Catalytic Performance of Palladium Supported on Sheaf-Like Ceria in the Lean Methane Combustion

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Abstract: Sheaf-like CeO₂ (CeO₂-S) in microscale was prepared by the hydrothermal method, and then etched with KOH aiming to obtain an imperfect fluorite structure (CeO₂-SK) with high content of oxygen vacancies and oxygen mobility. With CeO₂-S and CeO₂-SK as supports respectively, a modified colloidal deposition method was employed to obtain Pd/CeO₂ catalysts for being used in lean methane combustion. According to the inductively coupled plasma (ICP), N₂ physisorption and scanning electron microscopy (SEM) results, the Pd supported catalysts are very similar in their Pd loading, surface area and morphologies. SEM and transmission electron microscopy (TEM) results revealed various nanorods exposed CeO₂ (110) and (100) facets on Pd/CeO₂-SK surface after KOH etching. Raman spectra and H₂-temperature programmed reduction (H₂-TPR) results indicated that Pd/CeO₂-SK catalyst has a much higher content of catalytic active PdO species than Pd/CeO₂-S catalyst. It was also found that the catalytic performance of Pd/CeO₂ in lean methane combustion depends greatly upon the exposing crystal planes and oxygen vacancies content of sheaf-like CeO₂, and Pd/CeO₂-SK exhibits higher activity than Pd/CeO₂-S. The larger amount of CeO₂ (110) and (100) planes on Pd/CeO₂-SK surface can enhance the formation of oxygen vacancies, active Pd species and migration of lattice oxygen, which all evidently improve the redox ability and catalytic activity of the Pd/CeO₂-SK catalysts in lean methane combustion.

Keywords: lean methane combustion; sheaf-like; palladium; ceria

1. Introduction

Currently, a great amount of coal mine methane needs to be utilized owing to the huge annual output of coal in the world [1,2]. The high concentration methane can be recovered into chemical feedstock; however, sometimes low concentration methane is discharged directly into the atmosphere without any treatment, which not only causes energy waste, but also brings serious environmental problems due to the global warming potential of CH₄ is about 21–26 times higher compared with CO₂ [3–5]. Catalytic combustion of methane is viewed as an effective measure to treat lean methane due to its high combustion efficiency and low emission of toxic products, such as CO and NOₓ [6,7]. It is well known that the inertia of methane makes it difficult to oxidize at low
temperatures. Thus, the design and preparation of catalysts with high activity in lean \( \text{CH}_4 \) combustion at low temperatures still face great challenge.

Among the various catalysts, Pd supported catalysts are considered as one of the most promising candidates for methane combustion and activation owing to their extraordinarily high catalytic performance at low temperatures [7,8–11]. Furthermore, literature research has revealed that the rate limited step in methane combustion is the initial scission of the C–H bond [12], and palladium has the ability to split C–H bond [13]. According to Farrauto et al. the catalytic performance of palladium catalyst depends, to a great extent, on the nature of the support and the palladium-support interactions [14]. Thus, various oxide materials have been selected as carriers to prepare palladium supported catalysts for lean methane combustion.

Recently, ceria has attracted considerable attentions owing to its high oxygen storage capacity and remarkable redox properties [15–18], which permits effective oxygen adsorption and activation for \( \text{CH}_4 \) oxidation. Hence, many Pd/CeO\(_2\) catalysts with exceptionally high activities for \( \text{CH}_4 \) combustion at low temperatures have been synthesized and investigated in that the synergistic interaction between palladium and CeO\(_2\) may result in higher catalytic performance of Pd species [19–21]. Meanwhile, several reports have shown that the CeO\(_2\) morphology also has great influence on the catalytic activity of palladium loaded catalysts. This may be due to the fact that different shapes of ceria supports usually expose distinct ceria facets, which ultimately affects the palladium–CeO\(_2\) interaction. Tan et al. [22] found that Pd loading on (110)-faced CeO\(_2\) nanocubes exhibited much higher activity in formaldehyde oxidation compared with Pd loaded on (111)-faced CeO\(_2\) nanoctahedrals and CeO\(_2\) nanorods exposed (100) and (110) planes. Lei et al. [23] indicated that Pd supported on octahedral CeO\(_2\) were much more active than those supported on rod and cube CeO\(_2\) in lean \( \text{CH}_4 \) combustion owing to the synergistic effects between palladium species and (111) planes of octahedral CeO\(_2\) exposing. On the contrary, Guo et al. [9] believed that the larger activity of Pd/CeO\(_2\)-microspheres in lean \( \text{CH}_4 \) combustion was related to the exposed active (110) and (100) planes and its short porous channel. Up to now, various Pd/CeO\(_2\) catalysts with different shapes have been synthesized [9,22–25]; however, as far as we know, the preparation of ceria with sheaf-like morphologies in microscale and the shape effects of microscale ceria carrier on the catalytic activity of Pd/CeO\(_2\) catalyst in lean \( \text{CH}_4 \) combustion have been rarely reported.

Therefore, in this work, sheaf-like CeO\(_2\) (CeO\(_2\)-S) in microscale was synthesized by using the hydrothermal method. The as-made sheaf-like CeO\(_2\) was further etched with KOH to obtain an imperfect fluorite structure (CeO\(_2\)-SK) with high content of oxygen vacancies as well as oxygen mobility, which can improve the activity of supported Pd catalysts in lean \( \text{CH}_4 \) combustion at low temperatures. With CeO\(_2\)-S and CeO\(_2\)-SK as support respectively, Pd/CeO\(_2\) catalysts were synthesized by a modified colloidal deposition method as described previously with the aim to obtain a deep insight into the effect of the CeO\(_2\) support structure on the performance of Pd/CeO\(_2\) catalysts in lean \( \text{CH}_4 \) combustion [16,26,27]. The relationship between the crystal planes exposing and oxygen vacancies content of sheaf-like CeO\(_2\) and the catalytic activity of Pd/CeO\(_2\) catalyst in lean \( \text{CH}_4 \) combustion was investigated by the means of X-ray powder diffraction (XRD), \( \text{N}_2 \) physisorption, SEM, TEM, \( \text{H}_2 \)-temperature programmed reduction (H\(_2\)-TPR), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). This work provides a new thought to the design and preparation of novel and efficient catalysts in catalytic combustion of lean methane. Moreover, the obtained catalyst can also be applied to the catalytic oxidation of other volatile organic compounds such as CO, formaldehyde and benzene. The other advantages of this study are that the preparation process of CeO\(_2\) is simple and easy for mass production—the obtained Pd/CeO\(_2\)-SK catalyst can completely oxidize lean methane (1%) at 375 °C when Pd loading is only 1%. All of these are conducive to improving the economic benefits of its practical application.

2. Materials and Methods

2.1. Materials
The Ce(NO$_3$)$_2$·6H$_2$O, polyvinyl pyrrolidone, urea, absolute ethanol, KOH, polyvinyl alcohol (PVA), and H$_2$PdCl$_4$ were supplied by Sinopharm Chemical Reagent Co.(Shanghai, China), Ltd. All of the chemicals were used as received, and employed without further purification.

2.2. Preparation of Catalysts

As aforementioned, the hydrothermal method was employed to obtain the sheaf-like CeO$_2$. In a typical preparation process, 10.0 mmol Ce(NO$_3$)$_2$·6H$_2$O, 10 g polyvinyl pyrrolidone and 0.3 mol urea were dissolved in a mixture, which contains 50 mL of deionized water and 50 mL of absolute ethanol. This mixed solution was stirred for 0.5 h, and then put into an autoclave for 24 h at the temperature of 120 °C. After cooling, the precipitates were collected by filtration, and washed by deionized water and absolute ethanol more than once. Finally, the obtained precipitates were calcined for 4 h at the temperature of 500 °C after they were dried at 80 °C in air overnight. The obtained product was labeled as CeO$_2$-S.

Then, 1.5 g dried CeO$_2$-S prepared under the above conditions was added in 100 mL water. By adding KOH, the mixed solution had a final KOH mole concentration of about 4 mol/L and then the mixed solution was stirred for 40 min. Thereafter, the mixed solution was transferred into the autoclave, and then placed into a drying oven for 24 h at the temperature of 120 °C. Similarly, after cooling, the product was collected by filtration, washed by deionized water several times, dried at 80 °C in air overnight, and calcined at 500 °C for 4 h. The obtained product was marked as CeO$_2$-SK.

Sheaf-like CeO$_2$ supporting Pd catalysts were synthesized by a modified colloidal deposition method. Firstly, polyvinyl alcohol (PVA) was injected into 100 mg/L H$_2$PdCl$_4$ solution and sufficiently dissolved. Secondly, a certain amount of NaBH$_4$ aqueous solution was added rapidly to obtain the colloidal palladium solution. Then, CeO$_2$ powder was added into the above colloidal palladium solution and stirred for 24 h to achieve a designated content of 1 wt.% Pd on the CeO$_2$ support. Finally, the obtained solid materials, viz., the Pd/CeO$_2$-S and Pd/CeO$_2$-SK, were collected by going through the identical procedure of filtration, washing, drying and calcination as compared with CeO$_2$-S and CeO$_2$-SK. According to a previous report, the presence of chlorides can affect the redox behavior of cerium oxide [28]. Therefore, in order to reduce the chlorides in the Pd/CeO$_2$ catalysts, the washing times of the two Pd/CeO$_2$ catalysts were kept the same during the washing process, and both of them were washed until the filtrate had no white precipitate after AgNO$_3$ detection.

2.3. Catalytic Activity Measurements

The activity test for methane combustion over the catalysts was carried out in a quartz tube flow microreactor whose internal diameter is 6 mm. For each test, 200 mg of 40–60 mesh fresh catalyst was placed in the microreactor between two quartz glass wool layers. The reaction gas contained 1% CH$_4$, 19% O$_2$ and balanced Ar; and had a total flow rate of 100 mL/min, equivalent to a weight hourly space velocity (WHSV) of 30,000 mL/g·h. The outlet gaseous mixture was analyzed online using a gas chromatograph (GC-2010, Shimadzu, Japan) to determine the component concentrations. The whole test process took about 2.5 h.

2.4. Catalyst Characterization

The catalysts surface area was analyzed by a TriStar 3000 Gas Absorption Analyzer (Micromeritics Instrument Co., Atlanta, GA, USA) and N$_2$ physisorption at −195.8 °C. The samples were degassed at 200 °C and 6.7 Pa for 2 h prior to the measurement. The Pd content in the catalysts was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES; PerkinElmer Co., Waltham, MA, USA). X-ray powder diffraction (XRD) patterns of the catalysts were detected by an X-ray diffraction system (Bruker Corporation, Billerica, MA, USA) using Cu Ka radiation (154.06 pm, 40 kV and 40 mA). The diffraction spectra were collected over the 2θ range of 5–85° at a scanning rate of 4°/min.
The morphologies of the catalysts were analyzed at an operating voltage of 200 kV by a JSM-7001F scanning electron microscopy (SEM; JEOL Company, Tokyo, Japan). Meanwhile, characterization was also carried out by using both transmission electron microscopy (TEM; JEM-2010, JEOL Company, Tokyo, Japan) and high-resolution transmission electron microscopy (HRTEM; JEM-2010, JEOL Company, Tokyo, Japan) operating at 200 kV. To prepare the specimen for HRTEM, the catalyst sample was crushed to a fine powder and then a holey carbon film copper grid was dipped into the crushed powder.

Meanwhile, a Micromeritics AutoChem II 2920 Chemisorption Analyzer (Micromeritics Instrument Co., Atlanta, GA, USA) with a TCD detector was adopted for H2-temperature programmed reduction (H2-TPR). Typically, approximately 50 mg catalysts were reduced under a 10 vol % H2-Ar mixture. Before the H2-TPR analysis, the catalysts were treated under an air flow at 500 °C for 30 min, followed by purging with pure N2 at the same temperature for 30 min and then cooled down to 0 °C. After that, the reduction process took place in the temperature range of 0–900 °C.

In addition, Raman spectra were obtained using a Horiba Jobin Yvon LabRam HR800 Dual Microscope with a 514 nm Ar ion laser under ambient temperature. The X-ray photoelectron spectroscopy (XPS) analysis of the catalysts was performed on a spectrometer (ULVAC PHI-5800, Chanhassen, MN, USA) with the X-ray source of Al Kα. The standard binding energy of C 1s = 284.6 eV was used as the reference to shift the binding energies of the samples.

3. Results

3.1. XRD Results and Textural Properties

The XRD patterns of sheaf-like CeO2 supports and the Pd loaded catalysts are shown in Figure 1. Typical diffraction lines of ceria fluorite structure (JCPDS 34-0349) are observed for all of the samples. However, no distinct diffraction line for Pd species is detected in Figure 1, indicating that palladium species are finely dispersed on CeO2 surface and its size might be small.

![Figure 1. X-ray powder diffraction (XRD) patterns of (a) CeO2-S, (b) CeO2-SK, (c) Pd/CeO2-S and (d) Pd/CeO2-SK.](image)

| Samples    | Pd Loading (wt.%) | S\text{BET} (m^2/g) | Average Pore Size (nm) | Pore Volume (cm^3/g) |
|------------|-------------------|----------------------|------------------------|----------------------|
| CeO2-S     | -                 | 66.5                 | 4.2                    | 0.0626               |
Table 1 summarizes the Brunauer–Emmett–Teller surface area, average pore volume and pore size of sheaf-like CeO$_2$ supports as well as the corresponding supported Pd catalysts. It showed that the surface area of CeO$_2$-S support (66.5 m$^2$/g) was very similar to that of CeO$_2$-SK support (70.6 m$^2$/g). After the deposition of Pd component, the surface areas of the obtained Pd catalysts remained almost unchanged as compare with that of the corresponding carriers. Meanwhile, as shown in Table 1, the Pd contents in both of the two Pd-containing catalysts were close to the designated value (1 wt.%).

|          | Surface Area (m$^2$/g) | Average Pore Volume (µm$^3$) | Pore Size (µm) | K       |
|----------|------------------------|-----------------------------|----------------|---------|
| CeO$_2$-SK | -                      | 70.6                        | 5.0            | 0.0654  |
| Pd/CeO$_2$-S | 0.94         | 65.6                        | 4.1            | 0.0602  |
| Pd/CeO$_2$-S | 0.93         | 68.7                        | 4.6            | 0.0636  |

3.2. SEM Results

SEM images of sheaf-like CeO$_2$ supports as well as the Pd loaded catalysts are displayed in Figure 2. Clearly, the Pd loaded catalysts maintained the original morphology of those CeO$_2$ carriers. The obtained CeO$_2$-S support (Figure 2a) resembled a wheat bundle composed of many filamentous crystals, which was bandaged in its middle and fanning-out at both ends. Similar structures have been observed for CuO and Bi$_2$S$_3$ in the literature [29,30]. The average diameter of the individual nano-filament was about 10 nm and the bundles length was about 6–8 µm. Moreover, a smooth surface of the sheaves particles could be observed. However, after KOH etching, the surface of CeO$_2$-SK bundled particles become rough due to the formation of a large number of nanorods (Figure 2c,d).

![Figure 2](image_url)

**Figure 2.** Scanning electron microscopy (SEM) images of (a) CeO$_2$-S, (b) CeO$_2$-SK, (c) Pd/CeO$_2$-S and (d) Pd/CeO$_2$-SK (the inset is a magnified SEM image).

3.3. TEM and HRTEM Results

Figure 3 presents the TEM and HRTEM images of supported Pd catalysts. It can be seen from Figure 3a,c that both Pd supported catalysts show a sheaf-like structure, and an abundance of nanorods were observed on the Pd/CeO$_2$-SK surface; which was in accordance with the above SEM images. Moreover, as shown in Figure 3b, the complete structure of Pd/CeO$_2$-S was too big, and therefore the HRTEM images were observed for the typical edge part of Pd/CeO$_2$-S. The lattice plane spacing calculated from the HRTEM images was about 0.19 and 0.28 nm, which could be indexed as the (110) and (100) planes of CeO$_2$, respectively. In the Pd/CeO$_2$-SK HRTEM image (Figure 3d), the
lattice fringes were clear and their spacing values were 0.19 and 0.28 nm, respectively; which were also attributed to (110) and (100) planes of CeO$_2$. Although both Pd/CeO$_2$-S and Pd/CeO$_2$-SK catalysts exposed mainly the (110) and (100) crystal faces of CeO$_2$, Pd/CeO$_2$-SK had a larger amount of nanorods on its surface after KOH etching, and finally Pd/CeO$_2$-SK owned more content of (110) and (100) CeO$_2$ planes than Pd/CeO$_2$-S. In addition, because the diffraction contrast of Pd and CeO$_2$ was similar, no Pd particles were observed on both of the two Pd-containing catalysts [19].

**Figure 3.** Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images of (a,b) Pd/CeO$_2$-S and (c,d) Pd/CeO$_2$-SK.

### 3.4. H$_2$-TPR Results

**Figure 4.** H$_2$-temperature programmed reduction (H$_2$-TPR) profiles of (a) CeO$_2$-S, (b) CeO$_2$-SK, (c) Pd/CeO$_2$-S and (d) Pd/CeO$_2$-SK.

**Table 2.** Quantitative analysis of the H$_2$-TPR profiles of sheaf-like CeO$_2$ supports and the Pd loaded catalysts.

| Samples   | Peak Position (°C) | H$_2$ Uptake (µmol/g) | Theoretical H$_2$ Uptake (µmol/g) |
|-----------|-------------------|------------------------|----------------------------------|
| CeO$_2$-S | 460               | 1170                   | 2904                             |
Theoretical H\textsubscript{2} uptake was determined as the quantity of H\textsubscript{2} required for the reduction of Pd catalysts and corresponding CeO\textsubscript{2} supports by assuming that CeO\textsubscript{2} and PdO are stoichiometrically reduced to Ce\textsubscript{2}O\textsubscript{3} and Pd, respectively.

The H\textsubscript{2}-TPR profiles of sheaf-like CeO\textsubscript{2} supports and the Pd loaded catalysts are shown in Figure 4; the results of a quantitative analysis of the H\textsubscript{2}-TPR profiles are listed in Table 2. Obviously, the H\textsubscript{2}-TPR profiles of the two sheaf-like CeO\textsubscript{2} supports are similar to each other. It can be seen that two main reduction peaks existed at 0–900 °C, and the peaks were believed to be related to the reduction of surface oxygen of CeO\textsubscript{2} (at about 460 °C with a H\textsubscript{2} uptake of 1170 μmol/g for CeO\textsubscript{2}-S and 985 μmol/g for CeO\textsubscript{2}-SK) and bulk CeO\textsubscript{2} (at about 840 °C), respectively [16,31,32].

After loading the Pd component, the redox ability of CeO\textsubscript{2} is changed. The CeO\textsubscript{2} surface oxygen redox reduction peaks centered at 460 °C shift to 450 °C for both of Pd-containing catalysts, implying the promoted reducibility for Pd catalysts. Moreover, a new peak appears at around 210 °C for the Pd/CeO\textsubscript{2}-SK catalyst. It can be assigned to the reduction of PdO although its reduction temperature is higher compared with pure PdO [23]. As reported by Fu et al., this phenomenon could be mainly owing to the interaction between CeO\textsubscript{2} and PdO [33]. Noticeably, the PdO species reduction peak is not observed in Pd/CeO\textsubscript{2}-S, indicating that Pd/CeO\textsubscript{2}-SK owns a much higher fraction of PdO species than that of Pd/CeO\textsubscript{2}-S.

SEM and TEM results show that both Pd/CeO\textsubscript{2}-S and Pd/CeO\textsubscript{2}-SK catalysts exhibit sheaf-like morphologies, but Pd/CeO\textsubscript{2}-SK possesses more nanorods enclosed mainly by CeO\textsubscript{2} (100) and (110) facets. Previous studies reveal that the migration of lattice oxygen from bulk to surface on the (110) and (100) facet-dominated catalyst is much easier compared with that on the (111) facet-dominated one [16,34]. Therefore, the difference in their redox ability may be attributed to the exposure of larger amount of CeO\textsubscript{2} (110) and (100) planes on Pd/CeO\textsubscript{2}-SK surface compared with Pd/CeO\textsubscript{2}-S.

3.5. Raman Spectroscopy

The Raman spectra of sheaf-like CeO\textsubscript{2} supports and the Pd loaded catalysts are shown in Figure 5. For ease of observation, the Pd/CeO\textsubscript{2}-SK data is enlarged four times. For CeO\textsubscript{2} supports, the main bands at 460 cm\textsuperscript{-1} correspond to the F\textsubscript{2g} Raman active mode of CeO\textsubscript{2} fluorite structure [19,35–37]: the weak bands at about 597 cm\textsuperscript{-1} are assigned to the defect induced mode (D-mode), which should be associated with the existence of oxygen vacancies caused by Ce\textsuperscript{3+} ions in the CeO\textsubscript{2} lattice [19,22,38]; the bands at 257 cm\textsuperscript{-1} are ascribed to the second order transverse acoustic mode (2TA-mode) [19].
After incorporating Pd component, the $F_{3g}$ band of Pd catalysts is broader and slightly weaker compared with CeO$_2$ supports, which is a sign of enhanced Pd–support interaction. Meanwhile, the surroundings environment of CeO$_2$ surface is possibly changed by the introduction of Pd through an epitaxial contact between Pd and CeO$_2$ supports. In addition, the observed widening and weakening of the $F_{3g}$ band for the Pd-containing catalysts may be related to their lower crystallite size or the larger content of oxygen vacancies in ceria [39]. However, the Pd/CeO$_2$ catalyst and the corresponding CeO$_2$ support have a similar particle size as seen from the SEM images. Thus, the above changes of the CeO$_2$: $F_{3g}$ band in Pd-containing catalysts can be related to the larger fraction of oxygen vacancies on CeO$_2$ surface. Noticeably, the Pd/CeO$_2$-SK catalyst exhibited slightly intenser D-mode peak than Pd/CeO$_2$-S, indicating that the former has a higher proportion of oxygen vacancies. Another obvious difference between the Raman spectra of supported Pd catalysts and the parent CeO$_2$ carriers is a typical PdO band appeared at about 650 cm$^{-1}$ on Pd catalysts, which can be ascribed to the B$_{3g}$ mode of square planar [PdO] subunits in PdO [19,40,41]. However, the intensity of this PdO band decreased greatly for Pd/CeO$_2$-S catalyst, reflecting the lower content of PdO species on Pd/CeO$_2$-S; which agreed well with the H$_2$-TPR results. Furthermore, early studies showed that the reaction mechanism of CH$_4$ combustion reaction over Pd-based catalysts usually follows the Mars–van Krevelen mechanism [42–44]. During the reaction, the decomposition and reformation of PdO species has been observed (PdO→Pd→PdO) [14]; that is, CH$_4$ firstly reacts with O bounded with Pd to create CO$_2$/H$_2$O and oxygen vacancies, the generated oxygen vacancies are then supplemented by the gaseous oxygen or the bulk lattice oxygen. Obviously, the Pd oxides in Pd/CeO$_2$ catalysts are very important for the lean CH$_4$ combustion reaction. Misch et al. and Gholami et al. also discovered that PdO exhibits higher activity than that of metallic Pd in CH$_4$ oxidation process [45,46]. Therefore, the higher content of PdO species on Pd/CeO$_2$-SK may also imply higher activity compared with Pd/CeO$_2$-S.

As reported in the literature, the degree of oxygen vacancies on CeO$_2$ is related to the ratio of peak areas of D-mode to $F_{3g}$ [22,39]. In this way, a higher D/$F_{3g}$ ratio means a larger content of oxygen vacancies. The D/$F_{3g}$ ratio of sheaf-like CeO$_2$ carriers as well as the Pd loaded catalysts is presented in Table 3. It shows that the D/$F_{3g}$ ratio of CeO$_2$-SK support (0.104) and Pd/CeO$_2$-SK catalyst (0.136) is much larger than that of CeO$_2$-S (0.068) and Pd/CeO$_2$-S (0.093), which reveals that the former samples own more amounts of oxygen vacancies. As mentioned above, after KOH etching, numerous nanorods are formed on the CeO$_2$-SK surface, and these nanorods enclosed by CeO$_2$ (100) and (110) facets. Sayle et al. demonstrated that the formation energy of oxygen vacancies on ceria planes is ranked in the descending order of (111), (100) and (110) [47], indicating that the

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**Figure 5.** Raman spectra of (a) CeO$_2$-S, (b) CeO$_2$-SK, (c) Pd/CeO$_2$-S and (d) Pd/CeO$_2$-SK (its data is enlarged four times).
anion vacancies are more easily formed on CeO₂ (110) and (100) planes. As a result, the CeO₂-SK support and Pd/CeO₂-SK catalyst exhibit higher D/F₂g ratio, and a larger amount of oxygen vacancies are created on their surface.

### Table 3. Raman spectra and X-ray photoelectron spectroscopy (XPS) results of sheaf-like CeO₂ supports and the Pd loaded catalysts.

| Samples       | D/F₂g Content (%) | Pd⁰ Content (%) | Ce³⁺ Content (%) | Oads/Olatt Ratio |
|---------------|-------------------|-----------------|------------------|-----------------|
| CeO₂-S        | 0.068             | -               | 16.5             | 0.55            |
| CeO₂-S K      | 0.104             | -               | 19.3             | 0.97            |
| Pd/CeO₂-S     | 0.093             | 50.0            | 17.4             | 0.48            |
| Pd/CeO₂-SK    | 0.136             | 45.8            | 21.0             | 0.63            |

3.6. XPS Results

The oxidation states and surface composition of the elements present in the as-made catalysts were analyzed by the XPS measurements. Figure 6 illustrates the Pd 3d XPS profiles of the two Pd loaded catalysts. Clearly, two Pd 3d⁵/₂ peaks at 336.2, 337.4 eV and two Pd 3d³/₂ peaks at 341.2 and 342.4 eV are observed for the Pd/CeO₂-S catalyst, respectively. The peaks located at 336.2 and 341.2 eV can be attributed to the metallic Pd, and the peaks centered at 337.4 and 342.4 eV are related to the Pd oxides [22,48]. As for Pd/CeO₂-SK catalyst, the Pd 3d⁵/₂ peaks and 3d³/₂ peaks shift to slightly lower binding energy. As shown in Table 3, approximately 50.0% of Pd species existed on the surface of Pd/CeO₂-S in the form of metallic Pd; whereas, this value decreased to 45.8% for Pd/CeO₂-SK. The results revealed that the concentration of PdO species on Pd/CeO₂-SK surface was higher than that on Pd/CeO₂-S, which was consistent with the surface content of PdO observed from the Raman analysis.

![Figure 6. Pd 3d XPS spectra of (a) Pd/CeO₂-S and (b) Pd/CeO₂-SK.](image)

The Ce 3d XPS spectra of sheaf-like CeO₂ supports and the Pd loaded catalysts are presented in Figure 7. It can be seen that the XPS spectra of CeO₂ carriers and the Pd loaded catalysts exhibited ten peaks. The peaks labeled U and V belong to the spin-orbit components of Ce 3d₅/₂ and Ce 3d₃/₂, respectively [49,50]. In addition, the peaks marked by U, V, U”, V”, U’” and V’” are of Ce³⁺, while
those denoted by $U^0$, $U'$, $V^0$ and $V'$ are Ce$^{3+}$characteristic peaks \[51, 52\]. This reveals that two types of cerium oxides are present on the surface of all the samples, i.e., Ce$^{4+}$ and Ce$^{3+}$. It is generally believed that the surface Ce$^{3+}$ results from the surface defects and surface oxygen vacancies, which have a positive impact on the lean methane combustion. Thus, the calculation of Ce$^{3+}$ content is necessary for estimating the surface oxygen vacancies content. The area ratio \[S_1/(S_1 + S_2)\] of the Ce$^{3+}$ peaks area ($S_1$) to the total area ($S_1 + S_2$, Ce$^{4+}$ peaks area labels $S_2$) of Ce 3d peaks is used to detect the surface Ce$^{3+}$ content. Thus, a higher \[S_1/(S_1 + S_2)\] ratio reflects a larger Ce$^{3+}$ concentration.

The calculated results are listed in Table 3. Clearly, CeO$_2$-SK support (19.3) and Pd/CeO$_2$-SK catalyst (21.0) exhibited higher Ce$^{3+}$ content than those in CeO$_2$-S (16.5) and Pd/CeO$_2$-S (17.4), further confirming that more oxygen vacancies existed on the CeO$_2$-SK support and Pd/CeO$_2$-SK catalyst, coinciding with the Raman spectra results. Moreover, the loading of Pd also enhanced the Ce$^{3+}$ concentration in the obtained Pd-containing catalysts. This phenomenon implies that the valence of elements of the CeO$_2$ surface was changed owing to the interaction between Pd and CeO$_2$.

![Figure 7. Ce 3d XPS spectra of (a) CeO$_2$-S, (b) CeO$_2$-SK, (c) Pd/CeO$_2$-S and (d) Pd/CeO$_2$-SK.](image)

Figure 8 presents the O 1s XPS spectra of sheaf-like CeO$_2$ supports and the Pd loaded catalysts. As seen from Figure 8, all of the samples have two typical peaks with different energies. The peak at 529.3–529.7 eV stands for the lattice oxygen species (O$_{\text{latt}}$), while the other one at about 531.9–532.5 eV is related to the surface adsorbed oxygen (O$_{\text{ads}}$) \[49\], which is usually considered active for oxidation reactions. As such, the ratio between the two kinds of oxygen species (O$_{\text{ads}}$/O$_{\text{latt}}$) was quantified based on the area of O$_{\text{latt}}$ and O$_{\text{ads}}$ (Table 2). The O$_{\text{ads}}$/O$_{\text{latt}}$ ratio was 0.55 for CeO$_2$-S, whereas it dramatically increased to 0.97 for CeO$_2$-SK; implying a greater tendency to form adsorbed oxygen species on the CeO$_2$-SK surface. According to the above characterization results, after KOH etching, a large number of nanorods enclosed mainly by CeO$_2$ (110) and (100) planes were produced on the CeO$_2$-SK surface, which then promoted the creation of oxygen vacancies. These oxygen vacancies were easy to absorb oxygen to form active adsorbed oxygen species, and ultimately enhance the redox ability and catalytic performance of the obtained catalysts. In addition, it also could be seen from Table 3 that the addition of Pd caused a slight decrease of O$_{\text{ads}}$/O$_{\text{latt}}$ ratio, though Pd/CeO$_2$-SK exhibit higher O$_{\text{ads}}$/O$_{\text{latt}}$ ratio than Pd/CeO$_2$-S. This might be due to the fact that a few chemisorbed oxygen sites are occupied by Pd components.
3.7. \( \text{CH}_4 \) Combustion Catalytic Activity

The catalytic activities of the sheaf-like CeO\(_2\) supports and the corresponding supported Pd catalysts in lean methane combustion are shown in Figure 9. In these tests, only CO\(_2\) and H\(_2\)O as products were detected, indicating the good selectivity of the obtained catalysts in the complete oxidation of CH\(_4\).

It can be seen from Figure 9, CeO\(_2\)-S and CeO\(_2\)-SK supports show poor activity in lean methane combustion and the \( \text{CH}_4 \) conversion values at 500 °C are only 71.9% and 79.9%, respectively. After deposition Pd component, the \( \text{CH}_4 \) conversion of the Pd-containing catalysts was increased significantly, suggesting the important role of Pd in lean methane combustion. Moreover, it also shows that the activity of the as prepared Pd catalysts depended largely on the structural feature of CeO\(_2\) supports such as its exposing crystal face; the Pd/CeO\(_2\)-SK catalyst shows a high activity, superior to the Pd/CeO\(_2\)-S catalyst. Over the Pd/CeO\(_2\)-SK catalyst, \( \text{CH}_4 \) conversion reached 91% at 350 °C and 100% at 375 °C, while the full conversion of \( \text{CH}_4 \) was achieved at 425 °C for Pd/CeO\(_2\)-S catalyst.

**Figure 8.** O 1s XPS spectra of (a) CeO\(_2\)-S, (b) CeO\(_2\)-SK, (c) Pd/CeO\(_2\)-S and (d) Pd/CeO\(_2\)-SK.

**Figure 9.** Methane conversion for the catalytic combustion over sheaf-like CeO\(_2\) supports and the corresponding supported Pd catalysts.
Long-term tests were also performed for CH\textsubscript{4} catalytic combustion over the Pd/CeO\textsubscript{2}-S and Pd/CeO\textsubscript{2}-SK catalysts at 375 °C, as shown in Figure 10. Clearly, the Pd/CeO\textsubscript{2}-S catalyst displays a CH\textsubscript{4} conversion about 90% and that of the Pd/CeO\textsubscript{2}-SK catalyst is approximately 100% during the 120 min test process. Both of the two Pd-containing catalysts show good thermal stability. Moreover, as shown in Figures S1 and S2 in the Supplementary Information, there are no structural changes for the Pd/CeO\textsubscript{2}-S and Pd/CeO\textsubscript{2}-SK catalysts after the long-term tests, in comparison with the fresh ones.

![Figure 10. Long-term stability test for CH\textsubscript{4} catalytic combustion over Pd/CeO\textsubscript{2}-S and Pd/CeO\textsubscript{2}-SK catalysts at 375 °C.](image)

The above characterization results can explain the outstandingly activity of Pd/CeO\textsubscript{2}-SK catalyst in the lean methane combustion. According to the ICP, N\textsubscript{2} physisorption and SEM results, the Pd supported catalysts were very similar in their Pd loading, surface area and morphologies. SEM and TEM results show that Pd/CeO\textsubscript{2}-SK surface had numerous nanorods enclosed by CeO\textsubscript{2} (100) and (110) facets after KOH etching, which is beneficial to the formation of oxygen vacancies. These oxygen vacancies help absorb oxygen to form active adsorbed oxygen species and ultimately improve the reduction ability and catalytic performance of Pd/CeO\textsubscript{2}-SK. Moreover, as seen from the H\textsubscript{2}-TPR and Raman spectra results, the Pd/CeO\textsubscript{2}-SK catalyst possessed higher content of catalytic active PdO species than that of Pd/CeO\textsubscript{2}-S. As a result, the excellent performance of Pd/CeO\textsubscript{2}-SK in lean methane combustion was expected.

4. Conclusions

Sheaf-like CeO\textsubscript{2} in microscale was prepared by the hydrothermal method. The as-made sheaf-like CeO\textsubscript{2} was then further etched with KOH for obtaining an imperfect fluorite structure with higher content of oxygen vacancies as well as improved oxygen mobility. With the as-made and etched sheaf-like CeO\textsubscript{2} as supports respectively, two Pd/CeO\textsubscript{2} catalysts were obtained for lean methane combustion by a modified colloidal deposition method.

After KOH etching, CeO\textsubscript{2}-SK surface shows numerous nanorods enclosed by CeO\textsubscript{2} (100) and (110) facets and Pd/CeO\textsubscript{2}-SK exhibited much higher activity compares with Pd/CeO\textsubscript{2}-S; over the Pd/CeO\textsubscript{2}-SK catalyst, CH\textsubscript{4} conversion reached 100% at 375 °C, while the full conversion of CH\textsubscript{4} was achieved at 425 °C for Pd/CeO\textsubscript{2}-S catalyst. The larger proportion of CeO\textsubscript{2} (100) and (110) planes in Pd/CeO\textsubscript{2}-SK enhance the creation of oxygen vacancies and oxygen migration, which had a positive impact on the activity of lean methane combustion. Moreover, Pd/CeO\textsubscript{2}-SK catalyst had higher content of catalytic active PdO species compares with Pd/CeO\textsubscript{2}-S catalyst due to the interaction between the CeO\textsubscript{2} (100) and (110) planes and palladium species. All these contribute to the excellent activity of Pd/CeO\textsubscript{2}-SK in lean methane combustion.
Supplementary Materials: The following are available online at www.mdpi.com/2079-4991/10/1/31/s1: Figure S1: XRD patterns of the Pd/CeO$_2$-S and Pd/CeO$_2$-SK catalysts before and after the long-term test in lean methane combustion; Figure S2: SEM images of the Pd/CeO$_2$-S and Pd/CeO$_2$-SK catalysts after the long-term test in lean methane combustion.

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