH₄ oxidation under lean conditions, the mobility of surface oxygen also plays a pivotal role in the dissociation and reoxidation of PdO species and promotes catalytic activity to some extent. The presence of PdₓCe₁₋ₓO₂₋δ phases, which are not far from the PdO particles, readily generates more oxygen vacancy and defects than CeO₂ support (as shown in Figure 8). Additionally, the –Pd²⁺–O²⁻–Ce⁴⁺– linkage can stabilize PdO species to avoid growth at high temperatures, maximize the contact between active sites and reactants, and improve the utilization efficiency of active metals.

Among all the samples, 0.5% PdO/CeO₂-RE exhibits the best catalytic activity with a TOF as low as 400 °C. Meanwhile, kinetic parameters such as reaction rate, TOF and Ea further confirm that 0.5% PdO/CeO₂-RE has outstanding performance. In this work, sodium cyanoborohydride, as a mild reducing agent, has a weak reducing ability and could affect the size and occurrence state of surface Pd species. Compared with sodium borohydride, sodium cyanoborohydride is conducive to the formation of uniform ultrafine Pd nanoparticles. When the Pd loading is less than 0.5%, the distribution of Pd nanoparticles can be tailored to be 2.3 ± 0.6 nm, which is beneficial to enhance the interfacial interaction between Pd and CeO₂-R, and then affect the occurrence state of surface Pd species. During the calcination process, strong interaction promotes the formation of the PdₓCe₁₋ₓO₂₋δ...
phase at the interface. The H₂ consumption peak at 252 °C in the H₂-TPR profile shows that the presence of the Pd₁₋ₓCe₁₋ₓO₂₋₅ phase favors the oxygen mobility on the surface of CeO₂. Although the sample 0.3% PdO/CeO₂-Re has a higher specific surface area and smaller grain size in comparison with 0.5% PdO/CeO₂-Re, we believe that the high content of PdO species on the surface is responsible for the high activity, and the surface Pd atomic ratio of 0.5% PdO/CeO₂-Re (Table 2) is also high. In addition, it is worth mentioning that 0.5% PdO/CeO₂-RE and 0.5% PdO/CeO₂-IM have the same Pd loading, their reactivity is completely different, also reflecting the effect of the preparation method on the occurrence state of surface Pd species. Part of the Pd ions in 0.5% PdO/CeO₂-IM prepared by impregnation method penetrates the CeO₂ matrix, and it is difficult to completely oxidize to PdO at high temperature, as demonstrated by the XPS test.

![Figure 8](image_url)

**Figure 8.** Schematic representation of the CH₄ oxidation over the Pd/CeO₂ catalyst.

4. **Experimental Section**

4.1. **Catalyst Synthesis**

4.1.1. Synthesis of Ceria Nanorods Support (CeO₂-R)

The CeO₂-R was prepared by hydrothermal method given in the literature [35]. Both 4.0 m·mol cerium nitrate hexahydrate and 0.48 m·mol sodium hydroxide were dissolved in 10 mL and 70 mL deionized water, and it was stirred continuously for 30 min. The mixture was then transferred to a 100 mL Teflon-lined autoclave and heated to 100 °C for 24 h and the as-prepared sample was collected by filtration and washed with deionized water and ethanol alternatively. The product was dried at 100 °C for 6 h to obtain ceria nanorods (designated as CeO₂-R).

4.1.2. Synthesis of Pd/CeO₂ Catalyst

The Pd/CeO₂ catalyst was synthesized by reduction-deposition using sodium cyanoborohydride as a reducing agent. Normally, the required amount of palladium nitrate aqueous solution was added dropwise into the CeO₂-R suspension. After impregnation, the reducing agent sodium cyanoborohydride (1.5 times the moles of palladium) was dropped with vigorous stirring for 4 h, then dried overnight at 373 K. A battery of catalysts with different palladium loading (0.3%, 0.5%, 1.0%) was obtained by calcining at 450 °C for 4 h. The catalysts were named according to the Pd content and the preparation method. For example, 0.5% PdO/CeO₂-RE represents a catalyst with a Pd concentration of 0.5 wt% prepared by reduction method and calcinated at 400 °C, while 0.5% PdO/CeO₂-RE refers to a catalyst prepared with this process except for calcination. Besides, the reference 0.5% PdO/CeO₂-IM catalyst with Pd loading of 0.5 wt% was synthesized by the same procedure as above for 0.5% PdO/CeO₂-RE except that the reductant was added. The accurate content of palladium in the final catalyst was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).
4.2. Catalyst Characterization

XRD analysis of catalysts was carried out on a Rigaku TTRIII power diffractometer (Wilmington, MA, USA) operated at 30 kV and 15 mA with Cu Kα radiation source, the pattern data were collected in a 2θ range from 10 to 80° with a scan step of 2°/min. The mean crystalline size was calculated by the Scherrer equation based on the diffraction peak broadening [15,16].

H2-temperature-programmed reduction and CO chemical adsorption tests were conducted on Micro-meritics Chemisorb 2920II instrument (Norcross, GA, USA). In the H2-TPR test, 50 mg of sample was loaded at a quartz tube reactor, and pretreated at 150 °C in an Ar (80 mL/min) for 1 h, then the sample was reduced with 30 mL/min H2-N2 mixture and heated from 25 to 950 °C with a rate of 10 °C/min. The hydrogen consumption for each reduction peak is calibrated using the H2-TPR profile of copper oxide. For the CO chemical adsorption experiment, a 50 mg sample was pretreated at 200 °C for 1 h with 30 mL/min 10% H2-N2. After cooling down to room temperature, the sample was purged with He (30 mL/min) for 30 min, and then 5% CO/He was periodically introduced into the sample.

The specific surface area of synthesized samples was implemented on a Micromeritics NOVA 2000 instrument. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method.

Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) images were acquired on a JEM-2100 microscope (JEOL, Tokyo, Japan) with an operating voltage of 200 kV. The sample was ultrasonically dispersed in ethanol and a drop of the suspension was scooped onto a carbon film anchored by a 200-mesh copper grid.

X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo-Fisher Scientific ESCALAB 250 (Waltham, MA, USA) with a monochromatized Al Kα excitation source. The electron binding energies were calibrated by the C 1s peak of adventitious carbon at 284.8 eV. Besides, the Pd content of Pd/CeO2 catalyst was analyzed by PerkinElmer ICP-AES (Waltham, MA, USA).

4.3. Evaluation of the Catalytic Performance

The catalytic oxidation of CH4 was performed in a continuous flow fixed-bed reactor. About 100 mg sample was placed into the tubular reactor (inner diameter = 5 mm) with quartz-wool plugs. Prior to each test, the catalyst was pretreated at 150 °C for 2 h under H2 atmosphere and subsequently cooled to room temperature. Then, a mixture gas of 0.5 vol% of CH4 and 3 vol% O2 in synthetic air was injected into the quartz tube microreactor at a flow rate of 30 mL/min, which corresponds to a weight hourly space velocity of 18,000 mL·g⁻¹·h⁻¹. In addition, the effect of different weight hourly space velocity (24,000, 30,000 and 60,000 mL·g⁻¹·h⁻¹) on CH4 oxidation activity was also discussed. The reaction activity was evaluated at 150–600 °C. The effluent gas was measured using an in-line GC7890A gas chromatograph equipped with a flame ionization detector (FID). The CH4 conversion (XCH4) was calculated by the following formula:

\[
X_{\text{CH}_4}(\%) = \frac{[\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}}{[\text{CH}_4]_{\text{in}}} \times 100
\]  

where [CH4]in and [CH4]out are the CH4 concentration in the inlet and outlet gas, respectively.

In order to calculate the apparent activation energy, kinetic experiments were carried out at a temperature range of 200–1400 °C, and the WHSV was controlled at a range of 18,000–60,000 mL·g⁻¹·h⁻¹ to ensure that the CH4 conversion is below 15%, so as to eliminate internal and external diffusion as well as transport limitations. The reaction rates (rCH4 (mol·gPd⁻¹·s⁻¹)) and turnover frequency (TOF (s⁻¹)) were determined by the following formulas:

\[
r_{\text{CH}_4} = \frac{X_{\text{CH}_4} \cdot C_{\text{CH}_4} \cdot V \cdot P}{m_{\text{cat}} \cdot w_{\text{Pd}} \cdot R \cdot T}
\]
where $X_{CH_4}$ represents the conversion of $CH_4$, $C_{CH_4}$ is the concentration of $CH_4$ in the feed gas, $m_{cat}$ is the catalyst weight (g), $w_{Pd}$ is the Pd content in the catalyst determined by ICP-AES, $V$ is the total flow rate (mL/min), $R$ is the molar gas constant, $T$ is the room temperature (K), $M_{Pd}$ is the atomic weight of Pd, $D_{Pd}$ is the Pd dispersion measured by CO chemical adsorption at 25 °C. Combined with the Arrhenius equations, the apparent activation energy ($E_a$) was calculated by plotting $ln r$ vs. $1/RT$.

5. Conclusions

A series of Pd/CeO$_2$ catalysts with different surface Pd species occurrence states had been rationally engineered for lean methane combustion. The characterization of XRD, HRTEM, XPS, BET and H$_2$-TPR reveal that the surface Pd species in the form of Pd$^0$, PdO and Pd$_x$Ce$_{1−x}$O$_{2−δ}$ phase are highly dispersed on the rod-like CeO$_2$. Here, 0.5% PdO/CeO$_2$-RE behaves the remarkable catalytic activity with the lowest $E_a$ (61.6 kJ/mol), which was mainly due to the high concentration of PdO and Pd$_x$Ce$_{1−x}$O$_{2−δ}$ phase species on the surface. The Pd$_x$Ce$_{1−x}$O$_{2−δ}$ phase at the interface can contribute to the formation of oxygen vacancy and defect, promote the active oxygen species transfer between PdO and CeO$_2$. In brief, the presence of more PdO species and the oxygen vacancy provided by the Pd$_x$Ce$_{1−x}$O$_{2−δ}$ phase are responsible for excellent catalytic activity.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal11070772/s1, Figure S1: $N_2$ adsorption-desorption isotherm of the as-synthesized catalysts, Table S1: H$_2$ consumption of CeO$_2$-R and Pd/CeO$_2$ catalysts.

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