



Electrochemical reductive degradation of chlorobenzene using galvanically replaced Pd/Fe nanoscale particles



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HIGHLIGHTS

- Synthesis of Pd/Fe nanoscale particles through electrodeposition and galvanic replacement.
- Enhanced catalytic reduction of chlorobenzene compared to bulk Pd.
- Observed different reactivity from varied forms of hydrogen.
- Proposed conceptual model of dechlorination mechanism in Pd/Fe system.
- Elucidated explanation of synergist effect in Pd/Fe system.

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ABSTRACT

Nanoscale Pd/Fe particles were fabricated on glassy carbon substrates by electrodeposition of Fe and the subsequently underwent galvanic replacement with Pd. Heterostructure was found by various characterizations of Pd/Fe particles. The process of electrochemical reduction of chlorobenzene on Pd/Fe particles were studied by cyclic voltammetry and constant-potential electrolysis. The removal rate of chlorobenzene on Pd/Fe particles reaches up to 90% within 120 min using electrolysis at -0.1 V in 0.1 M H_2SO_4 . Consequently, it shows that nanoscale Pd/Fe particles exhibited higher catalytic activity than bulk Pd for chlorobenzene reduction.

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1. Introduction

There has been much discussion over chlorobenzene (CB), a typical halogenated aromatic compound, owing to its hazardous and enduring properties. When accumulated in human body, it can affect the function of central nervous system and even cause cancer, teratogenesis, mutagenesis [1–3]. Also, the presence of chlorine greatly reduces the activity of and stabilizes the benzene ring, making it harder to be dechlorinated.

Plenty of studies and degradation methods, such as photocatalytic oxidation, Fenton oxidation, H_2O_2 oxidation, Mn catalytic oxidation and ultrasonic oxidation, have been developed in order to reduce the CB effectively [4–11]. Electrochemical degradation method, thanks to its less cost [12] and more efficient treatment, has attracted tremendous attention in recent years [13,14].

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Pd is considered as the preferred electrode material for electrocatalytic hydrogenolysis of CB because it is able to absorb large amounts of hydrogen. Pd nanoparticles are used as opposed to the typical bulk Pd electrode because it has better catalytic ability [15]. Moreover, in comparison with monometallic systems, bimetallic counterparts bear superior catalytic ability. For example, Chen and her coworker claimed to have found significant enhancement in catalytic reduction of nitrobenzene by Fe/Au nanoparticles, while the single Fe nanoparticles were revealed to be much less efficient [16]. So Pd is usually used along with other metals to form bimetallic systems such as Pd/Sn, Pd/Fe, Pd/TiO₂, Pd/Au [17–20]. In the present study, nanoscale Pd/Fe particles were fabricated through cyclic voltammetric deposition of Fe followed by a galvanic replacement reaction with Pd. Recently, Pd nanoparticles or its mixed-metal systems were applied in dechlorination of chlorinated compounds, oxidation of gaseous pollutants, catalysts used for automobile exhaust purification and fuel cell electrodes [21–24]. To the best of our knowledge, it is rarely reported that they are used as electrochemical catalysts to treat hazardous pollutants.

The goal of this paper is to investigate the electrochemical behavior of CB on nanoscale Pd/Fe particles, which are fabricated at the optimal experimental condition. The main objectives are to (1) characterize the nanoscale Pd/Fe particles using spectroscopic techniques, (2) investigate the electrochemical reduction of chlorobenzene in acid electrolytes using Pd/Fe and bulk Pd respectively and compare the different behaviors, and (3) elucidate synergist effect and mechanism of CB reduction on Pd/Fe bimetallic system.

2. Experimental

All the chemicals used were of analytical grade and aqueous solutions were prepared with ultra-pure water (resistivity >18.2 M Ω). The diameter of both Glassy carbon (GC) electrode and bulk Pd electrode is 5 mm (geometric area = 0.196 cm²). All electrodes were polished to a mirror-like surface before application, and then sonicated in ultrapure water. The Fe particles were electrodeposited onto the surface of GC electrode from deoxygenated 0.1 M Na₂SO₄ containing 20 mM FeSO₄ (pH 3.0–3.5), and a cyclic voltammetry program was applied from –0.95 V to –1.25 V (vs. SCE) at a scan rate of 0.025 V/s for 10 cycles. Subsequently, the electrode was cleaned and immersed in the 1 mM H₂-PdCl₄ solution for 30 min. Because the standard potential of Fe²⁺/Fe (–0.440 V vs. SHE) is lower than that of PdCl₄²⁻/Pd (+0.62 V vs. SHE), Fe was spontaneously replaced by Pd.

Cyclic voltammetry and constant-potential experiments were carried out using a CHI 760D electrochemical workstation at room temperature (25 °C) and a conventional three-compartment electrochemical cell with an effective volume of 40 mL (25 mL solution was used for each experiment) was used too. A bright platinum plate (1 cm × 1 cm) and a saturated calomel electrode (SCE) served as counter and reference electrodes, respectively. The electrolytes were de-oxygenated by bubbling N₂ for 30 min before all tests.

The concentration of chlorobenzene was analyzed by high-performance liquid chromatography (HPLC) on a Agilent 1200 HPLC system (Agilent, USA) equipped with a reversed phase ZORBAX Eclipse XDB-C18 column (4.6 mm × 150 mm, 5 μ m), where a variable wavelength detector (VWD) was used and the detection wavelength was 210 nm for chlorobenzene. The HPLC mobile phase was the mixture of water and methanol (70:30) at a flow rate of 0.8 mL/min. Surface morphologies were observed by an S-4800 FESEM (Hitachi, Japan) and a JEM-2010 HRTEM (JEOL, Japan) and the elemental composition analysis of the Pd/Fe particles was performed using an Oxford energy dispersive X-ray (EDX) system attached to the HRTEM.

3. Results and discussion

3.1. Characterization of nanoscale Pd/Fe particles

The surface properties of Pd/Fe particles were characterized by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). In Fig. 1(A), Fe particles (denoted as Fe/GC) consist of large amount of tiny particles homogeneously distributed over the entire glassy carbon surface, some of which aggregated together. All these smooth particles are cubic in shape with size of about 150 nm. Fig. 1(B) presents that nanoscale Pd/Fe particles (denoted as Pd/Fe/GC) have been transformed into irregular shape with rough, porous surfaces. Such floc-like structures, when seen using higher resolution, are made of lots of smaller particles each 100 nm or below. So it can be verified that not only the size but the surface morphology have changed dramatically after the replacement, and smaller Pd/Fe particles with their porous and rough surfaces contribute to a larger overall surface area and porosity, which will be beneficial for the adsorp-

tion of hazardous pollutants and hydrogen. We were able to approximate the surface coverage of GC substrate based the particle size and the number as obtained by SEM analysis, with a result of 40–50%. Fig. 1(C) depicts the TEM image of Pd/Fe particle after the galvanized replacement within 30 min. As it can be seen that every single Pd/Fe nanoparticle is about 150 nm in size, with porous surface, and made up of numerous super tiny particles (about 10 nm in size) aggregated together, which can be seen in the micrograph taken at higher resolution. The chemical composition of the as-prepared Pd/Fe particles was determined by EDX analysis with a composition ratios of Pd:Fe of 11:1. This high proportion of Pd indicates that galvanic replacement process was relatively fast and extensive. Further study showed that galvanic replacement reaction of Pd and Fe were accomplished within 30 min. The XRD pattern (Fig. 2) of nanoscale Pd/Fe particles shows five peaks centered, respectively, at 40.38°, 46.96°, 68.3°, 82.52°, and 86.98°, which correspond, respectively, to the (111), (200), (220), (311), and (222) crystal planes of the standard Pd sample but do not match well the five standard peaks in peak position. Specifically, the five peaks were shifted to a larger angle direction (about 0.3°) as compared with those of pure Pd sample. This is perhaps due to the existence of Fe in bimetallic system which may make the lattice spacing smaller and theta angle bigger according to Bragg equation. And there are no peaks of Fe or other impurities observed in Fig. 2 which may result from (1) the relatively fast extensive diffusion of Pd atoms in the galvanic replacement process, the remaining content of Fe were limited on the electrode while most of Fe dissolved in the ionic liquid; (2) the signal of Pd and glassy carbon is strong enough to overshadow the weak signal from Fe.

Since it was neither core/shell (no hollow interior with a shell found) nor alloyed structure (no homogeneous mixture of Pd and Fe found), it was assumed that nanoscale Pd/Fe particles are inclined to be heterostructure achieved by one-step galvanic replacement involving Fe nanoparticles as a sacrificial template and PdCl₄²⁻ ions as a secondary metal consuming Fe in aqueous solution. In the formation of Pd/Fe heterostructure, the nucleation process of Pd crystal is relatively slow and if the initial size of Pd crystal nucleus is smaller than the critical size, Pd crystal is more likely grow on some special facets displaying high reactivity of Fe crystal nucleus rather than on the original Pd crystal nucleus to form core/shell-like structure where oxidized Fe²⁺ ions diffused out continuously across the mixed interface of Pd and Fe, while there also exists separate nucleation of the two metals, both of which share a mixed interface during the growth process. Pd/Fe bimetallic heterostructure can also be confirmed by the XRD analysis, in which new Bragg reflection indicating new compounds cannot be found but the characteristic diffraction peak of Pd can be detected.

3.2. Electrochemical behavior of nanoscale Pd/Fe particles

3.2.1. Electrochemical characteristics of Pd/Fe/GC electrode in acid electrolytes

The electrochemical characteristic of the Pd/Fe/GC electrode with comparison to bulk Pd electrode was investigated using a 0.1 M H₂SO₄ solution. The active surface area of the Pd/Fe/GC electrode could be determined by the charge corresponding to the stripping of the Pd oxide using a reported value of 424 μ C/cm² [25]. An active surface area of 0.707 cm² was calculated for Pd/Fe/GC, smaller than that of bulk Pd, which was 0.785 cm². The smaller active surface area might due to the incomplete coverage of the GC electrode by Pd/Fe particles. Fig. 3 shows CV curves of the bulk Pd electrode, which could be divided into three regions, namely hydrogen region (–0.4–0.2 V), double-layer region (0.2–0.3 V), and oxygen region (0.3–1.1 V). In hydrogen region,

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