



The roughened silver–palladium cathode for electrocatalytic reductive dechlorination of 2,4-Dichlorophenoxyacetic acid

Ma Chun'an*, Ma Hao, Xu Ying'hua*, Chu You'qun, Zhao Feng'ming

State Key Laboratory Breeding Base of Green Chemistry–Synthesis Technology, College of Chemical Engineering and Materials, Zhejiang University of Technology, Hangzhou City, Zhejiang 310032, China

ARTICLE INFO

Article history:

Received 31 July 2009

Received in revised form 11 September 2009

Accepted 11 September 2009

Available online 16 September 2009

Keywords:

Pd/Ag electrode

2,4-Dichlorophenoxyacetic acid

Electrocatalytic hydrogenation

Reductive dechlorination

Dechlorination mechanism

ABSTRACT

The roughened silver–palladium (Pd/Ag(r)) electrode was fabricated by a convenient metallic replacement reaction, and its electrocatalytic property towards reductive dechlorination of 2,4-Dichlorophenoxyacetic acid (2,4-D) in basic aqueous solution have been evaluated. Experimental evidence is presented that Pd/Ag(r) exhibited powerful electrocatalytic activity for dechlorination of 2,4-D. In addition, a new dechlorination mechanism of 2,4-D was proposed, in which the formation of adsorbed 2,4-D on Ag is a key step.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Electrocatalytic hydrogenation (ECH) using palladium modified cathodes is suggested as a very promising approach for the detoxification of chlorinated organic compounds (COCs) [1–9]. This method ensure the completed removal of chlorine atoms under mild experimental conditions, and that the chlorine-free organic compounds usually have much less toxic properties, could be disposed by more convenient and economic manner, for example by biodegradation. Unfortunately, it is very difficult to achieve high current efficiency in ECH dechlorination of COCs using palladium modified cathodes.

It has been found that the cathode substrates have a major effect on the efficiency of ECH dechlorination of chlorinated compounds. Therefore, large numbers of materials were used as catalyst support (i.e. cathode substrates), including various carbon materials [1–5], different metal materials [6–8] and polypyrrole [9]. These supports mainly play a role in physical separation of the catalytic particles and prevention of their agglomeration, however, their synergistic effect on the ECH dechlorination seems to be inappreciable.

Silver, as a cathode catalyst, has recently been received much attention for its extraordinary electrocatalytic activities towards

the reduction of halogenated organic compounds [10–14]. The electrocatalytic process probably is related to the formation of bridge-like R...X...Ag adsorbed intermediate, although the catalytic mechanisms of silver in the reduction process still need to be explored. Considering this fact, perhaps, Simonet's group chose silver as the cathode substrates to prepare a new cathode material (palladized silver), which exhibited more powerful electrocatalytic activities than silver electrode towards the reduction of alkyl bromides and alkyl iodides [15,16].

The objective of the present study is to evaluate the feasibility of palladized silver as the cathode for destruction of COCs and the synergistic effect of silver on the ECH process of COCs. Roughened silver (Ag(r)) rather than polished one (Ag(p)) was used as the cathode substrate in order to prepare the Pd/Ag(r) electrodes with the large surface areas and high degree of dispersity of palladium. The electrocatalytic properties of Pd/Ag(r) electrodes were investigated using 2,4-D as a model compound since it is more difficult to reduce than most of COCs and has the good solubility in aqueous solutions.

2. Experimental

Pd/GC and Pd/Ti electrodes were obtained by means of a potentiostatic deposit (keeping potential at -0.25 V for 1.0 h and at -0.45 V for 15 min) from a aqueous solution of palladium chloride (0.1 M HCl + 2.0 mM PdCl₂). Pd/Ag(p) and Pd/Ag(r)-1# electrodes were made by a metallic replacement reaction (exposing to a

* Corresponding authors. Tel./fax: +86 0571 88320813.

E-mail addresses: science@zjut.edu.cn (M. Chun'an), xuyh@zjut.edu.cn (X. Ying'hua).

2.0 mM PdCl₂ + 0.1 M HCl aqueous solution for 1.0 h); Pd/Ag(r)-2# electrodes were prepared by a metallic replacement reaction (exposing to a 2.0 mM PdSO₄ + 0.1 M H₂SO₄ aqueous solution for 1.0 h). Ag(r) electrodes were obtained by ORC treatment [10]. The surface morphology and composition of the electrodes were determined by SEM (Hitachi S-4700 II) equipped with EDS (Thermo NOANVANTAGE ESI). As showed in Fig. 1, the surface of Ag(p) and Ag(r)-1# electrodes are covered with a compact film and a porosity film, respectively, after the metallic replacement reaction. The two films are composed of four elements (O, Cl, Pd and Ag) and three elements (O, Pd and Ag), respectively, and their approximate content are 1.21, 3.13, 9.49, 86.17 wt% and 1.29, 10.29, 88.41 wt%. According to the literature [15], these Pd and Ag probably exist as alloy, i.e. Pd as a solute is dissolved in Ag solutions. Such a dissolved state would ensure a high degree of dispersity of Pd on the Pd/Ag(r) electrode.

Voltammetric investigations and preparative electrolyses were carried out by PAR 273A potentiostat. A three-electrode-cell composed of an aqueous saturated calomel electrode (SCE), a platinum sheet (0.5 × 1 cm²) used as the counter electrode and a working

electrode (Ø 2 mm) was used for voltammetric investigations. Preparative electrolyses were carried out in a two-compartment cell, divided by a cation-exchange membrane (Nafion 117), the catholyte and anolyte volumes were approximately 40 cm³; the cathode consisted either of a rectangular palladized GC plate (4 × 3 × 0.1 cm³) or of a rectangular palladized metal mesh (4 × 3 × 0.1 cm³). Quantitative analysis of the dechlorinated products and the remaining 2,4-D was performed by using a Waters HPLC system with same mode as described in [10]. All electrochemical experiments were carried out at 298 K and all potentials are relative to SCE.

3. Results and discussion

3.1. CV experiments

Fig. 2a shows cyclic voltammograms of Ag(r), Pd/GC, and Pd/Ag(r)-1# electrodes in blank NaOH aqueous solutions. As can be seen, the potential of hydrogen evolution detected on the three-electrodes are evidently different from each other. In the potential

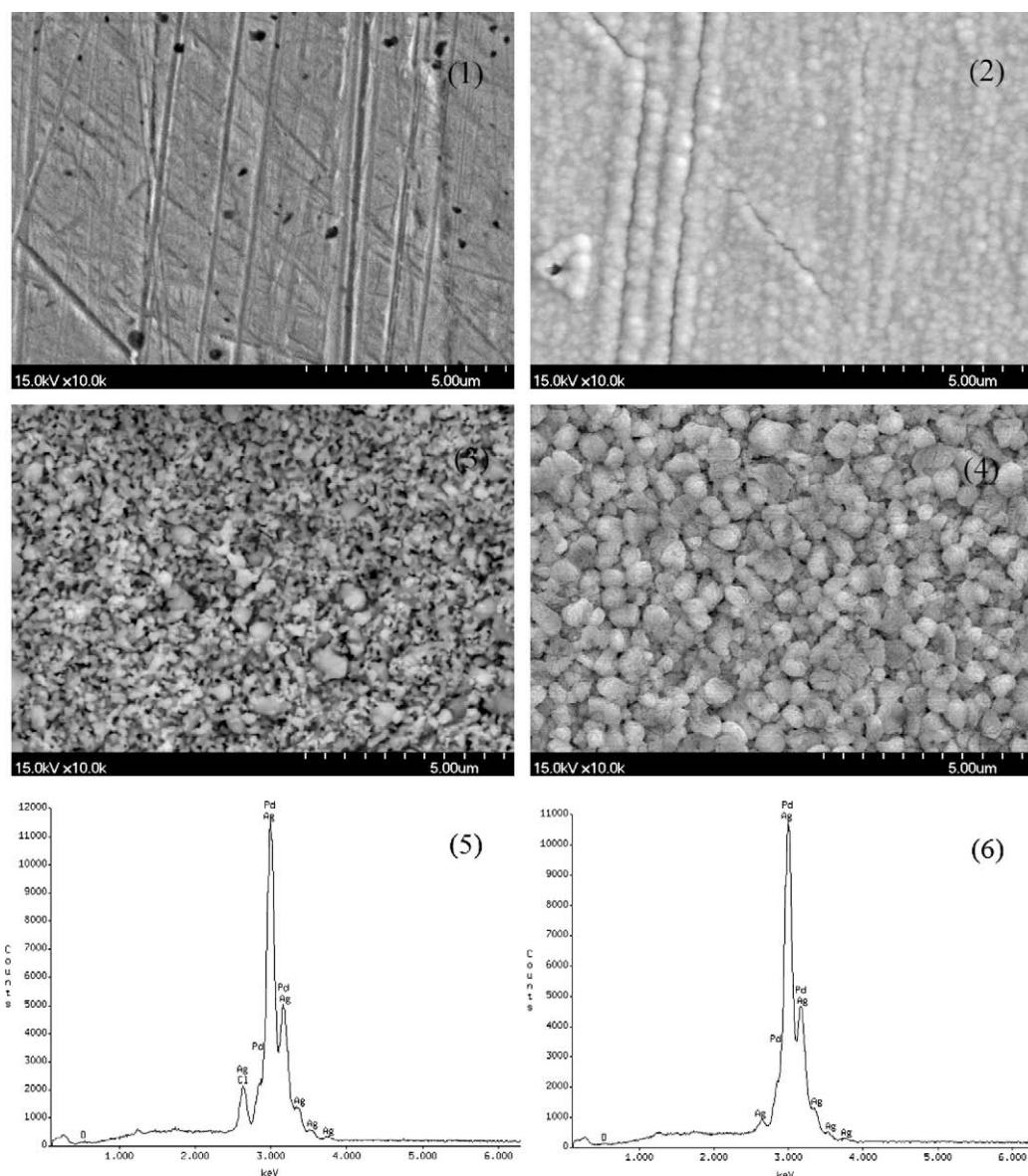


Fig. 1. SEM images: (1) Ag(p) electrode, (2) Pd/Ag(p) electrode, (3) Ag(r) electrode, (4) Pd/Ag(r)-1# electrode; and EDS: (5) Pd/Ag(p) electrode, and (6) Pd/Ag(r)-1# electrode.

Download English Version:

<https://daneshyari.com/en/article/180527>

Download Persian Version:

<https://daneshyari.com/article/180527>

[Daneshyari.com](https://daneshyari.com)