

Article

Catalytic Oxidation of Chlorobenzene over Pd-TiO₂/Pd-Ce/TiO₂ Catalysts

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Abstract: A series of Pd-TiO₂/Pd-Ce/TiO₂ catalysts were prepared by an equal volume impregnation method. The effects of different Pd loadings on the catalytic activity of chlorobenzene (CB) were investigated, and the results showed that the activity of the 0.2%-0.3% Pd/TiO₂ catalyst was optimal. The effect of Ce doping enhanced the catalytic activity of the 0.2% Pd-0.5% Ce/TiO₂ catalyst. The characterization of the catalysts using BET, TEM, H₂-TPR, and O₂-TPD showed that the oxidation capacity was enhanced, and the catalytic oxidation efficiency was improved due to the addition of Ce. Ion chromatography and Gas Chromatography-Mass Spectrometer results showed that small amounts of dichlorobenzene (DCB) and trichlorobenzene (TCB) were formed during the decomposition of CB. The results also indicated that the calcination temperature greatly influenced the catalyst activity and a calcination temperature of 550 °C was the best. The concentration of CB affected its decomposition, but gas hourly space velocity had little effect. H₂-TPR indicated strong metal-support interactions and increased dispersion of PdO in the presence of Ce. HRTEM data showed PdO with a characteristic spacing of 0.26 nm in both 0.2% Pd /TiO₂ and 0.2% Pd-0.5% Ce/TiO₂ catalysts. The average sizes of PdO nanoparticles in the 0.2% Pd/TiO₂ and 0.2% Pd-0.5% Ce/TiO₂ samples were 5.8 and 4.7 nm, respectively. The PdO particles were also deposited on the support and they were separated from each other in both catalysts.

Keywords: chlorobenzene; Pd-TiO₂/Pd-Ce/TiO₂ catalysts; catalytic oxidation; synergistic effect; metal/metal oxide-support interactions

1. Introduction

Volatile organic compounds (VOCs) contribute greatly to air pollution, such as chemical smog and atmospheric haze, and seriously affect the health of the population. Chlorobenzene (CB) is a flammable organic compound that is used in dyes, pesticides, paints, rubber additives, and intermediates in organic synthesis [1–3]. Excessive amounts of atmospheric CB can cause environmental pollution and also affects human health [4,5]. Therefore, increasingly strict regulations have been implemented to control various chlorine-containing VOCs, including CB. Catalytic oxidation techniques have been used to treat environmental CB pollution because of their low reaction temperatures, high purification efficiencies, and low secondary pollution generation [6–9]. The key to catalytic oxidation is to obtain a high activity and stability, and catalysts with few by-products, strong anti-poisoning characteristics, and low prices have been developed [10].

Commercial catalysts for the catalytic oxidation of CB are based on either noble metals or supported transition metal oxides [11]. Many studies [12–15] have reported that noble metal catalysts with good oxidation properties can help reduce the CO selectivity, reduce the temperature of the Deacon reaction, and prevent the accumulation of HCl on the catalyst surface, which can improve the stability of the

catalyst. Bimetallic catalysts commonly show higher catalytic activities, selectivity, and anti-poisoning abilities compared with monometallic materials due to synergistic effects [10,16–21].

Dai et al. [22] studied the catalytic oxidation of CB over Ru/Ti-CeO₂ catalysts and showed that 1% Ru/Ti₅Ce₉₅ and 1% Ru/Ti₁₀Ce₉₀ catalysts reached a conversion rate of 90% at 220 °C. When tested at 225 °C for 100 h, the activity of the catalysts decreased in the first 10 h, and then increased before stabilizing at 90%. Liu [10] studied the catalytic oxidation of CB over noble metal catalysts Pd/TiO₂, Pt/TiO₂, Ru/TiO₂, and Rh/TiO₂, and the results showed that the $T_{90\%}$ of Pd/TiO₂ was 340 °C. In addition, the stability of the active component was increased by adding auxiliaries and reducing the surface area of carbon in the catalyst. F. A. Silva et al. [23] introduced Ce in Pt/Al₂O₃, Pt/Ce/Al₂O₃, and Pd/CeZrO₂/Al₂O₃ catalysts. It was proposed that the doping of Ce increased the thermal stability of Al₂O₃, which increased the dispersion of metals and improved the catalytic activity. The development of low-cost, high-performance catalysts is of great significance for practical industrial applications. Rare earth metals have been introduced into precious metal catalysts, and precious metal-rare earth metal two-way catalytic systems have been used to obtain excellent oxygen storage and release performance. Replacing precious metals with rare earths without reducing the catalytic performance due to a lower precious metal content remains challenging [24–27], and the precious metal loading in previous studies has generally been about 1%. Considering the high price of precious metals, a certain amount of rare earths has been considered to replace precious metals to prevent reducing the catalytic performance, especially at high space velocities. Due to the larger space velocity under actual working conditions, the experimental space velocity has been increased to 30,000 h^{−1} [3,28].

Hence, this work studies the performance of a series of Pd/TiO₂ catalysts and Pd-Ce bimetallic catalysts for the catalytic combustion of CB. The structural characteristics and chemical properties of the prepared catalysts were characterized and analyzed using TEM, BET, H₂-TPR, and O₂-TPD. In addition, the catalytic oxidation activity and reaction conditions of low concentrations of CB were investigated. The catalyst performance was evaluated by analyzing both the catalytic activity and by-product formation.

2. Results and Discussion

2.1. Catalyst Characterization

The nitrogen adsorption-desorption isotherms of TiO₂, 0.2% Pd/TiO₂, and 0.2% Pd-0.5% Ce/TiO₂ are shown in Figure 1. All the isotherms were classified as type IV, and an H3 lag loop appeared at relative pressures (p/p_0) from 0.6 to 1.0, indicating the mesoporous structure of the catalyst [29]. These results indicated the presence of large channel-like pores within a narrow pore size distribution range.

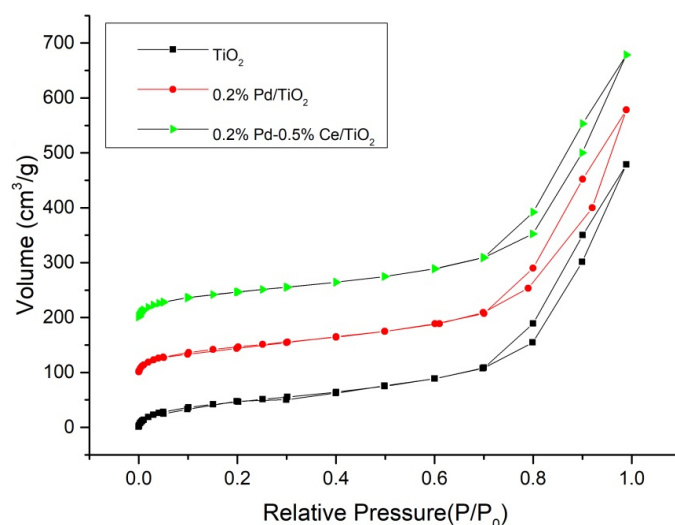


Figure 1. N₂ adsorption-desorption isotherms of TiO₂, 0.2% Pd/TiO₂, and 0.2% Pd-0.5% Ce/TiO₂.

In order to accurately determine the actual content of active components in the catalysts, 0.2% Pd/TiO₂ and 0.2% Pd-0.5% Ce/TiO₂ were selected for ICP-OES analysis. Two parallel samples were tested, and the average value was taken as the test result, which is listed in Table 1.

Table 1. Analytical content result of the catalysts.

Catalyst	Element	Calculated Value (%)	Actual Value (%)
0.2% Pd/TiO ₂	Pd	0.20	0.19
0.2% Pd-0.5% Ce/TiO ₂	Pd	0.20	0.18
	Ce	0.50	0.49

Table 1 shows that the actual loading of Pd and Ce was lower than the calculated loading, possibly because a certain amount of active components was lost during catalyst preparation. The textural parameters of the samples, such as the BET specific surface area, pore volume, and average pore size, are listed in Table 2. In Table 2, S_{BET} , pore volume, and pore size of the supported TiO₂ catalyst were 65.4 m²/g, 0.35 cm³/g, and 21.6 nm, and those of the 0.2% Pd/TiO₂ catalyst were 65.7 m²/g, 0.45 cm³/g, and 27.2 nm, respectively. These values indicated that the addition of Pd increased the specific surface area and pore volume of the catalyst. In addition, the introduction of Ce to 0.2% Pd/TiO₂ effectively increased the specific surface area and pore volume, which likely enhanced the catalytic performance. The effect of the active component addition on the surface morphology of the catalyst was also analyzed.

Table 2. BET surface area and pore structure of catalysts.

Sample	S_{BET} (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)
TiO ₂	65.4	0.35	21.6
0.2% Pd/TiO ₂	65.7	0.45	27.2
0.2% Pd-0.5% Ce/TiO ₂	75.1	0.51	26.9

Figure 2a,b shows representative TEM images of 0.2% Pd/TiO₂ and 0.2% Pd-0.5% Ce/TiO₂ samples, while Figure 2c,d show HRTEM images of 0.2% Pd/TiO₂ and 0.2% Pd-0.5% Ce/TiO₂. Both 0.2% Pd/TiO₂ and 0.2% Pd-0.5% Ce/TiO₂ showed PdO with a characteristic spacing of 0.26 nm. The 0.2% Pd-0.5% Ce/TiO₂ sample showed an expected spacing of 0.34 nm for CeO₂, as also found in the XRD results [30,31]. The average sizes of PdO nanoparticles in the 0.2% Pd/TiO₂ and 0.2% Pd-0.5% Ce/TiO₂ samples were 5.8 and 4.7 nm, respectively, indicating that the particle size of the PdO noticeably decreased after the addition of CeO₂, which improved the catalytic reaction [32]. Besides, from Figure 2, for Pd/TiO₂ and Pd-Ce/TiO₂ catalysts, we can see that the PdO particles were deposited on the support and they are separated from each other.

In addition, PdO exhibited irregular particle shapes. After doping with Ce, the catalyst particle size decreased, and the dispersion became more uniform, which indicated that the doping of Ce improved the dispersion of PdO. During catalyst preparation, pores were simultaneously formed in the shell and core. The presence of mesopores and cavities may facilitate more efficient transport of CB through the pores to reach active sites, which can improve the catalytic activity.

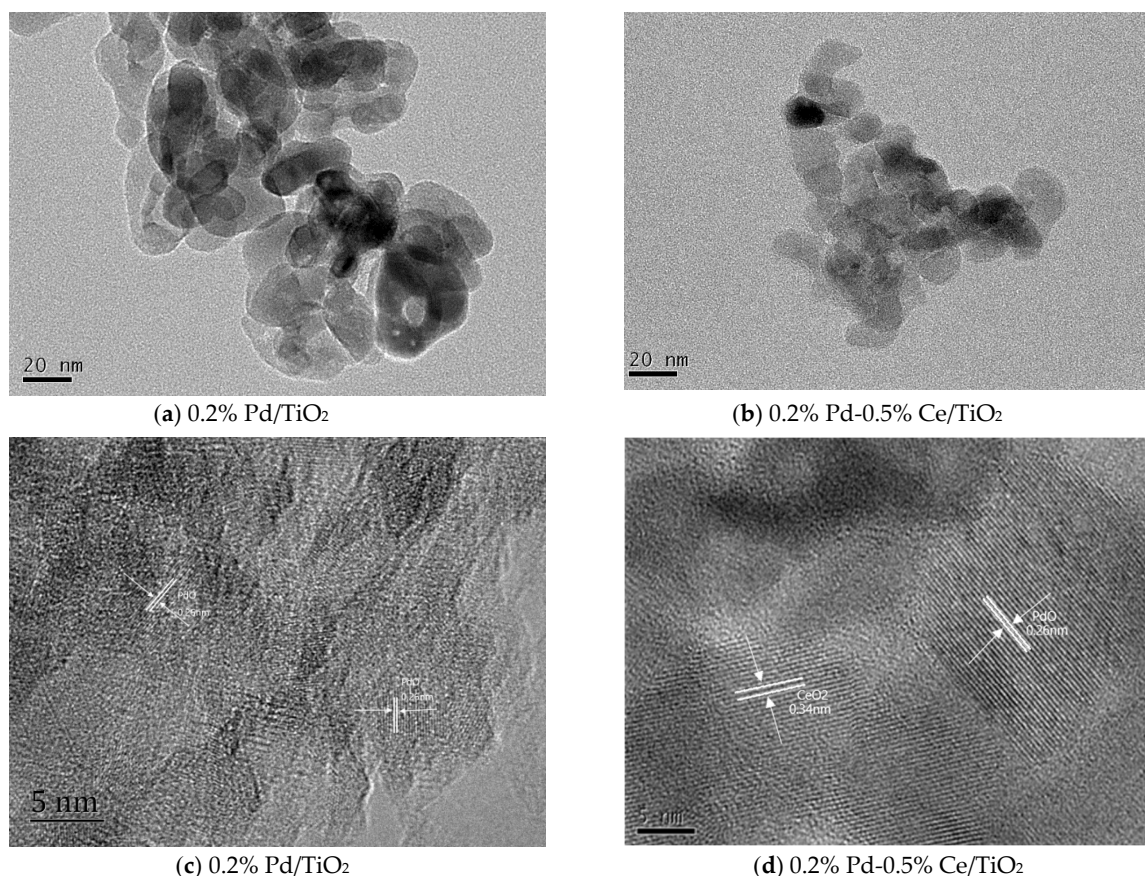


Figure 2. TEM images of 0.2% Pd/TiO₂ (a) and 0.2% Pd-0.5% Ce/TiO₂ (b); HRTEM images of 0.2% Pd/TiO₂ (c) and 0.2% Pd-0.5% Ce/TiO₂ (d).

Changes in the reductive properties are usually evaluated by H₂ temperature-programmed reduction (TPR), and the resulting TPR profiles can be differentiated both by the integral of the profiles and by a shift in the peak temperature. The former corresponds to the H₂ consumption, while the latter indicates the reducibility of the metal sites. Compared with the support, the TiO₂ reduction peaks shifted to a lower temperature. The H₂-TPR profiles of Pd/TiO₂ and pure TiO₂ catalysts are shown in Figure 3. A reduction peak appeared in the TiO₂ carrier, which corresponded to TiO₂ reduction at 429 °C, indicating that the carrier itself possessed a certain catalytic activity. The addition of Pd helped decrease other oxidation processes [33]. Two reduction peaks appeared in the Pd/TiO₂ catalyst, and the peak at 237 °C was attributed to the reduction of PdO. This temperature was higher than that reported in the literature, possibly due to strong interactions between PdO and the TiO₂ carrier. As the Pd loading increased, the PdO reduction peak strengthened, the peak area increased, and the TiO₂ reduction peak appeared forward. The H₂ consumption increased upon increasing the Pd loading. When the Pd content in the Pd/TiO₂ catalyst reached 0.4%, the PdO reduction peak overlapped with the TiO₂ reduction peak, which coincided with reference 34 [34]. The catalytic activity was closely related to the H₂-TPR test results. If the catalyst was easily reduced, it had a relatively high oxygen mobility, which resulted in a relatively high oxidation activity. According to the peak fitting results, 0.2% Pd/TiO₂ and 0.3% Pd/TiO₂ catalysts had the largest reduction peak areas and best theoretical activities, which was consistent with the actual test results.

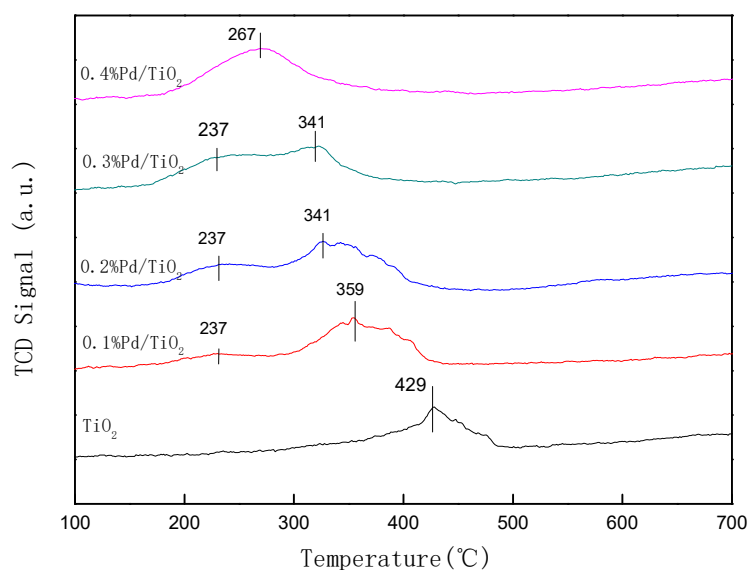


Figure 3. H₂-TPR profiles of Pd/TiO₂ catalysts.

Furthermore, Figure 4 shows that the Pd/TiO₂ catalyst had two reduction peaks in its H₂-TPR profile, the peak at 237 °C was attributed to the reduction of PdO, and the peak at 341 °C was attributed to the reduction of TiO₂. Figure 4 also shows that the PdO and TiO₂ reduction peaks overlapped, and the position of the PdO reduction peak appeared later. According to the position of the peak, it was concluded that the dispersion of precious metal was increased after adding Ce, which also increased the low-temperature activity of the catalyst. In addition, the small peak at 521 °C was attributed to the reduction of highly-dispersed CeO₂ on the surface. Additionally, the active sites reduced at lower temperatures were separate clusters with smaller sizes. The reduction peak area of the catalyst greatly increased below 250 °C, and the reduction peak at approximately 300 °C was fitted to the surface oxygen of CeO₂ and the reduction of secondary surface oxygen [35].

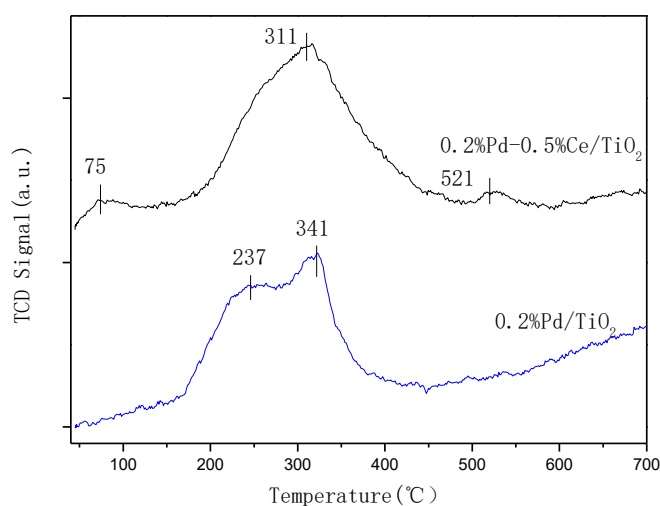


Figure 4. H₂-TPR profiles of Pd-Ce/TiO₂ catalysts.

The O₂-TPD profiles of 0.2% Pd/TiO₂, 0.2% Pd-0.5% Ce/TiO₂, and 0.2% Pd-3% Ce/TiO₂ catalysts are shown in Figure 5. Three different types of desorption peaks were observed in the Pd/TiO₂ catalyst at the starting and ending temperatures (0–800 °C), and desorption peaks appeared at 100, 300–600, and 600–800 °C. In general, physically-adsorbed oxygen species and chemisorbed oxygen species were more easily desorbed than lattice oxygen species, so the desorption peak appearing below 600 °C was

due to catalyst adsorption. The amount of desorbed oxygen corresponded to the number of holes on the surface, and the O vacancies served as a conversion medium between the gas phase oxygen and the lattice oxygen. The desorption peak appearing after 600 °C corresponded to the lattice oxygen.

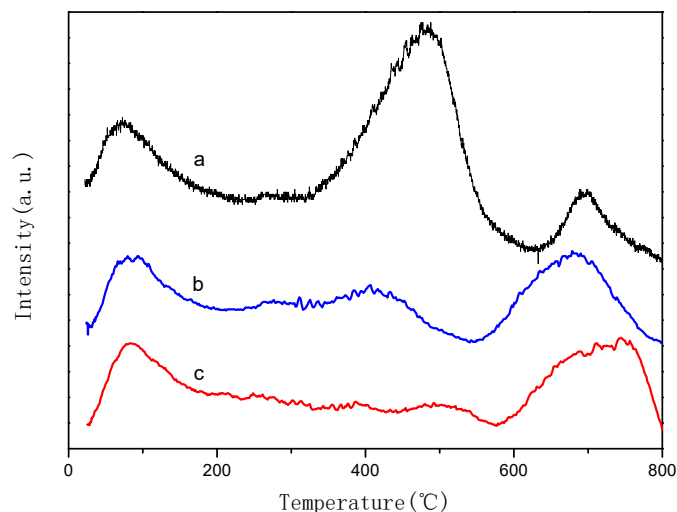


Figure 5. O₂-TPD profiles of (a) 0.2% Pd/TiO₂, (b) 0.2% Pd-0.5% Ce/TiO₂, and (c) 0.2% Pd-3% Ce/TiO₂.

Figure 5 also shows that the introduction of Ce to the 0.2% Pd/TiO₂ catalyst had no significant effect on the physically-adsorbed oxygen near 100 °C, while the surface-adsorbed oxygen from 300–600 °C was significantly decreased. As the Ce content increased, the desorption peak of surface-adsorbed oxygen gradually decreased. Since the CB catalytic experiments were carried out from 200–450 °C, the activity might be affected, but it was still superior to the 0.2% Pd-0.5% Ce/TiO₂ catalyst activity, and the performance of the 0.2% Pd-3% Ce/TiO₂ catalyst was identical. However, after the introduction of Ce, the catalyst exhibited distinct desorption peaks corresponding to lattice oxygen species, and the intensity of the peak increased and appeared earlier. This indicates that the Pd-Ce/TiO₂ catalyst had more lattice oxygen species, as well as a higher oxygen mobility and redox activity.

2.2. Effect of Calcination Temperature on Catalytic Performance

As reported in some literatures [36,37], the calcination temperature can significantly affect the activity and selectivity of catalysts by changing the molecular structures of catalysts. Consequently, the effect of calcination temperature was investigated for the Pd/TiO₂ catalyst. The conversion of CB over Pd/TiO₂ catalysts prepared at different calcination temperatures is shown in Figure 6. Among all Pd/TiO₂ catalysts, the conversion rate of CB first increased and then decreased with the calcination temperature. Figure 6 shows that 500–550 °C was the best calcination temperature, indicating that this catalyst has an optimum specific surface area and pore structure, confirming the critical role of surface Pd/TiO₂ in enhancing the catalytic activity. The catalyst was not sufficiently calcined at low calcination temperatures, which resulted in insufficient exposure of active sites on the surface and a low crystallinity of the active components. Combined, these effects reduced the oxygen storage and active oxygen transfer abilities and led to a low catalytic efficiency. When the calcination temperature was too high, the supported active material was sintered, and the pore structures were collapsed, or small pores were blocked with increased calcination temperature, especially > 550 °C.

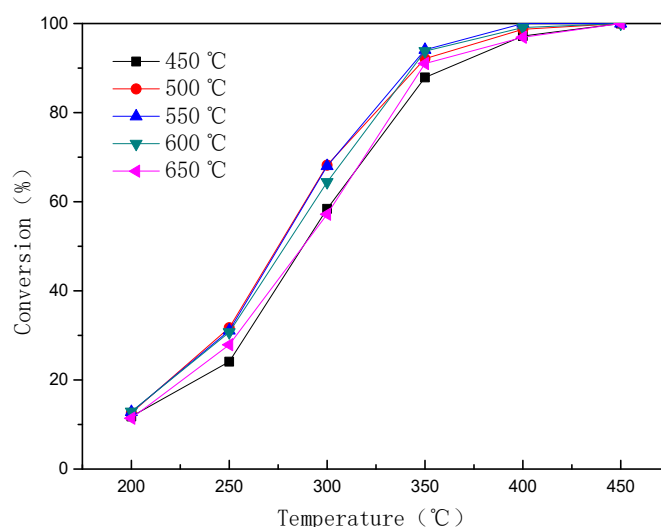


Figure 6. Catalytic oxidation activity of CB using catalysts prepared at different calcination temperatures. CB concentration = 2500 mg/m³; GHSV = 30,000 h⁻¹; catalyst amount = 2 g.

2.3. Effect of Pd Loading on the Catalytic Performance

The catalytic combustion of CB was studied over Pd-based and pure TiO₂ catalysts, and the experimental results are listed in Figure 7. Compared with the pure TiO₂ catalyst, the Pd-based catalysts showed higher activities, and the complete oxidation of CB was achieved below 410 °C over all Pd/TiO₂ catalysts, except for the pure TiO₂ catalyst. The CB conversion rate increased with the reaction temperature. The higher activity of the Pd/TiO₂ catalysts was attributed to the better reducibility of the TiO₂ support (Ti⁴⁺ to Ti³⁺) [11]. A two-step reaction scheme was proposed [38] in which CB is first oxidized by oxygen species supplied by Ti⁴⁺ which is transformed to Ti³⁺; secondly, the previously dissociated oxygen species present on the Pd sites re-oxidize Ti³⁺ to Ti⁴⁺.

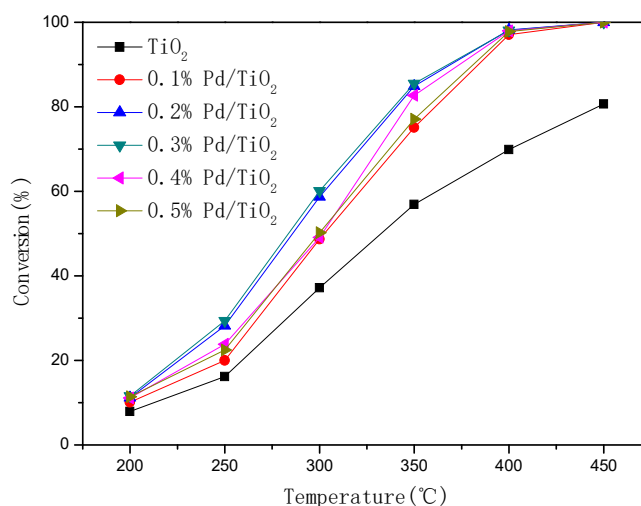


Figure 7. CB conversion of the x% Pd/TiO₂ catalysts with different Pd content. CB concentration = 2500 mg/m³; GHSV = 30,000 h⁻¹; catalyst amount = 2 g.

Moreover, the catalytic activities first increased and then decreased upon increasing the Pd loading, and the highest CB oxidation was achieved at Pd loadings of 0.2%–0.3%. The T_{50} was about 270–280 °C, and the T_{90} was about 370 °C, but the two kinds of catalysts showed negligible differences. However, it was found that the 0.1% Pd/TiO₂ catalyst showed a lower activity from 200 to 450 °C, which was ascribed to partial deactivation due to the lower PdO content. This shows that more active ingredients

provide more active sites, which facilitates the reaction. However, the maximum loading was not achieved because when the active component loading exceeded the dispersion threshold, excess crystal phase covered the active sites and the catalyst surface pores, which hindered the reaction progress and decreased the catalytic activity.

2.4. Effect of Ce Doping on the Pd/TiO₂ Catalyst

To test the effect of Ce loading on the catalytic activity of the Pd/TiO₂ catalyst and further reduce the precious metal content, 0.2% Pd/TiO₂ catalyst was investigated, and the influence of different Ce loadings on the 0.2% Pd/TiO₂ catalyst performance was also investigated. CeO₂ plays an important role as a co-catalyst in the catalytic combustion of chlorinated volatile organic compounds (CVOCs), because Ce has two stable oxidation states (Ce⁴⁺ and Ce³⁺), which allows oxygen to be stored and released by redox conversion between Ce⁴⁺ and Ce³⁺ [39,40]. The catalysts doped with CeO₂ have more mobile active oxygen species, so they have higher catalytic activities.

The catalytic combustion of CB was studied over Pd-Ce/TiO₂ and Pd/TiO₂ catalysts, and the experimental results are listed in Figure 8. Compared with the 0.2% Pd/TiO₂ catalyst, the 0.2% Pd-0.5% Ce/TiO₂ catalyst had a higher activity, and its T_{50} and T_{90} were 270 °C and 340 °C, respectively. The catalytic activity decreased with increasing Ce loading. The catalytic activity of the 0.2% Pd-0.5% Ce/TiO₂ catalyst was 67% at 300 °C, while the conversion on the 0.2% Pd-4% Ce/TiO₂ catalyst was only 49%. The lower activity may be due to Ce covering the precious metal Pd and occupying active sites. However, the addition of Ce significantly improved the thermal stability of the catalysts.

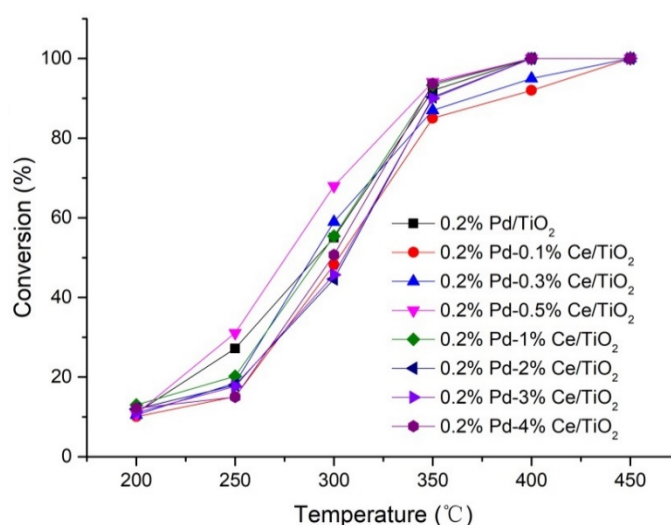


Figure 8. Effect of Ce loading on the catalytic oxidation of CB of 0.2% Pd/TiO₂. CB concentration = 2500 mg/m³; GHSV = 30,000 h⁻¹; catalyst amount = 2 g.

2.5. Effect of Inlet CB Concentration and Space Velocity on Catalytic Performance

The activity of the 0.2% Pd-0.5% Ce/TiO₂ catalyst was evaluated with the catalytic combustion reaction of CB under different inlet concentrations and space velocities, and the results are presented in Figures 9 and 10, respectively. As indicated in Figure 9, the conversion of CB decreased upon increasing the CB concentration, and complete conversion was achieved at 450 °C for all CB concentrations. This is important to the industrial use of these catalysts because the concentration of pollutants in actual working conditions is usually unstable. Upon increasing the initial CB concentration, the conversion of CB decreased at the same temperature, and the conversion curve gradually shifted towards a higher temperature, indicating that more molecules were converted at higher temperatures.

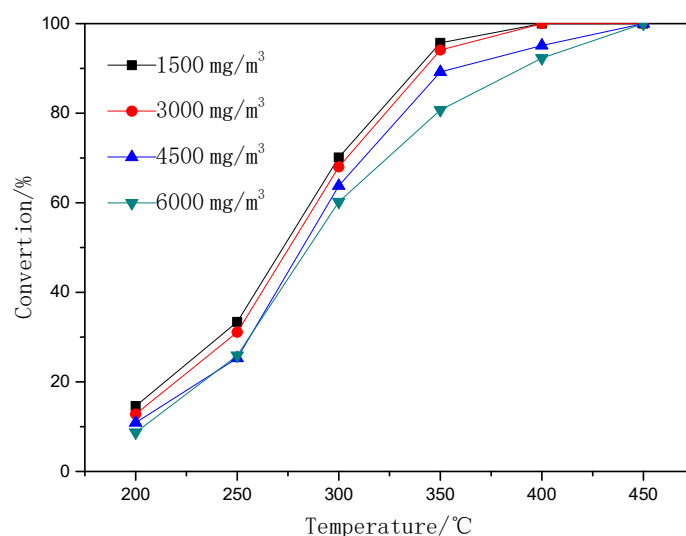


Figure 9. Catalytic oxidation of CB at different CB concentrations.

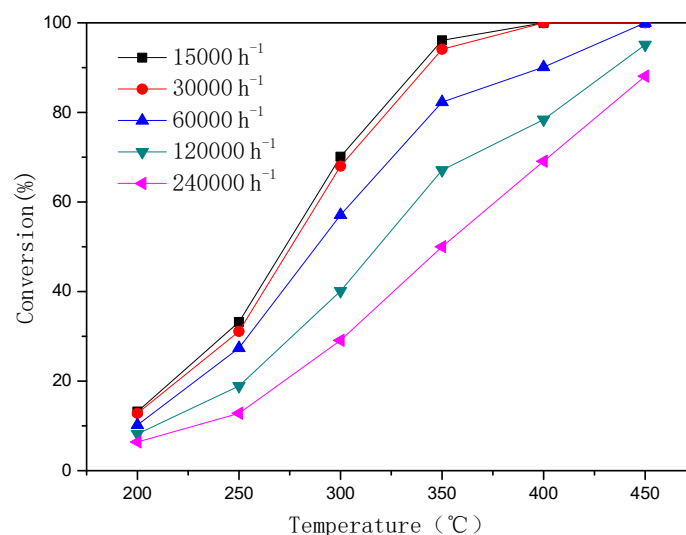


Figure 10. Catalytic oxidation of CB at different GHSVs.

Additionally, the conversion of CB decreased upon increasing the space velocity because the residence time for feed molecules through the catalyst bed decreased upon increasing the space velocity. A suitably high temperature is needed to achieve a sufficient conversion at higher space velocities. In our experiment, the highest CB conversion was only 85% when the space velocity was 240,000 h⁻¹. In addition, when the space velocity was lower than 30,000 h⁻¹, changing the space velocity had little effect on the catalytic activity of the CB conversion. This indicated that when the space velocity was low, the influence of extra molecular diffusion on the catalytic reaction process was eliminated. When the space velocity was higher than 30,000 h⁻¹, the reaction time between the CB mixed gas and the catalyst became shorter, the catalytic reaction was incomplete, and the catalytic activity decreased. Therefore, the best CB conversion could be obtained when the space velocity was 30,000 h⁻¹ in our experiment.

2.6. By-Product Generation in the Gas Effluent

Cl_{ad} served as the active Cl species to form HCl, Cl₂, or Cl-containing by-products during chlorination [10]. Thus, in this experiment, Cl_{ad} was detected with the absorption method. Figure 11 shows that the selectivity of Cl⁻ increased upon increasing the reaction temperature, and the selectivity of the 0.2% Pd-0.5% Ce/TiO₂ catalyst was higher than that of the 0.2% Pd/TiO₂ catalyst. At all reaction

temperatures, the highest Cl^- selectivity of the 0.2% Pd/TiO₂ catalyst was 15.3%, and that of the 0.2% Pd-0.5% Ce/TiO₂ catalyst was 16.2%. The low selectivity of Cl^- may have been due to the trapping method of gas effluent or the low concentration of inorganic Cl^- .

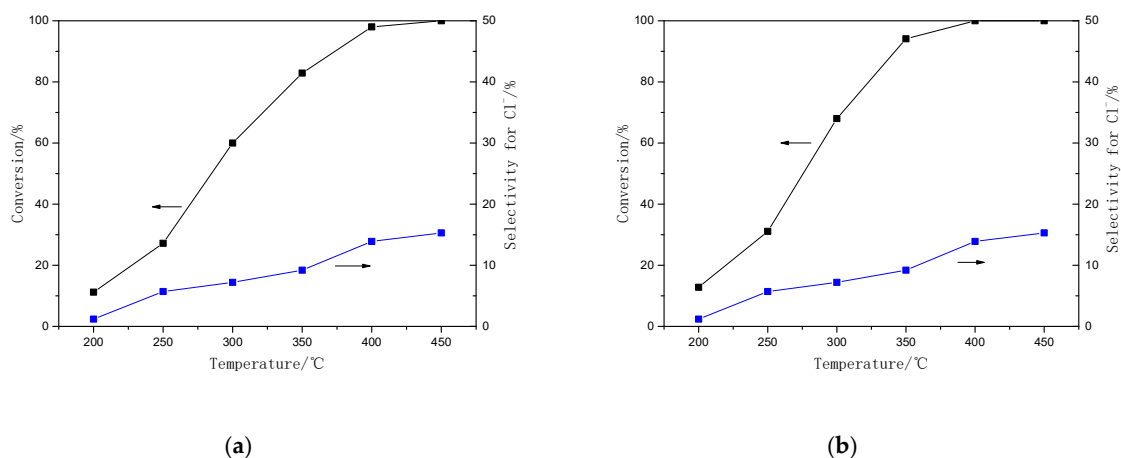


Figure 11. Cl^- selectivity over two catalysts. (a) 0.2% Pd/TiO₂; (b) 0.2% Pd-0.5% Ce/TiO₂

To evaluate the generation of organic by-products, GC-MS was employed. The outlet gas was collected using an adsorption column for 30 min, followed by degassing the column in a thermal analyzer equipped with a GC-MS. Figure 12 and Table 3 show that during the catalytic oxidation of CB by the Pd/TiO₂ catalyst, polychlorinated benzene by-products were detected above 300 °C. Dichlorobenzene (DCB) was produced from 300 to 350 °C, and trichlorobenzene (TCB) was produced at 400 °C. The Pd-Ce/TiO₂ catalyst detected DCB from the beginning of the catalytic oxidation of the CB reaction, and DCB and TCB from 350 to 400 °C. As the temperature continued to increase, the by-products were no longer observed. According to the formation of organic by-products, it was suspected that when the catalytic temperature was low, the catalytic reaction was incomplete, and the C–Cl bond was broken. However, the Cl species reacted with CB on the catalyst surface to form a DCB or TCB by-products. When the temperature was continuously increased to 450 °C, the by-products were not detected, but the formation conditions of polychlorobenzene are worth exploring. The immediate removal of Cl species was the key to studying the CB catalysts.

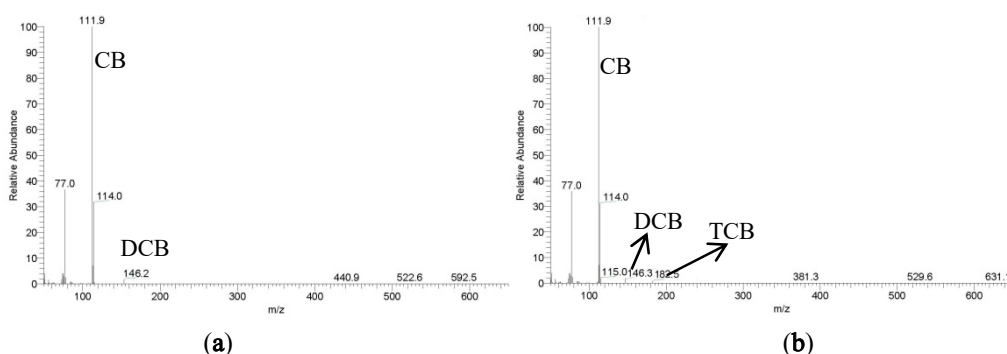


Figure 12. Organic by-products in the outlet effluents (350 °C). (a) 0.2% Pd/TiO₂; (b) 0.2% Pd 0.5% Ce/TiO₂.

Table 3. Formation of organic by-products at different temperatures.

	200 °C	250 °C	300 °C	350 °C	400 °C	450 °C	500 °C
0.2% Pd/TiO ₂	-	-	DCB	DCB	DCB/TCB	-	-
0.2% Pd-0.5% Ce/TiO ₂	DCB	DCB	DCB	DCB/TCB	DCB/TCB	-	-

In order to analyze the CO₂ selectivity of the catalysts, the CO_x (CO₂ and CO) yields were also collected. As shown in Figure 13, at 250 °C, the CO production and selectivity were the highest, at nearly 8%. However, when the temperature increased to 400 °C, no CO was detected, indicating that during CB catalysis, CO was formed and was oxidized to CO₂ at high temperatures and aerobic conditions. The amount and selectivity of CO₂ also increased with increasing temperature. At 200 °C, the selectivity of CO₂ was only about 30%, and after the temperature reached 400 °C, the selectivity of CO₂ was over 80%. As the catalytic temperature increased, the catalytic reaction proceeded more completely. The results were not significantly different from the CO₂ selectivity measured in the literature. In addition, the CO₂ selectivity was slightly higher after the addition of Ce.

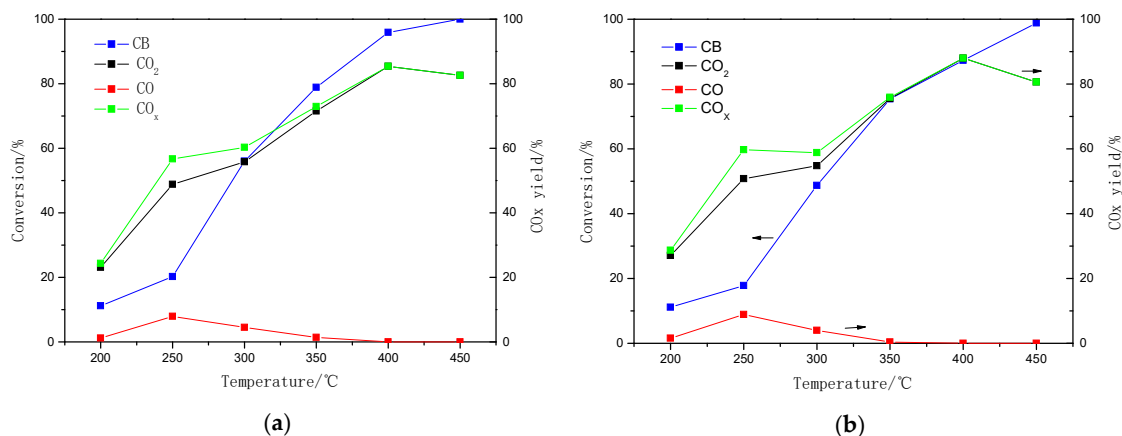


Figure 13. The CO_x selectivity over Pd-Ce/TiO₂ catalysts. (a) 0.2% Pd/TiO₂; (b) 0.2% Pd 0.5% Ce/TiO₂.

3. Experimental

3.1. Catalysts Preparation

Pd/TiO₂ catalysts with different Pd contents were prepared by an impregnation method. A quantitative palladium chloride solution was mixed in deionized water, and TiO₂ powder was slowly added as a carrier. The mixture was ultrasonically stirred for 3 h in a water bath at 60 °C, and the viscous solid was obtained. The mixture was dried in an oven at 105 °C for 2 h and then calcined in a muffle furnace at 550 °C for 3 h. The calcined material was naturally cooled, ground, pulverized, and sieved to 20–40 mesh for use.

Pd-Ce/TiO₂ catalysts with different Ce contents were prepared by an impregnation method. TiO₂ powder was added to a certain volume of Ce(NO₃)₃ and PdCl₂ solution, and then ultrasonically stirred for 3 h in a 60 °C water bath until the solution was viscous. Then, it was dried at 105 °C for 2 h and calcined in a muffle furnace at 550 °C for 3 h. The calcined material was naturally cooled, grounded, pulverized, and sieved to 20–40 mesh for use.

3.2. Catalysts Characterization

The specific surface area and pore structure of the catalysts were characterized by N₂ adsorption at 77 K using an automatic surface area and porosity analyzer (ASAP 2020, Micromeritics, Atlanta, GA, USA). The specific surface area, pore volume, and pore size of the samples were determined by the BET method and the BJH method. Hydrogen temperature-programmed reduction (H₂-TPR) was carried out on a chemisorption analyzer (PCA-1200, Beijing, China) with a flow-type reactor. Oxygen temperature-programmed oxidation (O₂-TPO) was carried out on a ChemBET Pulsar TPR/TPD chemical adsorption instrument (Quantachrome, Boynton Beach, FL, USA). Transmission electron microscopy (TEM) characterization was performed on a transmission electron microscope (H-800, Hitachi, Tokyo, Japan). ICP-OES analysis was carried out on an atomic emission spectrometer (IRIS Intrepid ER/S, Thermo, Waltham, MA, USA).

3.3. Catalytic Activity Measurement

Catalytic combustion reactions were carried out in a tubular quartz fixed-bed reactor (inner diameter 19 mm, outer diameter 22 mm) at atmospheric pressure. The raw material gas was purged from the dry air, and the mixed air was arranged in the bottle. Catalyst (2 g) was placed in the constant-temperature zone of the reactor with high-temperature-resistant quartz wool. The feed flow through the reactor was set at 2 L/min, and the gas hourly space velocity (GHSV) was maintained at 30,000 h⁻¹. The concentration of CB in the reaction feed was set at 2000–3000 mg/m³. The thermocouple, the temperature controller, and the heating electric furnace were combined to control the evaluation. The temperature of the reactor was measured using a thermocouple located at the surface of the catalyst, and the effluent gases were analyzed by an on-line gas chromatograph (GC) equipped with a flame ionization detector (FID) (6890N, Agilent, Palo Alto, CA, USA). Catalytic activity was measured from 200–450 °C and conversion data were calculated by the difference between the inlet and outlet concentrations. Conversion measurements and product profiles were taken after holding for 20 min at each test temperature.

Additionally, mass spectroscopy was used to determine the main intermediates and by-products. At different temperatures, the exhaust gas was absorbed by the absorption bottle containing the NaOH solution and then determined by ion chromatography to obtain the inorganic Cl⁻ concentration in the exhaust gas. The concentrations of CO₂ and CO in the exhaust gas were detected by a flue gas analyzer (Testo350M, Lenzkirch, Germany), and the organic by-products of the reaction were also detected by GC-MS (Trace DSQ, Thermo, Waltham, MA, USA). Intermediate product analysis was performed using electron ionization (EI) mode, 70 eV, and full scan.

4. Conclusions

A series of Pd/Pd-Ce/TiO₂ catalysts were prepared by an impregnation method, and their catalytic activities were analyzed. The activity of 0.2–0.3% Pd/TiO₂ catalysts was optimal. In order to reduce the costs of the catalysts, Ce was introduced into the 0.2% Pd/TiO₂ catalyst. Pd/Ce catalysts with different Pd/Ce mass ratios possessed high activities for the catalytic combustion of CB, and the 0.2% Pd–0.5% Ce/TiO₂ catalyst showed the best catalytic performance. The characterization of the catalyst using BET, TEM, H₂-TPR, and O₂-TPD showed that the oxidation capacity was enhanced and the catalytic oxidation efficiency was improved through the addition of Ce. Additionally, the hydrogen reduction peak shifted to the low-temperature region significantly, indicating a strong interaction between the Pd and the Ce. In addition, the catalytic products were analyzed using ion chromatography and GC-MS, and the results showed that small amounts of DCB and TCB were formed during the decomposition of CB. At the same time, the effects of calcination temperature, inlet CB concentration, and space velocity on the catalytic activity were investigated. The results showed that the calcination temperature had a great influence on the activity of the catalyst, and 550 °C was the best calcination temperature. When the inlet CB concentration was from 1500–6000 mg/m³, the decomposition of CB decreased upon increasing the CB concentration. When the space velocity was from 15,000–30,000 h⁻¹, the GHSV had little effect on the catalytic activity of CB, but the activity gap between the catalysts became more obvious upon increasing the GHSV.

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