

Article

Facile Synthesis of $(\text{NH}_4)_2[\text{Pd}(\text{C}_2\text{O}_4)_2]\cdot 2\text{H}_2\text{O}$ and Its Application as a New Precursor in the Preparation of Pd-Based Catalysts for VOC Oxidation

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Abstract

Developing a water-soluble and chlorine-free palladium compound to replace conventional PdCl_2 or $\text{Pd}(\text{NO}_3)_2$ as the precursor for Pd-based catalysts remains both challenging and of considerable significance for highly efficient degradation of volatile organic compounds (VOCs). Herein, we report a facile synthetic route to such a Pd compound, $(\text{NH}_4)_2[\text{Pd}(\text{C}_2\text{O}_4)_2]\cdot 2\text{H}_2\text{O}$ (denoted as Pd-X5), via a three-step reaction starting from PdCl_2 , under mild and readily controllable conditions, rendering the process amenable to industrial manufacture. The molecular structure of Pd-X5 was confirmed mainly by elemental analysis, FT-IR, and ^{13}C NMR. The overall yield was greater than 95% and the content of residual chloride was reduced to below 100 ppm. Pd-X5 exhibited high water solubility of 350 g L^{-1} . Subsequently, Pd-X5 was used as a catalytic precursor, and a Pd/ Al_2O_3 catalyst was prepared by an impregnation technique and evaluated for its catalytic performance in the degradation of VOCs. Compared with $\text{Pd}(\text{NO}_3)_2$ -derived Pd/ Al_2O_3 , the Pd-X5-based catalyst exhibited markedly enhanced activity for the oxidation of CH_4 and C_3H_8 at different temperatures and under different contents of water vapor, indicating that Pd-X5 is superior to $\text{Pd}(\text{NO}_3)_2$ as a catalytic precursor and has potential application in the production of Pd-based catalysts.

Keywords: $(\text{NH}_4)_2[\text{Pd}(\text{C}_2\text{O}_4)_2]\cdot 2\text{H}_2\text{O}$; water-soluble Pd(II) compound; catalytic precursor; Pd-based catalysts; VOC catalytic oxidation

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1. Introduction

Supported palladium catalysts are widely used in industrial processes, particularly for the oxidation of volatile organic compounds (VOCs) and automobile exhaust [1–6]. Wet impregnation is the most commonly employed preparation method, in which palladium salts serve as precursors for the active phase [7–11]. However, despite the availability of quite a number of commercial Pd compounds, only a few—most notably PdCl_2 and $\text{Pd}(\text{NO}_3)_2$ in acidic media—are suitable for impregnation [12–14]. The physicochemical properties of the precursor strongly influence metal dispersion, chemical state, and, ultimately, catalytic performance, making the proper selection of a precursor critical [15,16].

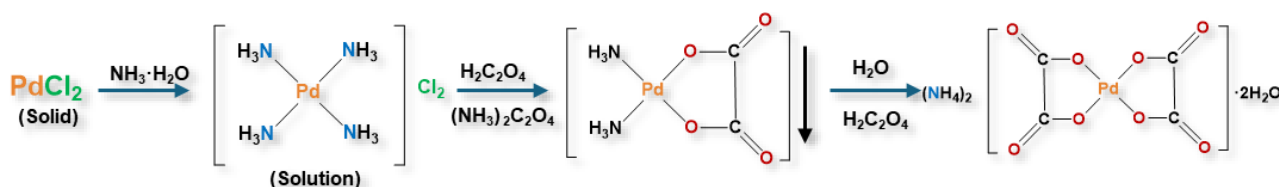
Accordingly, Pd/Al₂O₃ oxidation catalysts for VOC oxidation are typically prepared using Pd(NO₃)₂ [17–20] since chloride ions, even at low contents, will compromise the oxidation activity of palladium [21,22]. Nevertheless, Pd(NO₃)₂ is unstable in water and must be kept and sold in 10% HNO₃ solution, which can corrode the alumina support, disrupt surface modifications, and reduce Pd loading efficiency [23]. In addition, nitrate, mainly from HNO₃, undergoes thermal decomposition during drying and thermal treatment procedures of the catalysts, releasing harmful NO_x-containing gases [24]. Despite their importance, design and synthesis of new Pd catalytic precursors have received comparatively little attention in studies aimed at improving VOC oxidation performance.

(NH₄)₂[Pd(C₂O₄)₂] is a water-soluble palladium compound that is inherently free of chloride and other alkali or heteroatom impurities (e.g., K, Na, Li, P, and S) known to adversely affect palladium dispersion, redox behavior, and catalytic activity [12,25]. Owing to these advantages, (NH₄)₂[Pd(C₂O₄)₂] represents a promising precursor for the preparation of supported Pd catalysts, particularly for oxidation reactions sensitive to halide poisoning. However, previously reported synthetic routes for (NH₄)₂[Pd(C₂O₄)₂] remain confined to laboratory-scale (gram-level) production and typically afford low yields (<75%). Moreover, the residual chloride content in the resulting products often exceeds 0.2 wt%, failing to satisfy the stringent chlorine-free requirements for industrial palladium catalyst manufacture [26]. Therefore, developing a facile synthesis of (NH₄)₂[Pd(C₂O₄)₂] to increase yield, reduce residual chloride, and evaluate its performance as a catalytic precursor is of great importance for advancing Pd-based catalytic technologies.

Herein, a facile three-step synthesis of (NH₄)₂[Pd(C₂O₄)₂]·2H₂O (Pd-X5) from PdCl₂ was developed under mild and controllable conditions, enabling industrial-scale production. Pd-X5 was confirmed by elemental analysis, FT-IR, and ¹³C NMR, affording a yield above 95% with residual chloride below 100 ppm. The compound exhibits high water solubility (350 g L^{−1}), making it well suited to impregnation-based catalyst preparation. Using Pd-X5 as a precursor, Pd/Al₂O₃ catalysts were prepared and evaluated for VOC oxidation. Compared with Pd(NO₃)₂-derived Pd/Al₂O₃, the Pd-X5-based catalyst showed enhanced activity for CH₄ and C₃H₈ oxidation across various temperatures and water vapor concentrations, demonstrating its superiority as a Pd precursor and its potential for industrial Pd-based oxidation catalysts.

2. Results and Discussion

Ammonium bis(oxalato)palladium(II) (Pd-X5) was synthesized via a three-step route, as illustrated in Scheme 1. Specifically, poorly water-soluble PdCl₂ was first dissolved in aqueous ammonia to form a clear solution of [Pd(NH₃)₄]Cl₂. Subsequently, controlled substitution of two coordinated NH₃ ligands in the [Pd(NH₃)₄]²⁺ coordination sphere by one oxalate (C₂O₄^{2−}) anion, assisted by two protons provided by H₂C₂O₄, led to the formation of *cis*-[Pd(NH₃)₂(C₂O₄)], a poorly water-soluble intermediate. Finally, *cis*-[Pd(NH₃)₂(C₂O₄)] was quantitatively dissolved in an aqueous H₂C₂O₄ solution, yielding the target compound (NH₄)₂[Pd(C₂O₄)₂]·2H₂O with an overall yield of 95% based on PdCl₂. The purity of the obtained (NH₄)₂[Pd(C₂O₄)₂]·2H₂O was determined to be 98.6%, and the residual chloride content was as low as 97 ppm, which can be attributed to trace chloride originating from the PdCl₂ starting material.



Scheme 1. Synthetic route of $(\text{NH}_4)_2[\text{Pd}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$.

The structure of $(\text{NH}_4)_2[\text{Pd}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ was characterized by elemental analysis, UV–vis spectroscopy, FT-IR spectroscopy, and NMR spectroscopy (Figures S1–S3). The elemental analysis results were in good agreement with the calculated values. In the UV–vis spectrum, the absorption maximum at 380 nm can be assigned to a $d-d$ electronic transition within the ligand field of the $[\text{Pd}(\text{C}_2\text{O}_4)_2]^{2-}$ complex (Figure S1). The characteristic vibrational bands of $(\text{NH}_4)_2[\text{Pd}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ were observed in the FT-IR spectrum, and coordination of the oxalate ligands to Pd(II) was evidenced by the Pd–O stretching vibration at 569 cm^{-1} (Figure S2). In the ^{13}C NMR spectrum (DMSO- d_6), the carbon atoms of the oxalate ligands resonate as a singlet at 167 ppm [27], while the solvent DMSO accounts for the multiple resonances observed between 38 and 42 ppm (Figure S3). Although ^1H NMR spectroscopy could, in principle, provide evidence for the presence of NH_4^+ cations, the hydrogen atoms in NH_4^+ are highly exchangeable and readily undergo H/D exchange in D_2O , making the characteristic triplet difficult to observe in the ^1H NMR spectrum. Therefore, reliable ^1H NMR characterization of Pd-X5 is challenging. Nevertheless, the presence of NH_4^+ cations in the complex was confirmed by the absorption band at 3246 cm^{-1} in the FT-IR spectrum, which is characteristic of the $\nu(\text{N-H})$ vibration of NH_4^+ (Figure S2).

These chemical and spectroscopic data are fully consistent with the proposed structure of $(\text{NH}_4)_2[\text{Pd}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ (Figure S4). In this complex, the Pd(II) center is coordinated by two bidentate oxalate ligands to form the divalent anionic complex $[\text{Pd}(\text{C}_2\text{O}_4)_2]^{2-}$, with two ammonium cations located outside the coordination sphere.

As an ionic compound, $(\text{NH}_4)_2[\text{Pd}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ exhibits excellent water solubility ($>350\text{ g L}^{-1}$), sufficiently high for the preparation of various supported palladium catalysts. In addition, the compound is stable in both air and aqueous solutions at room temperature. The thermal decomposition behavior of $(\text{NH}_4)_2[\text{Pd}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ was investigated by TG/DTA analysis (Figures 1, S5, and S6). An initial weight loss of approximately 9% was observed between 50 and $115\text{ }^\circ\text{C}$, accompanied by an endothermic peak at around $100.2\text{ }^\circ\text{C}$, corresponding to the removal of two crystallization water molecules. Upon further heating, the complex underwent a two-step thermolysis process, occurring at $152\text{--}223\text{ }^\circ\text{C}$ under an Ar atmosphere and at $156\text{--}178\text{ }^\circ\text{C}$ under a simulated reaction (air) atmosphere. The total weight loss reached approximately 61%, consistent with complete decomposition of the complex, leaving metallic palladium as the final solid product, suggesting that $(\text{NH}_4)_2[\text{Pd}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ undergoes intramolecular self-redox at relatively low temperatures, thereby indicating a favorable profile as a catalytic precursor.

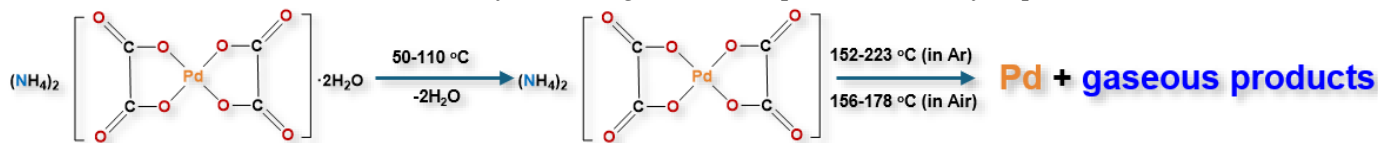


Figure 1. Temperature-dependent evolution of Pd species in Pd-X5 complex.

$\text{Pd}/\text{Al}_2\text{O}_3$, a Pd-based catalyst denoted as Pd-X5 catalyst, was prepared using an impregnation method with $(\text{NH}_4)_2[\text{Pd}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ as the Pd precursor. The detailed preparation procedure is shown in Figure S7. For comparison, a reference $\text{Pd}/\text{Al}_2\text{O}_3$, denoted as the $\text{Pd}(\text{NO}_3)_2$ catalyst, was also prepared by the same method using $\text{Pd}(\text{NO}_3)_2$ as the precursor. Photographs of the two Pd-based catalysts are given in Figure S8. It should be noted that Pd-X5 and $\text{Pd}(\text{NO}_3)_2$ were each formulated into a slurry together with Al_2O_3 powder and subsequently coated onto the ceramic substrate. This preparation route corresponds to that commonly used for commercial three-way oxidation catalysts [28]. The actual Pd loadings of the Pd-X5 and $\text{Pd}(\text{NO}_3)_2$ catalysts were determined by ICP–AES

analysis to be 0.098 wt% and 0.101 wt%, respectively. Further physicochemical characterization was difficult to perform without compromising the overall structural integrity of the two catalysts. Therefore, detailed mechanistic and kinetic investigations are beyond the scope of the present study and will be pursued in future work. The present work focused on the synthesis of a novel, chlorine-free, water-soluble Pd precursor and its application in the preparation of high-performance Pd-based oxidation catalysts.

To examine the influence of Pd precursors on catalytic performance, catalysts derived from two different Pd precursors were evaluated under industrially relevant VOC oxidation conditions over a temperature range of 300–500 °C and under water vapor concentrations of 0–20%. Here, the “0–20 vol% water vapor concentration” refers to the volume percentage relative to the hydrocarbon (or CO) gas. The catalysts were first tested in the oxidation of CH₄ and C₃H₈, two representative and particularly challenging components of VOCs [29–32], and subsequently in CO oxidation. The oxidation products of methane, propane, and CO were analyzed and confirmed to be exclusively CO₂ and H₂O, with no detectable organic byproducts observed, indicating complete oxidation under the investigated reaction conditions.

As shown in Table 1, CH₄ conversion over both Pd-X5- and Pd(NO₃)₂-derived catalysts increased monotonically with increasing temperature but decreased with increasing water vapor content. Notably, the Pd-X5 catalyst consistently exhibited higher CH₄ conversion than the Pd(NO₃)₂ catalyst across the entire temperature range. These results demonstrate that employing Pd-X5 as a precursor significantly enhances the catalytic performance of supported Pd catalysts for CH₄ oxidation. Since water vapor is ubiquitous in VOC-containing gas streams, achieving high low-temperature activity and robust water tolerance remains a major challenge for VOC oxidation catalysts [33,34]. Therefore, the influence of water vapor concentration on the catalytic performance of the Pd-X5 catalyst was further investigated. Although CH₄ conversion over Pd-X5 decreased with increasing water vapor concentration at 350 °C, it remained substantially higher than that of the Pd(NO₃)₂ catalyst under identical conditions. Even at a high water vapor concentration of 20 vol%, the Pd-X5 catalyst retained a CH₄ conversion of 5.1%, whereas the Pd(NO₃)₂ catalyst exhibited nearly zero activity at only 5 vol% water. Across the investigated temperature range, CH₄ conversion over Pd-X5 initially decreased slightly and then stabilized with increasing water vapor concentration, indicating good water tolerance. Moreover, the decline in CH₄ conversion with increasing water vapor over Pd-X5 was significantly less pronounced than that observed for the Pd(NO₃)₂ catalyst. Collectively, these results demonstrate that the Pd-X5 catalyst maintains appreciable activity and superior water tolerance under humid reaction conditions.

Table 1. CH₄ conversion over Pd-X5-derived and Pd(NO₃)₂-derived catalysts.

Temperature (°C)	Water Vapor Concentration (vol%)	CH ₄ Conversion (%)	
		Pd-X5-Derived Catalyst	Pd(NO ₃) ₂ -Derived Catalyst
350	0	25.2	1.8
	5	10.8	0
	10	7.3	0
	15	5.6	0
	20	5.1	0
400	0	47.3	26
	5	27.9	12.2
	10	22.7	10.2
	15	20.2	8.6
	20	18.6	7.8
450	0	72.8	55.4

	5	57.9	40
	10	51.6	34
	15	49.5	28.8
	20	49.3	25.6
500	0	91	77.4
	5	85.3	69.2
	10	83.9	65.2
	15	83.6	61
	20	83.9	57.6

As shown in Table 2, nearly complete C₃H₈ conversion was achieved over the Pd-X5 catalyst at a relatively low temperature of 350 °C under dry conditions (water vapor concentration = 0). Although both Pd-X5 and Pd(NO₃)₂ catalysts reached 100% C₃H₈ conversion at higher temperatures (450 and 500 °C), the Pd-X5 catalyst exhibited superior low-temperature activity. C₃H₈ conversion decreased with increasing water vapor concentration over both catalysts. Nevertheless, the Pd-X5 catalyst maintained a high C₃H₈ conversion of 70.7% at 350 °C even under 20 vol% water vapor, which was significantly higher than that of the Pd(NO₃)₂ catalyst (57.8%) under identical conditions.

Table 2. C₃H₈ conversion over Pd-X5-derived and Pd(NO₃)₂-derived catalysts.

Temperature (°C)	Water Vapor Concentration (vol%)	C ₃ H ₈ Conversion (%)	
		Pd-X5-Derived Catalyst	Pd(NO ₃) ₂ -Derived Catalyst
350	0	98.5	81.7
	5	89.5	59.2
	10	81.3	57.9
	15	75.3	57.9
	20	70.7	57.8
400	0	100	98.9
	5	98.6	96.9
	10	97.3	96
	15	96	95.2
	20	94.9	94.4
450	0	100	99.86
	5	100	99.65
	10	100	99.57
	15	100	99.46
	20	100	99.36
500	0	100	100
	5	100	100
	10	100	100
	15	100	100
	20	100	100

For CO oxidation, the experimental results are summarized in Table 3. Both catalysts exhibited excellent activity, achieving nearly 100% conversion at 350 °C. The presence of water vapor had no apparent effect on catalytic activity within the investigated concentration range. Moreover, no significant difference in performance was observed between the Pd-X5 and Pd(NO₃)₂ catalysts.

Table 3. CO conversion over Pd-X5-derived and Pd(NO₃)₂-derived catalysts.

Temperature (°C)	Water Vapor Concentration (vol%)	CO Conversion (%)
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		Pd-X5-Derived Catalyst	Pd(NO ₃) ₂ -Derived Catalyst
350	0	100	100
	5	99.9	100
	10	99.8	100
	15	99.6	100
	20	99.6	100
400	0	100	100
	5	100	100
	10	99.9	100
	15	99.9	100
	20	99.8	100
450	0	100	100
	5	100	100
	10	99.9	100
	15	99.8	100
	20	99.8	100
500	0	99.9	100
	5	100	100
	10	100	100
	15	100	100
	20	100	100

3. Experimental Section

3.1. General

All commercially available reagents were of analytical grade and used without further purification. PdCl₂ was purchased from Sino-Platinum Co., Ltd. (Kunming, Yunnan province, China). Elemental analyses (C, H, and N) were performed using a Carlo Erba analyzer Carlo Erba (Strumentazione, Milan, Italy), while palladium content was determined by conventional hydrogen reduction gravimetry. Ultraviolet–visible (UV–vis) spectra were collected on a Varian Cary-50 Bio spectrophotometer (Varian, Australia). Fourier Transform Infrared Spectroscopy (FT-IR) spectra were recorded in the 4000–400 cm^{−1} range using KBr pellets on a PerkinElmer 880 spectrometer (PerkinElmer, Waltham, MA, USA). ¹³C NMR spectra were obtained in dimethyl sulfoxide on Bruker AV400 and Avance III 500 MHz spectrometers (Bruker, Germany) to confirm the molecular structures of (NH₄)₂[Pd(C₂O₄)₂]·2H₂O. Thermal analyses (DTA/TG) were conducted using a Netzsch STA 449 F1 instrument (NETZSCH-Gerätebau GmbH, Selb, Germany). The actual Pd loadings of the Pd-X5 and Pd(NO₃)₂ catalysts were determined by inductively coupled plasma atomic emission spectroscopy (ICP–AES, Varian 710-ES). In addition, ion chromatography (IC, Thermo Fisher ICS-600 Thermo Fisher Scientific, Waltham, MA, USA) was employed to quantify chloride ions in the (NH₄)₂[Pd(C₂O₄)₂]·2H₂O precursor.

3.2. Synthesis of (NH₄)₂[Pd(C₂O₄)₂]·2H₂O

To a suspension of PdCl₂ (100 g, 0.565 mol) in 220 mL of ultrapure water at 60 °C, 180 mL of aqueous ammonia was added slowly. The mixture was stirred at 60 °C for approximately 2 h, during which almost all PdCl₂ dissolved, forming a yellowish solution. The solution was evaporated under reduced pressure to near dryness to remove excess ammonia and then redissolved in 500 mL of ultrapure water and filtered through a 0.2 μm membrane filter to afford a clear [Pd(NH₃)₄]Cl₂ solution.

A mixed aqueous solution containing H₂C₂O₄·2H₂O (0.565 mol) and (NH₄)₂C₂O₄·H₂O (0.565 mol) was added dropwise to the [Pd(NH₃)₄]Cl₂ solution under continuous stirring at 60 °C. The reaction was maintained for 5 h, during which a yellowish precipitate of *cis*-

$[\text{Pd}(\text{NH}_3)_2(\text{C}_2\text{O}_4)]$ gradually formed. The product was collected by filtration, thoroughly washed with ultrapure water, and dried at 60 °C for 4 h. The isolated yield was 96%, and the Pd content was measured to be 46.2% (calculated: 46.6%).

Subsequently, *cis*- $[\text{Pd}(\text{NH}_3)_2(\text{C}_2\text{O}_4)]$ (120 g, 0.525 mol) was added slowly to 350 mL of an aqueous solution containing $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (66.2 g, 0.525 mol) at 50 °C under continuous stirring. After 1 h, the solid was almost completely dissolved, yielding a deep red solution. Trace insoluble residues were removed by filtration, and the resulting filtrate was freeze-dried to afford a yellowish-brown crystalline product $(\text{NH}_4)_2[\text{Pd}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$, yield: 99% (184 g).

Found % (calculated for $(\text{NH}_4)_2[\text{Pd}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$): C 13.4 (13.6), H 3.42 (3.39), N 7.84 (7.90), Pd 29.6 (30.0). UV-vis: $\lambda_{\text{max}} = 380 \text{ nm}$, $\epsilon = 1.11 \times 10^2 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ (d-d electron transition). IR(cm^{-1} , KBr): 3528, 3464 [vs, $\nu(\text{O-H})$, H_2O], 3246 [w, $\nu(\text{N-H})$, NH_4^+], 1702 [vs, $\nu_{\text{as}}(\text{COO}^-)$], 1410 [(s, $\nu_{\text{as}}(\text{COO}^-)$], 1320, 1256 [vs, $\gamma(\text{COO}^-) + \delta(\text{NH}_4^+)$], 903, 825 [$\gamma(\text{NH}_4^+) + \delta(\text{COO}^-)$], 569 [m, $\nu(\text{Pd-O})$], 483 [m, $\nu(\text{five-membered chelating ring})$]. $^{13}\text{C-NMR}$ (DMSO, 400 MHz, ppm): 167 (COO^-).

3.3. Catalyst Preparation

Pd-based catalysts were prepared using an impregnation method; the preparative process is illustrated in Figure S7 [35]. Typically, 2 g of $\gamma\text{-Al}_2\text{O}_3$ powder, 0.5 g of mordenite powder, 1 g of La-Ce-Zr mixed oxide powder, and 0.0285 g of Pd-X5 were dispersed in 5 mL of ultrapure water to form a homogeneous slurry. A 2 mol L^{-1} $\text{Ba}(\text{OH})_2$ aqueous solution was then added dropwise to the slurry under continuous stirring until the pH reached 5. Subsequently, 5 g of ceramic support was impregnated with the prepared slurry at room temperature. The samples were dried at 100 °C for 1 h and then calcined at 400 °C for 3 h in static air to obtain the catalysts, denoted as Pd-X5 catalysts. For comparison, $\text{Pd}(\text{NO}_3)_2$ -based catalysts were prepared using the same procedure, with $\text{Pd}(\text{NO}_3)_2$ employed as the Pd precursor instead of Pd-X5, denoted as $\text{Pd}(\text{NO}_3)_2$ catalysts.

3.4. Catalytic Tests

The catalytic activities of the Pd-X5 catalyst and $\text{Pd}(\text{NO}_3)_2$ catalyst for VOC oxidation were evaluated in a quartz tubular fixed-bed continuous-flow reactor (8 mm inner diameter, 50 mm length) using 8 g of catalyst per test. The reactions were carried out under different reaction atmospheres at a gas hourly space velocity (GHSV) of 20,000 $\text{mL} \cdot \text{h}^{-1}$.

Three representative reaction atmospheres were employed. The first reaction atmosphere consisted of 1000 ppm CH_4 , 5 vol% O_2 , a controlled concentration of water vapor, and N_2 as the balance gas, corresponding to an $n(\text{CH}_4):n(\text{O}_2)$ ratio of 1:50. The second atmosphere contained 1000 ppm C_3H_8 , 5 vol% O_2 , a controlled concentration of water vapor, and N_2 as the balance gas, with an $n(\text{C}_3\text{H}_8):n(\text{O}_2)$ ratio of 1:50. The third atmosphere comprised 4000 ppm CO , 5 vol% O_2 , a controlled concentration of water vapor, and N_2 as the balance gas, corresponding to an $n(\text{CO}):n(\text{O}_2)$ ratio of 1:12.5. Gas flow rates in each stream were regulated using precalibrated mass flow controllers. The reaction temperature was monitored in real time by a thermocouple inserted directly into the fixed catalyst bed [36].

The reactor effluent was dried using magnesium chloride and subsequently analyzed online by an Agilent 7890A gas chromatograph equipped with two thermal conductivity detectors (TCDs) and a flame ionization detector (FID). The detector temperature was maintained at 393 K and H_2 was used as the carrier gas. The catalytic conversions of CH_4 , C_3H_8 , and CO were calculated according to Equation (1), as described below.

$$\text{Conversion} = \frac{[X]_{\text{in}} - [X]_{\text{out}}}{[X]_{\text{in}}} \quad (1)$$

where $[X]_{in}$ and $[X]_{out}$ are the inlet and outlet concentrations of CH_4 , C_3H_8 , and CO , respectively.

4. Conclusions

In summary, a facile synthetic method was developed for $(NH_4)_2[Pd(C_2O_4)_2] \cdot 2H_2O$ (denoted as Pd-X5) starting from $PdCl_2$, affording a high yield of 95% and reducing the residual chloride content to below 100 ppm. All synthetic steps proceeded under mild and readily controllable conditions, rendering the process suitable for industrial production. Pd-X5 undergoes intramolecular self-redox at relatively low temperatures (156–178 °C) in an air atmosphere, generating metallic palladium and benign gaseous products (NH_3 and CO_2). Compared with $Pd(NO_3)_2$ -derived catalysts, the Pd-X5-based catalyst exhibited significantly enhanced activity and superior water resistance in CH_4 and C_3H_8 oxidation. These results indicate that Pd-X5 is a more suitable catalytic precursor to produce high-performance Pd-based oxidation catalysts. Extensive physicochemical characterization for this industrial catalyst produced from Pd-X5 as a catalytic precursor was not feasible in the present study because it would have compromised its integrity. Nevertheless, our future work will focus on elucidating the structure–activity relationship, reaction mechanism, and kinetic behavior of the Pd-X5-derived catalyst to further reveal the reason for its superior catalytic performance.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/catal16070603/s1>, Figure S1. UV-Vis spectra of Pd-X5 in water ($C=1.17$ mmol/L). Figure S2. IR spectra of Pd-X5 (KBr pellet). Figure S3. ^{13}C NMR spectra of Pd-X5 (in DMSO). Figure S4. Chemical structure of ammonium bis(oxalato)palladium(II), referred to as Pd-X5. Figure S5. DTA/TG curves of Pd-X5 in Ar atmosphere. Figure S6. DTA/TG curves of Pd-X5 in simulated atmosphere. Figure S7. Preparative process of the Pd-based catalyst for VOCs degradation. Figure S8. A picture of Pd-X5 catalyst and $Pd(NO_3)_2$ catalyst.

Author Contributions: Conceptualization, C.Y., W.L. and Y.D.; methodology, Y.F. and J.J.; software, Y.F. and A.G.; validation, G.L. and Q.C.; formal analysis, Y.F. and Y.D.; investigation, Y.F. and C.Y.; resources, Y.F., C.Y. and Y.D.; data curation, Y.F., A.G. and C.Y.; writing—original draft preparation, Y.F.; writing—review and editing, C.Y. and Y.D.; project administration, C.Y. and Y.D.; funding acquisition, C.Y. and Y.D. All authors have read and agreed to the published version of the manuscript.

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