Codoping of phosphorus and nickel enhance electrocatalytic dechlorination performance of Pd-based catalyst

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Abstract. Chlorinated aromatic compounds are important raw materials or intermediates in many industries, but they are highly toxic and difficult to degrade in the natural environment. Electrocatalytic dechlorination technology can transform chlorinated compounds with high toxicity into substances with low toxicity and easy degradation, so it has broad application prospects. Compared with other metal catalysts, Pd-based catalysts have the highest electrocatalytic dechlorination activity. However, the high price of palladium limits the large-scale application of this technology. Hence, Ni doping strategy was used to reduce the usage of Pd in this paper, Pd-Ni and Pd-Ni-P catalysts were successfully prepared, and electrocatalytic dechlorination performance of 4-chlorophenol was studied. The results showed that the Pd-Ni-P catalyst had the highest dechlorination activity, the mass activity was 1.69 times that of pure palladium catalyst, and the use of Pd was reduced by 26.67%.

1. Introduction

Chlorinated organic compounds are highly toxic, difficult to degrade and widely distributed, which are the priority pollutant in water [1]. Electrochemical wastewater treatment technology is a new technology developed in recent years. Due to its advantages of green, low cost and easy automatic control, it has shown great vitality in the field of water pollution treatment. Compared with electrochemical oxidation, electrochemical reduction technology is more suitable for the treatment of chlorinated organic wastewater. This is because the toxicity of chlorinated organic compounds mainly comes from the chlorine atoms, the chlorinated organic compounds will be converted into hydrocarbons with low toxicity and easy degradation by removing the chlorine atoms.

In recent years, the research results of many scholars have confirmed the feasibility of this technology, and confirmed that Pd catalyst has the highest electrocatalytic reduction dechlorination activity, but the price of Pd is expensive, which limits the large-scale application of this technology. Therefore, this paper prepared Pd-Ni bimetallic catalyst to reduce the use of Pd, and introduced P to improve the electrocatalytic dechlorination activity of Pd-Ni catalyst [2], finally, the electrocatalytic dechlorination catalyst with high activity and low palladium content was successfully prepared, which provided research ideas for the subsequent preparation of low-cost electrocatalytic dechlorination catalyst.
2. Materials and Methods

2.1. Chemical reagents
Palladium acetylacetonate (Pd(acac)₂), oleylamine (OAm), borane-tert-butylamine complex (BTB), nickel acetylacetonate (Ni(acac)₂), trioctylphosphine (TOP), tetrabutylammonium bromide (TBAB), n-hexane, anhydrous ethanol and 4-chlorophenol (4-CP) were purchased from Adams Chemical Co. Ltd., Nafion solution (5 wt.%) were purchased from sigma Aldrich, Toray carbon paper was used as the working electrode substrate in electrocatalytic dechlorination.

2.2. Preparation of nanoparticles catalysts
(1) Preparation of pure Pd NPs catalyst [3], 1.0 mmol of Pd(acac)₂ and 36 mL of OAm were added into a 100 mL three port flask and stirred evenly in argon flow, then heated to 60 ℃ and kept for 30 min. 0.9 g BTB was dissolved into 9 mL OAm and added into the three port flask, then raised the temperature to 90 ℃ and kept for 1 h. The solution after reaction was cooled and centrifuged for precipitation, the pure Pd NPs catalyst was obtained.
(2) Preparation of Pd-Ni NPs catalyst, 1.0 mmol Pd(acac)₂, 0.5 mmol Ni(acac)₂ and 0.5 mmol TBAB were dissolved in a mixture solution of 2 mL OA and 40 mL OAm at room temperature, and the mixture was stirred for 30 min under an argon gas flow. Then, the reaction solution was heated to 270 ℃ with a constant heating rate of 10 ℃ · min⁻¹, and kept at this temperature for 30 min. The resultant solution was cooled down to room temperature, and the Pd-Ni NPs was separated by centrifugation.
(3) Preparation of Pd-Ni-P NPs catalyst, the Pd-Ni-P NPs catalyst was synthesized by one pot method. In short, 20 mL TOP was added into a 100 ml three port flask, and argon was bubbled to remove the air in the flask. Then 0.64 mmol Pd(acac)₂ and 0.32 mmol Ni(acac)₂ were added, stirred and dissolved, then 20 mL OAm was added, and then heated to 300 ℃ for 30 min. After cooling rapidly in air, excess ethanol was added, and the Pd-Ni-P NPs was separated by centrifugation.

2.3. Characterization of catalysts
X-ray diffraction patterns were recorded on an X’Pert PRO MPD system. Transmission electron microscope and Energy dispersive spectroscopy mapping analyses were taken on a JEOL-2100F system. X-ray photoelectron spectroscopy were measured on an AMICUS ESCA 3400. The content of Pd, Ni and P were measured by the Agilent ICP-OES 720.

2.4. Electrocatalytic dechlorination
Electrocatalytic dechlorination experiments were carried out by using three electrodes system, the working electrodes were carbon paper loaded with 6 mg catalyst, the reference electrode were mercurous sulfate electrode and the counter electrode were carbon rod. The cathode electrolyte was a mixed solution of sodium sulfate (50 mmol/L) and 4-chlorophenol (50 mg/L), and the anode electrolyte was sulphuric acid solution (50 mmol/L). All the electrocatalytic dechlorination experiments were carried out under the voltage of - 0.85 V. 0.5 mL cathode electrolyte was taken every 0.5 h to determine the content of 4-CP by high performance liquid chromatography (Waters E2695). The dechlorination efficiency (DE) calculation method was shown in formula (1):

\[ \text{DE} (%) = \frac{(C_0 - C_t)}{C_0} \times 100\% \]  

(1)

where \( C_t \) is 4-CP concentration (mg/L) at time t (h), \( C_0 \) was the initial 4-CP concentration (50 mg/L). A pseudo-first-order kinetic equation was used to describe the electrocatalytic dechlorination of 4-CP:

\[ \ln \frac{C_t}{C_0} = -k \times t + b \]  

(2)

where \( C_t \) denotes the 4-CP concentration at time t and \( C_0 \) is the initial concentration of 4-CP, k is the apparent dechlorination rate constant (h⁻¹). Mass Activity (MA) was the ratio of apparent rate constant to mass of Pd in catalyst, the formula is as follows:
MA (h⁻¹ · mg⁻¹) = k / m                            (3)

where MA is the mass activity (h⁻¹·mg⁻¹), k is the apparent dechlorination rate constant (h⁻¹), m is Pd mass in nanoparticles.

3. Results and discussion

3.1. XRD patterns and TEM images

Figure 1. (a) XRD patterns; TEM images of (b) Pd NPs, (c) Pd-Ni NPs, (d) Pd-Ni-P NPs; electron diffraction patterns (e) and mapping diagrams (f-j) of Pd-Ni-P NPs.

Figure 1a is the XRD patterns of three Pd-based nanoparticles catalysts, the peaks at 39.51°, 45.71°, 66.64° and 80.30° correspond to the 111, 200, 220 and 311 crystal planes of pure Pd. The Pd-Ni NPs catalyst also has four peaks, but they all deviate to high angle, which indicates the successful synthesis of Pd-Ni alloy. There is only one peak in the pattern of Pd-Ni-P NPs catalyst, corresponding to Pd (111) crystal plane, the peaks of 200, 220 and 311 crystal plane of Pd disappeared. This is because phosphorus can induce the transformation of crystalline Pd to amorphous Pd [4], and the crystal structure of pure Pd is destroyed, the electron diffraction pattern of Pd-Ni-P NPs (figure 1e) also confirms this conclusion, which has only Pd (111) diffraction ring. figure 1b-d are the TEM images of the three catalysts, three Pd-based catalysts are all spherical with average sizes of 6.3 nm, 5.9 nm and 5.2 nm, respectively. Figure 1f-j are the mapping element analysis diagrams of Pd-Ni-P NPs catalyst, Pd, Ni and P are evenly distributed in the nanoparticles, indicating the successful synthesis of Pd-Ni-P ternary catalyst.
3.2. XPS spectrum of Pd-Ni-P NPs catalyst

![Figure 2](image)

There are peaks of P 2p, Pd 3d and Ni 2p in the XPS survey spectrum of Pd-Ni-P NPs (figure 2a), which means that Ni and P are successfully doped into Pd nanoparticles, the atomic proportions of the three elements are 9.08%, 7.23% and 8.52% respectively. The ICP results show that the mole ratio of Pd-Ni-P is 2.06/0.83/1.00, while that of Pd-Ni catalyst is 2.11/0.91. In figure 2b, 335.35 eV is the 3d5/2 peak of Pd (0), which is positively shifted by 0.15 eV relative to pure Pd 3d5/2 (335.20 eV), this may be due to the introduction of P, which leads to the shift of Pd electron cloud [5]. The peak at 337.84 eV is 3d5/2 peak of Pd (II) specie, which mainly comes from the reaction of Pd on the surface of nanoparticles with oxygen in air. The peak at 856.60 eV is the 2p3/2 peak of Ni (II) and the peak at 861.95 eV is the satellite peak of Ni in the Ni 2p spectrum (figure 2c). In figure 2d, the peak at 130.10 eV is P species bonded with Ni, and the peak at 133.66 eV is P (V) species, due to the oxidation of phosphorus atoms on the surface of nanoparticles [6].

3.3. Dechlorination performance

Figure 3a shows the electrocatalytic dechlorination efficiency of three Pd-based catalysts. The dechlorination rate of pure Pd NPs catalyst could reach 89.66% after 3 h, but the dechlorination rate decreased slightly after doping Ni, which was 76.83% after 3 h, indicating that Ni was an inert component in the process of electrocatalytic dechlorination. This is because the electrochemical dechlorination of chlorinated aromatic compounds generally follows the indirect reduction mechanism:

\[
\begin{align*}
M + H^+ + e^- & \rightarrow M-H_{ads} \quad (4) \\
M + R-Cl & \rightarrow MCl-R \quad (5) \\
M-H_{ads} + MCl-R & \rightarrow MH-Cl + MH-R \quad (6) \\
MH-Cl & \rightarrow M + HCl \quad (7)
\end{align*}
\]
Figure 3. (a) Dechlorination efficiency, (b) apparent rate constant, (c) mass activity of Pd NPs, Pd-Ni NPs and Pd-Ni-P NPs catalysts; (d) circular stability of Pd-Ni-P NPs catalyst.

MH-R → M + HR (8), M stands for electrocatalyst. Therefore, the electrocatalytic dechlorination catalyst must have the ability to activate H⁺ or H₂O to produce active H_ads, which has strong reducibility and can realize the hydroreduction of chlorinated aromatic organic compounds. According to the research of Pan et al. [7], nickel phosphide has excellent ability to activate H⁺ or water, therefore, the phosphating treatment of nickel may improve the electrocatalytic dechlorination activity of Pd-Ni NPs catalyst. The experimental results confirmed our conjecture that Pd-Ni-P NPs catalyst could completely remove 4-CP within 3 hours, and the introduction of phosphorus could further reduce the amount of precious metal palladium by 26.67%. The pseudo first-order kinetic fitting results show that the apparent rate constants are 0.76 h⁻¹, 0.47 h⁻¹ and 0.95 h⁻¹ for pure Pd NPs, Pd-Ni NPs and Pd-Ni-P NPs catalyst respectively (figure 3b), and the apparent rate constant of Pd-Ni-P NPs catalyst is 1.25 times of pure Pd NPs catalyst. The results of mass activity (figure 3c) also show that the mass activity of Pd-Ni-P catalyst is 1.69 times that of Pd, therefore, the introduction of phosphorus can not only significantly improve the dechlorination rate of Pd-Ni NPs catalyst, but also reduce the use of precious metal Pd. In the actual use of the electrocatalytic dechlorination technology, the stability of catalyst is an important index. In this paper, the Pd-Ni-P NPs catalyst was tested five times, and each time lasting for 3 h (figure 3d). The dechlorination rate of the fifth experiment was 97.35%, which was only 2.65% lower than that of the first experiment, this indicated that Pd-Ni-P NPs catalyst had good stability.

4. Conclusions
Electrocatalytic dechlorination is a promising technology for the treatment of wastewater containing chlorine. However, the high cost of electrocatalyst Pd limits its large-scale industrial application. Doping the second metal is an effective method to reduce the content of palladium in Pd-based catalyst, but the introduction of Ni will reduce the dechlorination activity of Pd. Therefore, the third element is introduced to phosphatize Ni, the dechlorination activity of Pd-Ni catalyst is improved and the amount of Pd used was further reduced, the mass activity of Pd-Ni-P NPs catalyst is 1.69 times that of pure Pd NPs catalyst.

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