Efficient Reduction of Cr (VI) to Cr (III) over a TiO2-Supported Palladium Catalyst Using Formic Acid as a Reductant

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Abstract: Cr (VI) has been considered to be a harmful environmental pollutant due to its toxicity, mobility and strong oxidation. It has become challenging to remove Cr (VI) from wastewater. In this work, a series of supported palladium-based catalysts were synthesized via a facile wet chemical reduction method. Among all the as-synthesized catalysts, Pd/TiO2 (P25) showed the optimized catalytic activity for the reduction of Cr (VI) to Cr (III) using formic acid (HCOOH) as the reductant. More than 99% of K2Cr2O7 (50 mg/L) was reduced completely within 30 min at 25 °C. The structural properties of the Pd/TiO2 catalyst (such as particle size, hydrophilicity and stability) and the synergetic effect of metal and support played significant roles in the reduction of Cr (VI) to Cr (III). Meanwhile, several pivotal parameters such as Cr (VI) concentration, catalyst loading, HCOOH concentration and temperature were investigated in detail. Furthermore, this catalyst was also active for the reduction of nitro compounds with HCOOH as the reductant at room temperature. Finally, the reasonable reaction mechanism of the Pd/TiO2/HCOOH system for the reduction of Cr (VI) to Cr (III) was put forward.

Keywords: heavy metal; reduction of Cr (VI); Pd/TiO2; formic acid

1. Introduction

Heavy metal pollution is increasingly becoming a major environmental problem because of metals’ non-biodegradability and mobility. The toxicity and biomagnification of heavy metals can detrimentally affect the health of organisms [1,2]. Among many heavy metal pollutants, Cr (VI) is considered to be the third-largest environmental pollution source and the second most abundant heavy metal in hazardous waste due to its acute toxicity, high water solubility and strong oxidation, and is released by industrial and agricultural activities [3,4]. Therefore, the removal of Cr (VI) from water/wastewater is challenging. In contrast, it has been revealed that Cr (III) is relatively more inert and has less toxicity and weaker migration abilities than Cr (VI), and is an essential trace element for humans [5]. In addition, Cr (III) can be removed from waters through the formation of hydroxide species at appropriate pH values [6]. Thus, the conversion of Cr (VI) to Cr (III) is an effective approach to reduce Cr (VI) compounds in the environment.

Nowadays, several strategies are used for reducing Cr (VI) to Cr (III), including chemical [7], electrochemical [8], biological [9–11] and photocatalytic methods [12]. Among all these methods, catalytic reduction is considered to be the most valuable approach and has gained significant interest due to its relatively high activity, selectivity and cost-effectiveness. More importantly, catalytic reduction does not require complex systems [13], large amounts of organic additives or extra energy (such as light, electricity or heat), and can provide mild and safe reaction conditions using various reducing agents,
such as sodium borohydride [14], hydrazine [15], pinacol [16,17], ammonium borane [18] and formic acid [19]. From the perspective of atomic economy and environmental friendliness, formic acid (HCOOH), a green water-soluble chemical obtained from renewable biomass, is regarded as a promising reductant for the reduction of Cr (VI) to Cr (III) [20]. Additionally, compared to other reductants, HCOOH is nontoxic and stable, and can be used as a safe and economical reductant [21,22]. Particularly, in the catalytic reduction reaction, HCOOH can generate H2 and CO2(HCOOH→H2 + CO2), and Cr (VI) can be effectively reduced to Cr (III) by H2 in the presence of catalysts (Cr2O72-+3H2 + 8H+→7H2O +2Cr3+) [23].

The development of efficient catalysts is the key to achieving high catalytic performance in the reduction of Cr (VI) to Cr (III) using HCOOH as water-soluble reducing agents. To date, numerous heterogeneous metal nanoparticles have been shown to perform effectively in the reduction of Cr (VI) [24]. Pd nanoparticles, as the acid-resistant component, are effective active components in HCOOH dehydrogenation. Furthermore, Pd-based catalysts have high activity in many reductions through adsorption and activation of H2 [25,26]. Nevertheless, the preparation processes of Pd-based catalysts are rather complicated, and catalytic activity, stability and atom utilization need to be further improved [27,28]. In principle, it is a common strategy to use a suitable support to improve the catalytic performance of Pd nanoparticles based on support effects. In our work, we took TiO2 as a suitable support for optimizing the catalytic activity of Pd nanoparticles based on its special properties [29–31]: (1) TiO2 is a supporting material in the stabilization of metal nanoparticles against aggregation; (2) TiO2 has good stability and hydrophilicity, which are suitable for the reduction of Cr (VI) in acidic conditions. Motivated by these promising results, we expect that TiO2-supported Pd nanoparticles could achieve high activities in the reduction of Cr (VI) to Cr (III) using HCOOH as water-soluble reducing agents.

In this work, we report the synthesis, characterization and catalytic application of Pd nanoparticles supported by TiO2 for the reduction of Cr (VI) to Cr (III) using HCOOH as the reductant. For comparison, CeO2, ZnO, Al2O3, SiO2, g-C3N4 and Titanium Silicalite (TS-1) were also employed as supports for the Pd nanoparticles’ catalyst in the reduction of Cr (VI) under the same conditions. In comparison with the existing supported palladium-based catalysts, the as-synthesized Pd/TiO2 catalysts, especially Pd/P25, showed a good catalytic ability in the reduction of Cr (VI) to Cr (III). The catalytic stability, and the possible mechanisms in the catalytic reduction of Cr (VI), were also investigated. Furthermore, this catalyst was also active in the reduction of nitro compounds (a class of organic pollutants) with HCOOH as the reductant at room temperature.

2. Results and Discussion

2.1. Characterization of the Prepared Sample

A series of supported palladium-based catalysts were synthesized via a facile wet chemical reduction method with a Pd loading of 1 wt% at room temperature, in which PdCl2 was used as the metal source and NaBH4 was used as the reducing agent. Among all the as-synthesized catalysts, Pd/TiO2(P25) showed the optimized catalytic performance, and therefore, the Pd/TiO2 catalyst was selected as the model catalyst for the detailed characterization. First, X-ray diffraction (XRD) measurements can reveal the characteristic diffraction peaks of the prepared sample (Figures 1 and S1). As shown in Figure 1, the XRD pattern of TiO2 and Pd/TiO2 presented a well-defined P25 crystal, with the characteristic diffraction peaks of anatase (101) and rutile (110), and there were no structural changes after the loading of Pd [32,33]. The absence of any crystal phase containing Pd indicated the presence of highly dispersed and small-sized Pd species in the catalyst, which can provide more active atoms with high surface energy and be conducive to catalytic reaction.
In addition, the Fourier Transform Infra-Red (FTIR) characterization of the P25 and Pd loading on TiO$_2$ with different phases (P25, anatase TiO$_2$, rutile TiO$_2$, and nano TiO$_2$) was conducted (Figures 2a and S2). All spectra showed a wide absorption peak at 500–700 cm$^{-1}$, induced by the characteristic absorption peak of TiO$_2$ [34]. The typical peak at 2300 cm$^{-1}$ corresponded with the telescopic vibration of Ti-O [35]. The peaks at 3400 cm$^{-1}$ and 1600 cm$^{-1}$ originated from the telescopic and bending vibration absorption of hydroxyl, respectively. The prepared sample has rich surface hydroxyl, which can improve hydrophilicity and adaptability to an aqueous solution. No obvious difference was observed in the FTIR spectra of the TiO$_2$ before and after the loading of Pd, indicating the stability of the TiO$_2$. The pure P25 and Pd/TiO$_2$ was further characterized by Raman spectroscopy, and the result is shown in Figure 2b and Figure S3. It is obvious that the characteristic peak signals of TiO$_2$ at 146, 396, 522 and 639 cm$^{-1}$ were enhanced by the Pd loading, which was attributed to the surface plasmon resonance effect between Pd and TiO$_2$ [36,37]. The Raman result confirms that there are intense interactions between Pd and TiO$_2$.

The morphology of the Pd/TiO$_2$ catalyst was observed by Transmission Electron Microscope (TEM), as given in Figure 3a,d. Figure 3a shows the distribution of the separated particles in TiO$_2$; Figure 3b presents a typical TEM image of the Pd/TiO$_2$ catalyst, suggesting that Pd nanoparticles are highly distributed on the surface of TiO$_2$. Further, HRTEM observation was investigated, as typically illustrated in Figure 3c. A lattice fringe spacing of 0.223 nm in the core part can be observed, which is consistent with Pd (111) [38]. The particle size of Pd nanoparticles was measured to be about 2.66 nm (Figure 3d). The element distribution of the prepared Pd/TiO$_2$ catalyst was investigated by TEM-mapping. As shown in Figure 3e,f, the Ti and Pd elements were uniformly distributed. In addition, the corresponding Energy Dispersive X-Ray Spectroscopy (EDX) spectrum showed the existence of the elements Ti and Pd in the catalyst. The percentage of Pd was about 1 wt%,
which is in agreement with the Inductively Coupled Plasma (ICP) result and close to the feed ratio. In short, Pd nanoparticles are evenly coated on the surface of TiO$_2$ nanoparticles.

To gain a deeper insight into the chemical state of the catalyst, the surface elements of the as-prepared Pd/TiO$_2$ catalyst were analyzed by X-ray photoelectron spectroscopy (XPS). The corresponding XPS survey spectrum showed the existence of Ti, O and Pd in the Pd/TiO$_2$ catalyst, as shown in Figure 4a, which is in agreement with the EDX analysis. In Figure 4b, two prominent Ti 2p bands of Pd/TiO$_2$ at 458.69 eV and 464.38 eV can readily be assigned to Ti 2p3/2 and Ti 2p1/2 peaks for pure TiO$_2$, respectively [39]. The split value between Ti 2p3/2 and Ti 2p1/2 was about 5.7 eV, which is consistent with the theoretical value for Ti in TiO$_2$ [39]. Moreover, there was a displacement of about 0.14 eV compared to the Ti 2p signal of pure TiO$_2$. The high-resolution O1s spectra of the Pd/TiO$_2$ catalyst showed two peaks at 529.94 and 531.25 eV, corresponding to the oxygen in TiO$_2$ and hydroxyl group (OH), respectively [40]. Meanwhile, the binding energy of O1s for the
Pd/TiO2 catalyst was lower than that of the TiO2. The change in the binding energy of Ti 2p and O1s before and after loading confirms that there is a charge transfer from TiO2 to Pd, which can improve the electronic properties of the Pd/TiO2 catalyst [41]. The XPS spectra of Pd 3d (Figure 4d) was observed at the Pd 3d5/2 peak at 334.50 eV and the Pd 3d3/2 peak at 339.75 eV, corresponding to the Pd²⁺ species [42]. However, the low intensity peaks at 336.20 eV and 341.30 eV may have originated from Pd⁰, while the presence of Pd²⁺ species may have originated from the surface oxidation of Pd nanoparticles [43].

![Figure 4](image)

Figure 4. (a) XPS survey spectrum and core-level spectra of (b) Ti 2p, (c) O 1s and (d) Pd 3d.

2.2. Catalysts Activity Studies

2.2.1. Evaluation of Catalytic Properties of Cr (VI) Reduction

The catalytic reduction properties of Cr (VI) were monitored by the change in Cr (VI) concentration with an ultraviolet spectrophotometer. As can be seen from Figure 5a, the Pd/TiO2/HCOOH catalytic system showed a good catalytic ability, and the reduction of Cr (VI) occurred in 25 min. To identify the catalytic properties of Pd/TiO2 relating to the reduction of Cr (VI), a series of control experiments were conducted for comparison, and the results are displayed in Figure 5b. Evidently, no reaction occurred in the control experiment (without a catalyst or HCOOH) under the same conditions, suggesting that the reduction of Cr (VI) is difficult to carry out using only HCOOH. Additionally, it was observed that the reduction of Cr (VI) was difficult to initiate using HCOOH and TiO2 with only 0.7% of Cr (VI) being converted within 30 min. Meanwhile, when Pd/TiO2 was used without HCOOH, less than 0.3% of Cr (VI) was converted after 30 min, indicating a negligible catalytic performance. Taken together, the Cr (VI) reduction reaction was carried out through the coordination of HCOOH and Pd/TiO2. In order to select palladium-based catalysts with excellent performance, we tested the catalytic activity of different supported palladium-based catalysts under the same reaction conditions (Figure 4c). Obviously, Pd nanoparticles supported on TiO2 showed the highest catalytic activity in the reduction of Cr (VI) (99% Cr (VI) conversion) under the same reaction conditions, which was much higher than those supported on other catalysts. Meanwhile, we also studied the effect of Pd loading on TiO2 with different phases in the catalytic reduction of Cr (VI) under the same reaction conditions. Figure 5d shows P25, anatase TiO2, rutile TiO2 and nano TiO2 were used as supports, and that the conversion rates of Cr (VI) in 30 min were 99%, 51%,
81% and 34%, respectively, suggesting that P25 acts as the best support for the Pd-catalyzed Cr (VI) reduction. More importantly, the as-prepared Pd/TiO2 catalyst shows an excellent catalytic performance compared with many heterogeneous palladium-based catalysts reported earlier (Table S1). Much literature has proved that TiO2, especially P25, is a promising combination as a support material for the optimization of catalytic activity [33,44]. Therefore, we decided to use P25 as the support for the further investigation of Pd nanoparticles catalysts in the catalytic reduction of Cr (VI).

![Figure 5](image)

Figure 5. (a) UV-vis spectra for the reduction of Cr (VI) to Cr (III) by using HCOOH (K2Cr2O7 50 mg/L, HCOOH 73 μL) with Pd/TiO2 catalyst (10 mg); (b) the control experiment on the catalytic reduction of Cr (VI); (c,d) the effects of different catalysts on the reduction of Cr (VI).

The parameters, such as Cr (VI) concentration, catalyst amount, HCOOH amount and reaction temperature, can affect the catalytic reduction efficiency of Cr (VI). Several critical experimental factors are presented in Figure 6, and the corresponding rate constants are displayed in Figure S4. The effect of the initial Cr (VI) concentration is illustrated in Figure 6a. The time for complete reduction of Cr (VI) dramatically increased as the initial concentration increased from 30 mg/L to 70 mg/L. The corresponding rate constant dropped from 0.147 min\(^{-1}\) to 0.055 min\(^{-1}\), which could be attributed to the need for more active sites the higher the concentrations of Cr (VI). Therefore, a high concentration of Cr (VI) could adversely affect the reduction efficiency.

The amount of catalyst is an important factor that influences the catalytic reaction. The catalytic performance of Pd/TiO2 in the reduction of Cr (VI) was investigated with regard to the amount of catalyst (Figure 6b). It is seen that the reduction efficiency of Cr (VI) increased significantly with increasing amounts of catalyst at room temperature. One can see that the rate constant increased slightly from 0.112 min\(^{-1}\) to 0.178 min\(^{-1}\). This is because the increase in catalyst dosage leads to the corresponding increase in palladium content, which provides more active metal sites for the catalytic reduction of Cr (VI).

Meanwhile, it was found that the HCOOH amount also had a positive effect on the catalytic reduction of Cr (VI). As can be seen from Figure 6c, with the increase in the HCOOH amount, the time required for the complete reduction of Cr (VI) gradually decreased, and the corresponding rate constant gradually increased. This is because as the
amount of HCOOH increases, the amount of H₂ generated by catalytic decomposition increases, the reduction efficiency of Cr (VI) increases and the reaction time shortens.

In addition, the effects of reaction temperature on the reduction of Cr (VI) in the Pd/TiO₂/HCOOH system are presented in Figure 6d. The reduction efficiency of Cr (VI) increased significantly with the environmental temperature. The rate constant was increased from 0.155 to 0.246 min⁻¹ as the reaction temperatures rose from 25 to 35 °C. This is mainly because the higher the reaction temperature, the more conducive it is to the decomposition of HCOOH and reduction of Cr (VI) [45].

![Figure 6](image)

**Figure 6.** Effects of (a) K₂Cr₂O₇ initial concentration, (b) Pd/TiO₂ amount, (c) HCOOH amount \( \text{nmol} \text{Cr₂O₇}^{-}/\text{nmol HCOOH} \), (d) the temperature on Cr (VI) reduction. The temperature-regulated reaction condition: 50 mL, K₂Cr₂O₇ 50 mg/L; HCOOH 109 μL; 15 mg Pd/TiO₂.

### 2.2.2. Pd/TiO₂ Catalyzed the Nitro Compounds Reduction

Nitro compounds, as a kind of common organic pollution, can cause a series of hazards. In this work, the Pd/TiO₂/HCOOH system was extended to the reduction of various nitro compounds, and the results are summarized in Table S2. All nitro compounds were efficiently converted into the corresponding primary amines over Pd/TiO₂ using HCOOH as the reducing agent at room temperature. In addition, we also studied the catalytic degradation of antibiotics. The UV spectrum showed that the catalyst has good degradation efficiency on chloramphenicol, which can be completely degraded within 6 min (Figure S5). This is mainly because palladium-based catalysts can effectively activate formic acid to produce hydrogen species and realize the reduction of nitro compounds [38].

### 2.3. Recyclability of Pd/TiO₂

The reusability of the Pd/TiO₂ was also evaluated. The conversion of Cr (VI) was decreased from 99% to 86% within 30 min after three cycles (Figure S6). The catalytic ability of Pd/TiO₂ decreased, which might come from the leaching of palladium ions from Pd/TiO₂. The structure of the recovered catalyst was measured using XRD and TEM. The results showed that the characteristic diffraction peaks of Pd/TiO₂ were still present (Figure S7), and the aggregation of small catalyst particles occurred (Figure S8). More
importantly, the profile of Ti 2p in used Pd/TiO₂ was quite similar to that of fresh Pd/TiO₂, and no peak shift or additional signal was detected (Figure S9a). In addition, compared with the initial state of the Pd 3d spectrum, the main peak of Pd 3d was consistent with that of the fresh catalyst (Figure S9b). This phenomenon means that a Pd/TiO₂ catalyst has good stability and reusability under reaction conditions.

3. Materials and Methods

3.1. Materials

All reagents of analytical grade or higher purity have not been further purified. The detailed descriptions of reagents are described in the Supplementary Materials.

3.2. Synthesis of Pd/TiO₂(P25)

Pd/TiO₂ with 1% Pd load was prepared by chemical reduction method. Firstly, 1.2 g TiO₂ was added to 80 mL deionized water at room temperature and stirred continuously. Then, 100 mL PdCl₂ (120 mg/L) aqueous solution was added and stirred for 1 h. Sodium hydroxide solution (0.1 M) was added drop by drop until pH was 9.5. After stirring for 2 h, 5 mL of the newly prepared NaBH₄ solution (the molar ratio of NaBH₄ to Pd was 15:1) was quickly added. After mixing for another 3 h, the precipitation was washed with a large amount of deionized water and ethanol until there was no Cl⁻ ion. Finally, the collected samples were dried overnight at 50 °C. Other catalysts were prepared in the same way with 1% palladium loading.

3.3. Characterization

X-ray powder diffractometry (XRD) was used to determine the crystal structure of the product. The X-ray was Cu-Kα line (λ = 1.542 Å, 40 Kv, 30 mV). The diffraction angle was measured as being between 10° and 80° (2θ), and the scanning rate was 5° min⁻¹. The structure of the samples was characterized by Talos F200x (Thermo Fisher Scientific, Waltham, MA, USA) transmission electron microscope, and the dispersivity and morphology of the metal nanoparticles were obtained by transmission electron microscope. X-ray photoelectron spectra (XPS) were acquired using an ESCALAB 250 spectrometer (Thermo Fisher Scientific, Al Kα, hν = 1486.6 eV). The binding energy was corrected by C1 s orbital, which was supposed to be at 284.8 eV. Fourier infrared spectroscopy (FTIR) mainly identifies the structure of the sample by the position and shape of the spectral absorption peak and analyzes the content of each component in the sample according to the intensity of the characteristic absorption peak. All spectra were measured between 400 and 4000 cm⁻¹. Horiba Scientific XlioRATMPLUS laser Raman spectrometer was used in this experiment, and the excitation wavelength was 514.5 nm. The UV-visible absorption spectra of degradation experiments were analyzed by a Shimadzu UV-2450PC spectrophotometer. The nitro compound was reacted, and the conversion rate was analyzed by gas chromatograph (Shimadzu Corporation of Japan, Kyoto, Japan, GC-2010).

3.4. Catalytic Reduction of K₂Cr₂O₇

In a typical process, 73 μL (1.7 × 10⁻³ mol) HCOOH was added to 50 mL K₂Cr₂O₇ (50 mg/L) solution, and stirred at room temperature for 15 min. Then, 10 mg of catalyst was loaded into the above mixed solution under continuous magnetic stirring. All the reaction solutions were taken at regular intervals and filtered with 0.22 μm membrane. The concentration of the residual solution was recorded by a UV-visible spectrophotometer at the maximum absorption wavelength of hexavalent chromium.

3.5. Catalytic Reduction of Nitro Compounds

As in a typical experiment, 1 mmol nitro compounds and 50 mg catalyst were mixed with 5 mL methanol solvent for 3 min at room temperature. Then, 260 μL of HCOOH was loaded into the solution. Subsequently, the reaction mixture was stirred for 30 min. After
the reaction was finished, the solutions were filtered using a filter, and the conversion of the nitro compounds and the primary amine yields were recorded by GC.

4. Conclusions

In this paper, a facile route to synthesize a series of supported palladium-based catalysts via a facile wet chemical reduction method was successfully realized. The resulting as-synthesized Pd/TiO₂ catalysts, especially Pd/P25, were found to have superior catalytic activity in the reduction of Cr (VI) with HCOOH as a reducing agent at room temperature, compared to the majority of the supported palladium-based catalysts in the same reaction, which can be ascribed to the ultrafine particle size of Pd nanoparticles, excellent hydrophilicity of TiO₂ and strong metal–support interactions. Further, the resulting Pd/TiO₂ catalyst possessed great cycling stability throughout the reusability experiments. Additionally, the catalyst also showed excellent catalytic performance in the reduction of nitro compounds using HCOOH as the reductant at room temperature. We believe that the simple design of Pd-based support nanomaterials may be extended as a potential catalyst to effectively remove other environmental pollutants.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/article/10.3390/catal12020179/s1, Table S1: Catalytic efficiency of various catalysts reported in the literature along with the present work for the reduction of Cr (VI) to Cr (III); Figure S1: XRD patterns of different phases TiO₂-supported palladium catalyst; Figure S2: FT-IR spectra of different phases TiO₂-supported palladium catalyst; Figure S3: Raman spectra of different phases TiO₂-supported palladium catalyst; Figure S4: Effects of various parameters (a) K₂Cr₂O₇ initial concentration, (b) Pd/TiO₂ amount, (c) HCOOH amount (nK₂Cr₂O₇:nHCOOH), (d) the temperature on Cr (VI) reduction; Table S2: Catalytic reduction of various nitro compounds to the corresponding primary amines over Pd/TiO₂; Figure S5: Monitoring of HCOOH-mediated reduction of chloramphenicol aqueous solution; Figure S6: Conversion efficiency of Cr (VI) after three cycles; Figure S7: XRD pattern of the Pd/TiO₂ after three runs for the reduction of Cr (VI) to Cr (III) using formic acid (HCOOH) as a reducing agent; Figure S8: TEM image of the Pd/TiO₂ after three runs for the reduction of Cr (VI) to Cr (III) using formic acid (HCOOH) as a reducing agent; Figure S9: XPS core level spectra of Ti 2p (a) and Pd 3d (b) for Pd/TiO₂ after three runs.

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