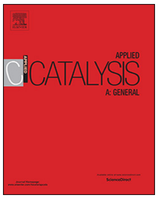
Applied Catalysis A, General 560 (2018) 84–93

Contents lists available at ScienceDirect

Applied Catalysis A, General

journal homepage: www.elsevier.com/locate/apcata



Insight into the mode of action of Pd-doped zero-valent iron nanoparticles @ graphene (Pd/FePs@G) toward carbon tetrachloride dechlorination reaction in aqueous solution

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ARTICLE INFO

Keywords:
Carbon tetrachloride
Pd/Fe bimetallic nanoparticles
Graphene
Inorganic anions
Reaction pathway

ABSTRACT

Herein, Pd/Fe bimetallic nanoparticles (Pd/FePs) were uniformly distributed on the surface of graphene sheet structure, and had good combination with the multilayer substrate. The nanocomposites could maintain high reactivity even after five times degradation reactions of carbon tetrachloride (CT) in succession, indicating that the modified technology had a positive effect on achieving high surface activity and prolonging the longevity. The structure evolution and compositional changes were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photo-electron spectroscopy (XPS). Also, humic acid (HA) as non-reactive adsorbate could preferentially occupy surface active sites of Pd/FePs to mediate the predominant radical species in the degradation process, which caused a 53% decrease in dechlorination rate of CT. These findings provided an important understanding of the stability and reactive mechanism involved in Pd/Fe bimetallic system toward CT degradation. Moreover, batch experiments were conducted to investigate the actual catalytic activity in view of the effects of common inorganic anions in aqueous solution. The results revealed that the presence of Cl^-, HCO_3^-, and HPO_4^{2-} was beneficial to the CT degradation while SO_4^{2-} and NO_3^- exerted the negative effects. Based on the detection results by means of gas chromatography (GC) and ion chromatography (IC), a possible degradation pathway was propose.

1. Introduction

Carbon tetrachloride (CT), as a chlorinated aliphatic hydrocarbon, has been widely applied to diverse fields in both industry and business such as degreasing agents, reactive intermediates and organic solvent over the past several decades. Unfortunately, CT was also known as a toxic [1] and relatively hydrophobic [2] organic compound and always contaminated the natural environment for a long time, and besides, for its high toxicity and carcinogenicity, CT could cause serious harm to humans, animals and vegetation [3], and thus was considered a priority pollutant [4] by United States Environmental Protection Agency (EPA). Even more remarkably, there was a strict regulation on the carbon tetrachloride concentration in drinking water, in which the maximum contaminant levels were at 2 μg L^{-1} in China and 5 μg L^{-1} in USA [5], respectively. However, the corresponding high detection rate in the soil and groundwater [6] that caused by a variety of improper industry processes has become current environmental concerns.

Nowadays, many scholars have devoted their efforts to develop innovative remediation techniques for removing CT from the environment, especially in water. These existing techniques including advanced oxidation technology [7], thermal oxidation [8], biodegradation [9] and reductive dechlorination [10–12] were increasingly explored for solving the environmental problems caused by halogenated organic compounds. Thereinto, zero-valent iron (ZVI), as an inexpensive and environmentally friendly reducing agent, was found to be effective for the treatment of carbon tetrachloride pollution as indicated by many controlled laboratory experiments [13,14]. Further research found that the nanoscale zero-valent iron (nZVI) possessed larger specific surface area and higher surface activity than micron-scale ZVI as well as their smaller particle sizes than most porous media pore throats [15–17], which was conducive to permeate subsurface to contact with the contaminant source zone. In addition, the dechlorination activity of monometallic nZVI particles toward CT could be greatly improved by impregnation with palladium metal to form so-called iron based bimetallic nanoparticles [18], which also exhibited higher reactivity than the other reported bimetallic systems [19,20]. Based on our previous

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https://doi.org/10.1016/j.apcata.2018.05.002
Received 31 January 2018; Received in revised form 24 April 2018; Accepted 1 May 2018

research, however, the removal efficiency of CT appeared a sharp decline in the Pd/Fe bimetallic system after multiple cycle experiments. The results attributed to the development of the deposited iron oxide and hydroxide on the Pd/FePs surface and thus formed a mixed-valence (Fe^{2+}-Fe^{3+}) oxide layer [21] which might cover the active reaction zone in addition to these Pd/FePs tended to aggregate under the action of magnetic and van der Waals force and then made particle sizes become larger. Hence, graphene as a supporting matrix was used to stabilize and assist the Pd/FePs in term of dispersibility, and the results shown that the modified method could not only further increase the corresponding specific surface area but also eliminate these nanoparticles agglomeration during the CT degradation process. More importantly, as we known that the conjugate structure [22] of graphene could provide the adsorption capacity of reactant molecules and facilitate the electrons mobility, thus enhancing the performance of Pd/FePs@G catalytic activity. The interesting behaviors attracted considerable attention because of the enhanced surface reactivity imparted by large specific surface as well as the stability and reusability, and further study was required for the evaluation for the role of nZVI and palladium metal.

Thus, the corresponding mechanism studies of the CT degradation in aqueous solution demonstrated that the Fe^0 component of Pd/FePs@G served as the electron donor, whereby palladium metal behaved as the catalyst for hydrogen formation, activation, and the subsequent formation of dissociated atomic hydrogen (•H), which in turn acted as the predominant radical species responsible for the dechlorination and hydrogenation of CT [23]. However, the well-known catalytic ability of palladium metal could not only promote water reduction and hydrogen generation, but also accelerated the reaction of Fe^0 with water due to the galvanic effect between iron and palladium metal [24], suggesting that the interaction of Pd/FePs@G with water also determined the longevity of this nano-material and the long-term degradation efficiency for CT. But so far, rather few studies have focused on the CT dechlorination reaction by using Pd/FePs@G under complex and changeable groundwater conditions, meanwhile, the corresponding possible reaction pathway for the CT reductive hydrodechlorination was inferred in our research.

The objectives of this study were to demonstrate our team's current achievements related to the use of Pd/FePs@G for CT degradation, and this work was mainly divided into the following sections: (1) concluded the reaction mechanism to clarify the role of each component of Pd/FePs@G for removal of CT; (2) verified the accuracy and credibility of the reaction mechanism by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XRD); (3) examined the effects of inorganic ions and HA on the CT degradation reaction to detect the stability of Pd/FePs@G; (4) illustrated a possible reaction pathway of CT dechlorination degradation by Pd/FePs@G.

2. Materials and methods

2.1. Preparation of Pd-doped zero-valent iron nanoparticles @graphene (Pd/FePs@G)

The Pd/FePs@G was synthesized by using a modified method from Wang and Zhang [25] by replacing $FeCl_3$ with $FeSO_4{\cdot}7H_2O$ in a 500 mL three-neck flask under nitrogen protection. Firstly, 0.14 g of GO was dissolved in deoxygenated DI water to form suspension with the assist of ultrasound at 45 KHz for 1 h. Then, 100 mL of 0.05 M $FeSO_4{\cdot}7H_2O$ aqueous solution was slowly added into above-mentioned suspension with uniform stirring for 10 h to ensure that ferrous irons were reduced and nZVI particles were successfully loaded on the GO surface by dropwise adding 200 mL of 0.20 M $NaBH_4$ aqueous solution. According to the following reaction:

$$Fe(H_2O)_6{}^{2+} + 2BH_4{}^- \rightarrow Fe^0\downarrow + 2B(OH)_3 + 7H_2\uparrow \qquad (1)$$

The reaction was ongoing for another 2 h after the termination of $NaBH_4$ dripping until the solution color from tawny to black without hydrogen foaming. Subsequently, in order to coat a thin layer of palladium metal by using K_2PdCl_6 aqueous solution on the surface of nZVI particles. Thus, the Pd-doped zero-valent iron nanoparticles were prepared by the method of reductive deposition according to the following equation:

$$Pd^{4+} + 2Fe^0 \rightarrow Pd^0\downarrow + 2Fe^{2+} \qquad (2)$$

Finally, the wet precipitates were obtained by repeatedly rinsing with deoxygenated DI water and anhydrous ethanol for three times, respectively. Washed Pd/FePs@G was freeze-dried with a freezer dryer and then stored in the anaerobic condition.

2.2. Batch experiments

The effects of different reaction conditions on CT degradation using Pd/FePs@G were investigated in batch experiments, which were conducted in 100 mL serum bottles sealed with Teflon stopper. Prior to the batch experiments, all glass containers were autoclaved for 2 h. The reactions were initiated by adding a desired dosage of Pd/FePs@G ($0.5\ g\ L^{-1}$, Fe:GO = 2:1 and Fe with 0.75 wt% Pd loading) and CT ($C_{initial} = 3\ mg\ L^{-1}$) aqueous solution. Also, CT dechlorination reactions were conducted in the presence of HA and common dissolved anions. Under the constant temperature, all bottles were stirred on the rotary shaker at 150 rpm to achieve mixing. And then the mixtures were taken at pre-determined times with filtered through 0.22 μm membrane filter and followed by diluting the CT filtrate with DI water. Finally, the removal efficiency of the CT molecules from the aqueous solution was monitored by gas chromatography.

2.3. Method of analysis

X-ray diffraction spectra were measured at room temperature by a Bruker AXS D8 Advance diffractometer with Cu/Kα radiation at 40 kV and 40 mA. The morphology of the prepared samples were observed with the Hitach SU8010 field-emission scanning electron microscope. X-ray photo-electron spectroscopy was used to record the surface chemistries of the obtained materials.

Chloridion was determined by the Dionex ICS-900 ion chromatograph equipped with a DS5 conductivity detector and an IonPac AS23 guard column (Dionex 4 × 250 mm) with an IonPacAG23 guard column (Dionex 4 × 50 mm). Total organic carbon (TOC) were detected by a Multi TOC Analyzer (2100, Analytik Jena AG Corporation). And the concentration of CT, CF and DCM were analyzed by the gas chromatography (Agilent 7890 A)/mass spectrometry (GC-2014, Agilent 5975 C).

3. Results and discussions

3.1. XRD, SEM, XPS study

The wide angle X-ray diffraction pattern of as-synthesized Pd/FePs@G was illustrated in Fig.1(a). As demonstrated in the XRD pattern, in the absence of the characteristic diffraction peaks locating at 10.3° and 26.4° corresponding to GO and graphite, it indicated the fact that graphene component of Pd/FePs@G behaved as the typical lamellar structure was consistent with the SEM observation. The above-mentioned analysis shown that fresh Pd/FePs@G consisted of two phases of zero-valent iron and magnetite, and the maximal reflection peak at $2\theta = 44.76°$ was classified as the characteristic peak of cubic Fe (JCPDS, file NO. 06-0696). Because of the extremely high activity of nZVI, its oxidation reactions were easy to occur whether it was exposed to the air or submerged in the aqueous media, leading to the structure with zero-valent iron in the inner and iron oxide in the outer of these