Effect of Particle Size and Crystal Surface of CeO₂ on the Catalytic Combustion of Benzene

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Abstract: In this study, three kinds of CeO₂ were synthesized, and supported PdOₓ (x = 0,1) catalysts were prepared for benzene catalytic combustion. The samples were characterized by XRD, N₂ adsorption/desorption, HRTEM, XPS and H₂-TPR. The results show that three kinds of CeO₂ with different structures can be formed by different preparation methods. This is mainly reflected in the differences in pore structure, particle size and crystal plane. CeO₂-DC obtained from directly calcined Ce(NO₃)₃·6H₂O had the largest pore volume and pore diameter and smallest particle size. CeO₂-DC was mainly exposed to the (200) plane. Combined with the results of the ability test, it could be concluded that when Pd²⁺ and Pd⁰ exist at the same time, the activity increases with an increase in the proportion of Pd²⁺. Meanwhile, the structure of CeO₂ affects the formation of oxygen vacancies, thereby affecting the adsorption and degradation of benzene. This article reveals that the particle size, crystal planes, oxygen vacancies and proportion of Pd²⁺ have a great impact on the catalytic combustion of benzene and allow a more comprehensive understanding of the structure–activity relationship, which can guide us to design high-efficiency catalysts targeted to obtain suitable CeO₂-based catalysts for the catalytic combustion of benzene.

Keywords: cerium oxide; benzene; catalytic combustion; particle size; crystal surface

1. Introduction

Volatile organic compounds (VOCs) are a main component of air pollution and have been increasing rapidly in recent years. Most VOCs not only harm the environment but also threaten human health due to their toxicity and carcinogenicity [1–3]. Aromatic hydrocarbons, as a kind of VOCs, are considered to cause great harm to the environment and are usually toxic and carcinogenic [4,5]. Benzene is a kind of carcinogen, which can be determined to be carcinogenic. Toluene, ethylbenzene and xylene are all possible carcinogens [6]. Among the aromatic hydrocarbons, benzene, toluene, ethylbenzene and xylene (BTEX) constitute the majority of the total industrial emissions [7]. Therefore, it is very urgent to develop an effective and suitable method to reduce the total amount of VOCs. The main methods for dealing with VOCs include adsorption, membrane separation, absorption and oxidative approaches (thermal incineration, biological degradation, photocatalytic decomposition, nonthermal plasma oxidation and catalytic combustion) [8–13]. Catalytic combustion has become the most widely used technology because of its characteristics of high catalytic efficiency, low energy consumption and low secondary pollution [14–16].

Catalytic combustion is a typical gas–solid catalytic reaction. In the reaction, VOCs need to be adsorbed on the surface of the catalyst, and then a catalytic degradation reaction is carried out. Supports with a high specific surface area (S BET) and rich pore structure can improve the adsorption property and the catalytic performance of VOCs [8]. Thus, it is important to identify excellent supports...
for the catalytic combustion of VOCs. Common supports include γ-Al₂O₃, cordierite, molecular sieves and pillared clays [17–21]. These supports have large S_BET and pore volume (Vₚ) but have no activity or low activity. Due to the low activity of the support, only the proportion, type and loading method of the active component can be improved, which limits the improvement of catalyst performance in the catalytic combustion of VOCs. In recent years, some researchers have found that using active supports can further promote the performance of catalysts [22–25]. For example, Jablonska et al. synthesized a new HY zeolite that can completely catalyze methanol combustion at 500 °C. After loading Pd, it can completely convert methanol below 150 °C, which is greatly improved compared with Pd/Al₂O₃ [25]. Li et al. synthesized a type of CoAl mixed oxide that can completely catalyze toluene conversion at 345 °C. After loading Pt, its activity is greatly improved, and toluene can be completely burned at 230 °C [26]. Therefore, the use of active supports instead of traditional supports provides a development direction for future research.

Compared with other active supports, rare-earth elements have many advantages in catalytic materials, such as increasing oxygen storage and releasing capacity, adjusting catalytic active sites and improving the dispersion of active components and the thermal stability of catalysts. Therefore, rare-earth oxides, as active supports, have been widely used in VOCs catalytic combustion reactions [24,27]. Wu et al. synthesized a series of LaCo composite oxides for the catalytic combustion of toluene. By introducing La, the valence state of Co can be adjusted, and the formation of oxygen vacancies can be promoted, which causes the catalyst to have good catalytic performance for toluene combustion [28]. Wu et al. prepared LaFeO₃ perovskite oxide for the catalytic combustion of toluene, which showed high catalytic activity [29]. Cerium oxide (CeO₂), one of the most significant rare-earth oxides, has attracted much attention in recent decades. Many researchers have applied CeO₂ as a catalyst in the catalytic combustion of VOCs [27,30–32]. Chen et al. synthesized a Ce metal–organic frameworks (MOF) catalyst which showed good catalytic activity for toluene oxidation [33]. Wang et al. synthesized a honeycomb CeO₂ catalyst. It had great differences in morphology and reducibility and exhibited high activity in the oxidation of o-xylene [24]. However, CeO₂ catalysts cannot achieve ideal catalytic performance due to the limitation of structure and physicochemical properties. Therefore, it is still necessary to use CeO₂ as a support to prepare catalysts. For combustion of light hydrocarbons, several works have pointed out that noble metals as active components exhibited excellent performance of catalytic combustion. Guo et al. successfully prepared a 3D ordered mesoporous CeO₂ catalyst loaded with biogenic Pd nanoparticles for the catalytic combustion of benzene. The experimental results show that the catalyst has good catalytic activity and can achieve 90% catalytic conversion at 187 °C [34]. Abbasi et al. prepared nanostructured Pt/Al₂O₃–CeO₂ catalysts for catalytic combustion of VOCs, and they exhibited high catalytic activity [35]. Lei et al. synthesized a Pd/CeO₂ catalyst for methane catalytic combustion. The experimental results show that the catalytic activity of the catalyst is greatly improved after loading Pd, which can completely catalyze combustion at 360 °C [31]. Nowadays, many researchers focus on the selection of active components and the role of rare-earth oxides as promoters. However, there is little research on the effects of pore structure, particle size, crystal surface and other physical indicators on the performance of catalysts and the structure–activity relationship.

In this paper, three kinds of CeO₂ with different physicochemical properties were prepared and used to prepare Pd/CeO₂ catalysts. Then, the influence of these properties on the catalytic combustion of benzene was discussed. XRD, N₂ adsorption/desorption, HRTEM, XPS and H₂-TPR tests were used to systematically analyze the structure–activity relationship.

2. Materials and Methods

2.1. Support Preparation

CeO₂ (particle size: 20–50 nm, 99.5% purity) was purchased from Aladdin and used as received, which is denoted CeO₂-P. Ce(NO₃)₃·6H₂O (99.5% purity, Aladdin) was directly calcined at 500 °C for 2 h to obtain CeO₂, which is called CeO₂-DC. Another CeO₂ was made by thermal decomposition of
Ce metal-organic frameworks (MOF), which is named CeO$_2$-MOF. The preparation method of Ce-MOF has been described in our previous articles [36].

2.2. Catalyst Preparation

The catalysts loaded with Pd nanoparticles (0.2 wt.%) were synthesized by high-temperature liquid reduction [37]. First, 2.0 g of CeO$_2$ and 100 mL of ethylene glycol (AR, 98%, Aladdin, Xi’an, China) were added to a three-necked flask with stirring for 30 min, and then 0.4 mL of H$_2$PdCl$_4$ (10 mg/mL) was added into the three-necked flask and stirred for 12 h. Then, the pH was controlled at 11.0. The reaction was heated to 165 °C for 3 h, and then the temperature dropped to room temperature. The product was washed with distilled water twice, then washed with ethanol (AR, 99.7%, Aladdin, Xi’an, China) once and then dried for 12 h at 60 °C. After that, the product was calcined in a muffle furnace (Shanghai Pudong Yuexinxue Instrument Factory, Shanghai, China) at 500 °C for 2 h to obtain a 0.2% Pd/CeO$_2$ catalyst. Pd/CeO$_2$-P, Pd/CeO$_2$-DC and Pd/CeO$_2$-MOF were obtained by the above method using CeO$_2$-P, CeO$_2$-DC and CeO$_2$-MOF, respectively.

2.3. Catalytic Performance Evaluation

The activity of the catalysts was evaluated on a WFS-3010 microreactor (Xianquan, Tianjin, China) with a benzene concentration of 1000 ppm and a space velocity of 20,000 h$^{-1}$. An amount of 200 mg catalyst (40–60 mesh) was loaded in the quartz reactor and pretreated at 400 °C in air for 0.5 h. After that, 1000 ppm benzene was added for the activity test. Online gas chromatography (Shimadzu, GC-14C, Kyoto, Japan) with a hydrogen flame ionization detector (FID) was used to detect the concentration of the organic substance entering the chromatograph. The chromatographic working conditions were as follows. The temperatures of the column and vaporization chamber were 80 and 120 °C, respectively. An N2000 online chromatography workstation (Saizhi Technology Co., Ltd, Hangzhou, China) was used to record data. The durability of catalysts was tested under the same working conditions of the activity evaluation, and the catalytic time was as long as 100 h.

2.4. Catalyst Characterization

The structure of catalysts and supports was characterized using XRD (PANalytical, Almelo, The Netherlands, Cu Kα radiation, 40 kV, 40 mA, speed of 0.02°/s). The particle size of samples was calculated from the XRD data using the Scherrer formula (Equation (1)):

\[
D = \frac{K \gamma}{B \cos \theta}
\]

where:

- \(D\) = Average thickness of particle perpendicular to crystal plane (nm);
- \(K\) = Scherrer constant;
- \(\gamma\) = X-ray wavelength (0.154 nm);
- \(B\) = Full width at half maxima (FWHM);
- \(\theta\) = Diffraction angle.

A Tristar II 3020 apparatus (Micromeritics Company, Norcross, GA, USA) was used to determine the nitrogen adsorption and desorption isotherms at −195.8 °C. The Brunauer-Emmett-Teller (BET) model was used to measure the \(S_{BET}\). Meanwhile, the Barrett-Joyner-Halenda (BJH) method was used to calculate the pore size and average pore diameter. Before the adsorption process, the samples were kept under vacuum at 200 °C for 4 h.

The morphology of the supports and the catalysts was obtained using high-resolution transmission electron microscopy (HRTEM, JEOL-2010F, Tokyo, Japan) operated at 200 kV. The chemical composition of the Pd/CeO$_2$ catalyst was detected using energy-dispersive X-ray spectroscopy (EDS) with an Oxford INCA instrument (OXFORD instruments, Abingdon, UK).
The valence states and the elemental proportions of samples were analyzed by X-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific, Waltham, MA, USA) on a Thermo ESCALAB 250 with Al Kα (hv = 1486.8 eV) as the excitation source. C1s was used as the internal reference to calibrate electron energies.

Temperature-programmed reduction (H$_2$-TPR) experiments were carried out in a CHEMBET-3000 apparatus prior to the measurement, and 200 mg catalyst was put into the quartz reactor and pretreated in air at 300 °C for 0.5 h. After being cooled to room temperature, the catalyst was raised from room temperature to 900 °C under H$_2$ flow (5 vol.% in Ar, 40 mL/min) at a heating rate of 15 °C/min. A gas chromatograph (TCD) (Shimadzu, GC-14C, Kyoto, Japan) was used to record and analyze data.

3. Results and Discussion

3.1. Catalytic Activity Evaluation

The catalytic activity of the CeO$_2$ supports and Pd/CeO$_2$ catalysts is shown in Figure 1. The results show that the performance of three different CeO$_2$ samples was obviously different, which indicated that the ability of CeO$_2$ was closely related to the preparation method. The catalytic combustion activity of benzene followed the sequence CeO$_2$-DC > CeO$_2$-MOF > CeO$_2$-P. The conversion rate of CeO$_2$-DC for benzene reached 91.7% at 320 °C. After loading Pd, the catalytic combustion ability of benzene was significantly improved. All the catalysts showed better catalytic ability than single CeO$_2$, indicating that the active component of PdO$_x$ plays an important role in benzene catalytic combustion. Catalytic activity decreases in the following order: Pd/CeO$_2$-DC > Pd/CeO$_2$-MOF > Pd/CeO$_2$-P. The complete conversion temperatures of benzene using Pd/CeO$_2$-MOF and Pd/CeO$_2$-P were 280 and 300 °C, respectively. Pd/CeO$_2$-DC showed the best performance of catalytic combustion, which could completely convert benzene at 260 °C. The catalytic activity data of the samples and related catalysts for benzene catalytic combustion are compared in Table S1. Although the Pd/CeO$_2$ catalyst synthesized by Guo et al. can achieve 90% benzene catalytic combustion at 187 °C, they used a higher content of Pd (2 wt.%) than Pd/CeO$_2$-DC [34]. Therefore, considering the comprehensive cost, Pd/CeO$_2$-DC has high application value.

![Figure 1](image.png)

Figure 1. Effect of different CeO$_2$ and Pd/CeO$_2$ on catalytic combustion of benzene.
CeO₂ will lead to the formation of surface lattice defects and the generation of reactive oxygen species [33]. However, no diffraction peak for the PdOₓ phase could be found, which may be attributed to the low loading content and the high dispersion of Pd.

3.2. Durability Test

The temperature of the conversion rate at 52% was selected for the life test of the catalyst. Figure 2 shows the results of the durability test of Pd/CeO₂-DC at 190 °C. After 100 h of reaction, the activity of the catalyst remained at approximately 49%, with no obvious decrease. It exhibited exceptional stable catalytic activity. Industrial chlorine-containing VOCs and water were widely distributed in waste gases. Figure 2 shows that when 3 vol.% water was added, its catalytic activity decreased because of competitive adsorption [38]. After introducing chlorobenzene at 100 ppm into the system, the catalytic activity further decreased. However, after water vapor and chlorobenzene were removed, the activity of the catalyst returned to its original level. The results show that the Pd/CeO₂-DC catalyst had a certain ability to resist chlorine poisoning that may be due to the interaction between PdOₓ and CeO₂-DC, which can timely release the combustion products of chlorobenzene and prevent chlorine poisoning. Meanwhile, it exhibited good resistance to moisture conditions. In addition, the catalyst maintained its catalytic activity over a long reaction time of 100 h.

![Figure 2. Durability test for catalytic combustion of benzene over the 0.2% Pd/CeO₂-DC catalyst.](image)

3.3. XRD Analysis

Figure 3 (XRD patterns of supports and catalysts) shows that the patterns of samples have characteristic diffraction peaks of CeO₂. All samples exhibited several peaks at 28.7°, 33.2°, 47.7°, 56.6°, 59.4°, 69.7°, 77.1° and 79.5°, pointing to the (111), (200), (220), (311), (222), (400), (331) and (420) crystal planes, respectively (JCPDS No. 34-0394) [26]. The XRD spectra of the precursor Ce-MOF are shown in Figure S1. From Figure 3, it can be found that the intensity and FWHM of the diffraction peak are different and decrease in the following order: CeO₂-P > CeO₂-MOF > CeO₂-DC. According to the Scherrer formula, the average particle size of the samples can be calculated as follows: CeO₂-P (34 nm) > CeO₂-MOF (11 nm) > CeO₂-DC (8 nm). This result indicates that CeO₂-DC prepared by direct calcining had the smallest particle size. As shown in Figure 3, it can be concluded that the crystallinity of CeO₂-P is the highest and that of CeO₂-DC is the lowest. Combined with their particle size, it can be inferred that the smaller the particle size of CeO₂, the poorer the crystallinity. It is well known that the lattice defects of CeO₂ increase with decreasing particle size, so the smaller particle size of CeO₂ will lead to the formation of surface lattice defects and the generation of reactive oxygen species [33].
However, no diffraction peak for the PdOₓ phase could be found, which may be attributed to the low loading content and the high dispersion of Pd.

![XRD patterns of the samples.](image)

**Figure 3.** XRD patterns of the samples.

### 3.4. HRTEM Analysis

Figure 4 shows the morphology and crystal plane structure of CeO₂ supports and their Pd-based catalysts. Figure 4a–c show that all CeO₂ synthesized by different preparation methods have the morphology of nanoparticles and show an irregular shape. The particle sizes of CeO₂-P, CeO₂-DC and CeO₂-MOF were 30–60, 3–10 and 10–30 nm, respectively. It was found that the particle size of CeO₂-DC was significantly smaller than that of CeO₂-P and CeO₂-MOF, which was consistent with the results of XRD analysis. The fine structure of three different Pd/CeO₂ was observed when the resolution was further improved. We can observe the lattice fringes of PdOₓ and CeO₂, as shown in Figure 4d–f. The lattice fringe spacing was calculated by Image J digital micrograph software. For Pd/CeO₂-P, the lattice fringe spacing is 0.215 nm, corresponding to the PdO (110) crystal plane (JCPDS No. 41-1107), and CeO₂-P mainly exposes the (311) and (200) crystal planes. For Pd/CeO₂-DC and Pd/CeO₂-MOF, the lattice fringe spacing is 0.225 nm, corresponding to the Pd (111) crystal plane (JCPDS No. 46-1043); CeO₂-DC mainly exposes (200) crystal planes with a lattice fringe spacing of 0.270 nm; and CeO₂-MOF has two crystal plane spacings of 0.191 and 0.270 nm, corresponding to the (220) and (200) crystal planes. The exposed crystal surface may affect the formation of oxygen vacancies, and different Pd/CeO₂ should have different chemical properties [33]. Through catalytic activity testing, we can assume that the (200) crystal plane of CeO₂ may play an important role in benzene catalytic combustion. The morphology of the recovered catalyst is shown in Figure S2. It can be found that the morphology of the catalyst has no obvious change after use, indicating that the catalyst has good stability.
In addition, the EDS spectrum of Pd/CeO$_2$-DC had Pd, O and Ce signals, as shown in Figure 4g, indicating that the active components of PdO$_x$ have been successfully loaded and highly dispersed in CeO$_2$-DC and the particle size of PdO$_x$ nanoparticles is about 2–3 nm.

3.5. N$_2$ Adsorption/Desorption Analysis

The pore size distribution and $S_{BET}$ of the catalyst have a great influence on the activity of catalytic combustion. It can be measured by N$_2$ adsorption/desorption, and the results are shown in Figure 5. It can be clearly seen in Figure 5a that all the samples showed a type IV isotherm, which indicates that there are mesoporous structures in the materials [39,40]. CeO$_2$-P and CeO$_2$-MOF showed a H3 hysteresis loop appearing at $P/P_0 = 0.4–1.0$, indicating that there are slit-shaped pores in the sample [41]. Additionally, CeO$_2$-DC exhibited a H1 hysteresis loop, indicating that there is a cylindrical order in the sample. The pore size distribution curve is shown in Figure 5b. From the pore size distribution curves, it can be clearly found that the average pore size of CeO$_2$-DC is approximately 11.0–12.7 nm and the $V_P$ is 0.23 cm$^3$/g. Meanwhile, the pore size does not change after loading PdO$_x$ nanoparticles, but the $V_P$ decreases slightly. Table 1 summarizes the physical properties of samples according to the N$_2$ adsorption/desorption isotherms. From Table 1, we can conclude that the $S_{BET}$ of three different CeO$_2$ is arranged as follows: CeO$_2$-MOF > CeO$_2$-DC > CeO$_2$-P. After the introduction of PdO$_x$ nanoparticles, $V_P$ decreased in varying degrees, and some catalysts formed a microporous structure, which may be due to the blockage of the pore channels by PdO$_x$ nanoparticles. However, the $S_{BET}$ of CeO$_2$-DC increases after loading with PdO$_x$ nanoparticles, which may be due to the fact that PdO$_x$ nanoparticles are mainly distributed on the surface of CeO$_2$-DC. The results of EDS in Figure 4g also show that PdO$_x$ is mainly distributed on the surface of CeO$_2$-DC and highly dispersed. Pd/CeO$_2$-DC has the highest $S_{BET}$ (80.4 m$^2$/g) and the largest $V_P$ (0.21 cm$^3$/g) among all catalysts. It is well known that higher $S_{BET}$ and $V_P$ can provide more active sites and promote catalytic activity. The results are consistent with the experimental results of the catalytic combustion performance.

Figure 4. Cont.
Figure 4. HRTEM images: (a) CeO$_2$-P; (b) CeO$_2$-DC; (c) CeO$_2$-MOF; (d) Pd/CeO$_2$-P; (e) Pd/CeO$_2$-DC; (f) Pd/CeO$_2$-MOF; (g) EDS mapping images of Pd/CeO$_2$-DC (The red, green and yellow dots represent O, Ce and Pd elements, respectively).
Figure 5. Textural properties of the samples: (a) N\textsubscript{2} adsorption/desorption isotherms; (b) pore size distributions.

Table 1. Characteristic data of the samples.

| Samples          | $S_{\text{BET}}$ (m$^2$/g) | $A_{\text{mes}}$ (m$^2$/g) | $V_P$ (cm$^3$/g) | $V_{\text{mic}}$ (cm$^3$/g) |
|------------------|-----------------------------|-----------------------------|------------------|-------------------------------|
| CeO$_2$-P        | 10.7                        | 10.7                        | 0.044            | -                             |
| CeO$_2$-DC       | 66.3                        | 66.3                        | 0.23             | -                             |
| CeO$_2$-MOF      | 90.5                        | 90.5                        | 0.14             | -                             |
| Pd/CeO$_2$-P     | 7.7                         | 5.9                         | 0.039            | 0.00074                       |
| Pd/CeO$_2$-DC    | 80.4                        | 77.3                        | 0.21             | 0.00059                       |
| Pd/CeO$_2$-MOF   | 73.8                        | 73.8                        | 0.13             | -                             |

\textsuperscript{a} The BET specific surface area. \textsuperscript{b} Calculated by the BJH method. \textsuperscript{c} Total pore volume estimated at $P/P_0 = 0.99$. \textsuperscript{d} Micropore volume calculated by the t-plot method.

3.6. XPS Analysis

The valence states of the elements on the surfaces of materials can be investigated using the XPS technique. Figure 6a shows the Pd 3d spectra of the catalysts. It was reported that the complex spectrum of Pd 3d can be decomposed into four peaks associated with the two spin orbitals. The peaks
of 339.3–342.9 and 335.3–337.1 eV can be allocated to Pd 3d3/2 and Pd 3d5/2, respectively [30]. It is obvious that Pd⁰ and Pd²⁺ were detected in the prepared Pd/CeO₂-DC and Pd/CeO₂-MOF catalysts, but only Pd²⁺ was detected in the prepared Pd/CeO₂-P catalyst. The percentage of Pd²⁺ species in the catalyst was obtained by calculating the fitted area of Pd²⁺/(Pd²⁺ + Pd⁰). The concentration of Pd²⁺ in catalysts is reduced in the following order: Pd/CeO₂-P (100%) > Pd/CeO₂-DC (71.1%) > Pd/CeO₂-MOF (57.1%). Many researchers found that Pd²⁺ plays an important role in hydrocarbon oxidation, indicating that Pd²⁺ is more active than Pd⁰ in the reaction [42]. However, it is worth noting that compared with other catalysts, Pd/CeO₂-P exhibited relatively low activity, indicating that single Pd²⁺ has a negative effect on benzene catalytic combustion [43].

| Catalyst       | Pd²⁺/(Pd²⁺ + Pd⁰) | Ce³⁺/(Ce³⁺ + Ce⁴⁺) | Pd/CeO₂-P | Pd/CeO₂-DC | Pd/CeO₂-MOF |
|---------------|-------------------|---------------------|-----------|------------|-------------|
| Pd/CeO₂-P     | 100%              | Ce⁴⁺                |           |            |             |
| Pd/CeO₂-DC    | 71.1%             | Ce³⁺/Ce⁴⁺           | Ce³⁺      |            |             |
| Pd/CeO₂-MOF   | 57.1%             | Ce³⁺/(Ce³⁺ + Ce⁴⁺)  |            | Ce³⁺       |             |

**Summary table of XPS characterization result of catalysts.**

Figure 6. XPS spectrum: (a) Pd 3d; (b) Ce 3d.

Figure 6b shows the Ce 3d spectra of the catalysts. Ce mainly exists in the form of Ce³⁺ and Ce⁴⁺ [44]. According to the equation of Ce³⁺/(Ce³⁺ + Ce⁴⁺), the ratio of Ce³⁺ on the catalyst was
calculated based on the peak area. To compare the concentration of Ce$^{3+}$ on the supports and catalysts, the concentration of Ce$^{3+}$ on the CeO$_2$ support was calculated. The results show that the proportion of Ce$^{3+}$/Ce$^{3+} + $ Ce$^{4+}$ on supports is reduced in the following order: CeO$_2$-DC (22.5%) > CeO$_2$-MOF (21.9%) > CeO$_2$-P (17.8%). After loading PdO$_x$, the concentration of Ce$^{3+}$ on the CeO$_2$ surface increased, which indicates that there is a strong interaction between PdO$_x$ and CeO$_2$. Pd/CeO$_2$-DC had the highest proportion of Ce$^{3+}$/Ce$^{3+} + $ Ce$^{4+}$. The proportion of Ce$^{3+}$/Ce$^{3+} + $ Ce$^{4+}$ decreased in the order: Pd/CeO$_2$-DC (24.8%) > Pd/CeO$_2$-MOF (23.1%) > Pd/CeO$_2$-P (18.1%). This was consistent with the higher activity of Pd/CeO$_2$-DC. The corresponding results are listed in Table 2. It has been reported that Ce$^{3+}$ can promote the formation of oxygen vacancies [35]. Therefore, a higher ratio of Ce$^{3+}$ means more oxygen vacancies on the surface of the catalyst, which can promote the interaction between PdO$_x$ and CeO$_2$, which is crucial for redox performance and catalytic activity. It is well known that CeO$_2$ has good oxygen storage performance and oxygen in the CeO$_2$ phase can be moved. Due to the strong interaction between PdO$_x$ and CeO$_2$, Pd/CeO$_2$-DC can transfer oxygen from CeO$_2$ to PdO$_x$, resulting in the appearance of more Ce$^{3+}$ and Pd$^{2+}$. Combined with the data of activity evaluation, it can be found that the difference in activity of Pd/CeO$_2$ catalysts with the same preparation method and the same Pd loading amount is mainly due to the different structure of CeO$_2$. CeO$_2$ prepared by different methods has different particle sizes and exposed crystal planes, which leads to different binding abilities between PdO$_x$ and CeO$_2$, resulting in the change of the valence state of Pd and CeO$_2$ on the catalyst surface, thus affecting the catalytic activity of the catalysts.

**Table 2. Summary table of XPS characterization result of catalysts.**

| Catalyst          | Pd 3d (eV) | Ce 3d (eV) | Pd$^{3+}$/Pd$^{2+}$ + Pd$^{0}$ (%) | Ce$^{3+}$/Ce$^{3+} + $ Ce$^{4+}$ (%) |
|-------------------|------------|------------|-----------------------------------|-----------------------------------|
| Pd/CeO$_2$-P      | 3d$^{3/2}$ | -          | 342.4                             | 883.7, 887.3                      |
|                   | 3d$^{3/2}$ | -          | 336.9                             | 898.6, 901.9                      |
|                   | 3d$^{5/2}$ | -          | 334.8                             | 894.0, 887.0                      |
| Pd/CeO$_2$-DC     | 3d$^{3/2}$ | 340.8      | 342.9                             | 883.2, 889.2, 897.9               |
|                   | 3d$^{5/2}$ | 335        | 337.1                             | 900.8, 907.5, 916.6               |
| Pd/CeO$_2$-MOF    | 3d$^{3/2}$ | 339.3      | 342.2                             | 883.3, 884.8                      |
|                   | 3d$^{5/2}$ | 335.3      | 336.8                             | 898.7, 902.4                      |

### 3.7. H$_2$-TPR Analysis

To study the redox ability of different CeO$_2$ and their Pd/CeO$_2$ catalysts, H$_2$-TPR was used. As shown in Figure 7, CeO$_2$ exhibits one or two reduction peaks at temperatures below 600 °C, which are attributed to the reduction of CeO$_2$ surface oxygen and subsurface oxygen. When the temperature is higher than 800 °C, the CeO$_2$ lattice oxygen is reduced. The total hydrogen consumption follows the sequence CeO$_2$-DC > CeO$_2$-MOF > CeO$_2$-P. The results show that CeO$_2$-DC has the best redox capacity, which is consistent with the catalytic activity. After loading PdO$_x$, a new peak appeared near 100 °C, and the peak disappeared between 423 and 523 °C, which indicates that there is a strong interaction between PdO$_x$ and CeO$_2$ which promotes the reduction of CeO$_2$. The peak at low temperature is caused by the reduction of PdO$_x$ and the co-reduction of oxygen adsorbed on the CeO$_2$ surface. Obviously, although Pd/CeO$_2$-DC shows a small acromion below 100 °C, neither Pd/CeO$_2$-P nor Pd/CeO$_2$-MOF has an acromion, which can be attributed to the strong binding with Pd-O-Ce, resulting in a higher PdO$_x$ reduction temperature. Therefore, the first reduction temperature of Pd/CeO$_2$-DC is the lowest (70 °C); that is, the PdO$_x$ species on CeO$_2$-DC is relatively easy to reduce, which leads to maintaining the palladium metal state and catalytic oxidation of benzene activity. It has been reported that the reducibility of catalysts is closely related to their catalytic activity, and catalysts with lower reduction temperatures usually show higher catalytic activity.
4. Conclusions

In this study, three kinds of CeO₂ were obtained by purchase, calcining of Ce(NO₃)₃·6H₂O and thermal decomposition of Ce-MOF, which exhibited different pore structures, particle sizes and crystal planes. CeO₂-DC had the largest pore volume and the smallest particle size, which promotes the formation of oxygen vacancies. Meanwhile, the Pd/CeO₂ catalysts were synthesized by high-temperature liquid reduction, and Pd/CeO₂-DC showed the best catalytic performance, excellent durability and resistance to poisoning in the catalytic combustion of benzene due to the good properties of CeO₂-DC, which could completely combust benzene at 260 °C. Moreover, the research indicates that the difference in binding ability between the exposed surfaces of CeO₂ and Pd can affect catalytic activity and that CeO₂ with the (200) crystal plane may play an important role in the catalytic combustion of benzene. Furthermore, the increase in the Pd²⁺ proportion can promote the catalytic activity when Pd⁰ and Pd³⁺ exist at the same time. These characteristics indicate that the catalyst has great potential in industrial applications. However, we must realize that although this catalyst has shown high catalytic activity in the laboratory, the industrial environment is more complex and changeable. Therefore, further research in environments with high concentrations and multiple mixed VOCs is urgently required.

Supplementary Materials: The following are available online at http://www.mdpi.com/1996-1944/13/24/5768/s1, Figure S1: The XRD diffraction pattern of the precursor Ce-MOF-120 of CeO₂-MOF, Figure S2: The morphology of recovered Pd/CeO₂-DC catalyst, Table S1: The catalytic activity data of the samples and related catalysts for benzene catalytic combustion.

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