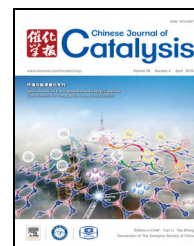


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Palladium nanoparticles assembled on titanium nitride for enhanced electrochemical hydrodechlorination of 2,4-dichlorophenol in water



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ABSTRACT

We report a one-pot surfactant-free wet-chemical reduction approach to the synthesis of palladium/titanium nitride (Pd/TiN) and Pd/carbon (Pd/C) composites, in which ~5 nm Pd NPs were uniformly dispersed on TiN or C. In terms of catalytic performance, Pd/TiN showed enhanced efficiency and stability compared with those of Pd/C and bare TiN in the electrocatalytic hydrodechlorination (EHDC) reaction of 2,4-dichlorophenol (2,4-DCP) in aqueous solution. The superior performance of Pd/TiN arises from the promotion effect of TiN. Strong metal-support interactions modified the electronic structure of Pd, which optimized generation of H_{ads}⁺ and 2,4-DCP adsorption/activation. The cathode potential plays a vital role in controlling the EHDC efficiency and the product distribution. A working potential of -0.80 V was shown to be optimal for achieving the highest EHDC efficiency and maximizing conversion of 2,4-DCP to phenol (P). Our studies of the reaction pathway show that EHDC of 2,4-DCP on Pd/TiN proceeded by 2,4-DCP → *p*-chlorophenol (*p*-CP), *o*-chlorophenol (*o*-CP) → P; however, Pd/TiN presented little selectivity for cleavage of *p*-C-Cl vs *o*-C-Cl. This work presents a new approach to enhancing Pd performance towards EHDC through the effects of a support. The strategy demonstrated here could also be extended to design highly efficient catalysts for other hydrogenation reactions.

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1. Introduction

Recently, widespread use of chlorinated phenols (CPs) in pharmaceuticals, agriculture, and the polymer industry has led to severe environmental concerns, with potential to threaten public health [1,2]. However, owing to the high stability of the

Cl–C bonds, these CPs are usually highly resistant to environmental degradation, and also difficult to mineralize by common disposal technologies, such as Fenton/H₂O₂ oxidation, bioprocess, and photocatalytic degradation [3–5]. To detoxify such CPs, one alternative and efficient strategy is to convert them into chlorine-free phenols via a reductive hydrodechlorination

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process, and the resultant phenols can then be completely mineralized through chemical oxidation or biological processes [6,7]. Among current hydrogenation methods [8,9], electrocatalytic hydrodechlorination (EHDC) has received growing attention owing to its high efficiency, mild reaction conditions, no requirements for other chemicals, and low secondary pollution risks [10–12].

In the EHDC process, atomic hydrogen (H^*), a strong reducing agent, is first formed by reduction of H^+ in aqueous solution. The atomic hydrogen then attacks chemically adsorbed CPs on the cathode surface, leading to cleavage of C–Cl bonds and subsequent substitution of Cl by H on the benzene ring. Metallic Pd has been found to be the most effective catalyst towards EHDC, owing to the low overpotential required for H^+ reduction, as well as the appropriate adsorption strength of the Pd– H^* . However, bulk Pd does not have high activity, and its low reserves requires us to reduce the usage of Pd in practical applications [13]. To improve the efficiency of Pd and lower the costs of the electrode, two leading strategies have been established: (1) introducing another cocatalyst, such as transition metals (Fe and Ni) [14,15], grapheme [16], and polymers (such as pyrrole-CTAB) [17]; and (2) maximizing the exposure of the Pd sites by shaping the Pd into a nanosized or a porous structure [18,19]. Constructing an active interface between the active metal and the support is another efficient strategy, which is often used to increase the catalytic activity of metals towards certain reactions [20–22]. However, until now, there have been few reports on the effects of supports on tuning the EHDC efficiency of Pd [23,24].

In this work, a surfactant-free wet-chemical reductive approach is developed to synthesize the Pd/titanium nitride (Pd/TiN) and Pd/carbon (Pd/C) composites. Through this approach, Pd NPs in the composite can be controlled to be quite uniform in terms of both size (~5 nm) and shape (spherical), and are also evenly dispersed on the support without any agglomeration. TiN was chosen owing to its good conductivity, chemical stability, and electronic structure. Indeed, Pd/TiN shows considerably enhanced EHDC efficiency and stability compared with those of Pd/C in the EHDC of 2,4-dichlorophenol (2,4-DCP one typical chlorinated phenol). Mechanistic studies have shown that the superior performance of Pd/TiN arises from the promotion effect of TiN. Its strong metal-support interactions with Pd can modify the electronic structure of Pd to optimize H^*_{ads} generation and 2,4-DCP adsorption/activation. We also investigated the cathode potential, which is an important operating parameter in terms of EHDC efficiency and the resulting product distribution. Our results demonstrated that –0.80 V was the optimal working potential to achieve the highest EHDC efficiency and maximum conversion of 2,4-DCP to P. Mechanistic studies showed that the EHDC of 2,4-DCP on Pd/TiN proceeds by 2,4-DCP → *p*-chlorophenol (*p*-CP), *o*-chlorophenol (*o*-CP) → phenol (P); however, Pd/TiN has low selectivity for cleavage of *p*-C-Cl vs *o*-C-Cl.

2. Experimental

2.1. Materials

TiN was obtained from Hefei Kaier Nano Company (China). Before use, it was treated with concentrated HCl for 3.0 h, washed with deionized water until the washings were neutral, and subsequently dried in an oven at 60 °C for 1.0 h. Carbon black (Vulcan XC 72R) was used as an alternative support material (denoted as C below), and purchased from Cabot. $Na_2[PdCl_4]$ and Nafion solution (5 wt%) were purchased from Sigma-Aldrich. $NaBH_4$, HCl, ethanol, 2,4-DCP, *p*-CP, *o*-CP, P, Na_2SO_4 , and chromatography grade methanol were supplied by the Sinopharm Group Chemical Reagent Co., Ltd. China. A 2,4-DCP stock solution was prepared by dissolving 5 g of 2,4-DCP in 1 L of methanol and was stored at 4 °C. Deionized water with a specific conductivity $>18.2 \text{ m}\Omega \text{ cm}^{-1}$ was used throughout the experiments. Carbon paper (Toray 090, with a thickness of 280 μm and a porosity of 0.78) was used as the working electrode substrate.

2.2. Preparation of cathode

The Pd/TiN composite was synthesized as follows: 40 mg of the treated TiN powders was dispersed into 80 mL of deionized water by intense sonication. A 0.8-mL portion of the $Na_2[PdCl_4]$ solution (13.8 mg mL^{-1}) was then dropwise added into the above TiN suspension, and sonicated for a further 30 min. The solution pH was adjusted to approximately 10 by adding a NaOH solution (1.0 mol L^{-1}). Under stirring, an aqueous solution of $NaBH_4$ (8.0 mg mL^{-1}) was slowly dropped into the above mixture over 20 min. After reaction for 1.0 h, a Pd/TiN composite was formed, and the product was collected by adding ethanol and centrifugation (10000 r min^{-1} , 8 min), further washed three times with deionized water and separated by centrifugation (10000 r min^{-1} , 8 min). The final product was dried in 60 °C for 12 h. The same method, substituting TiN with C could lead to the Pd/C composite.

To prepare the working electrode, 15 mg Pd/TiN or Pd/C powders were dispersed in a solvent mixture of 2.5 mL ethanol and 25 μL Nafion by intense sonication to form a catalyst ink. This ink was then transferred onto a carbon paper (area: $2 \text{ cm} \times 2 \text{ cm}$) under an infrared heat lamp, which accelerated the evaporation of liquid and promoted the formation of a uniform film.

2.3. Electrocatalytic hydrodechlorination of 2,4-dichlorophenol in water

EHDC of 2,4-DCP was conducted in a two-compartment electrochemical cell, which was separated by a proton-exchange membrane Nafion-117 to prevent Cl^- flowing into the anode cell to generate Cl_2 . The catalyst-loaded carbon paper served as the working electrode, while an Ag/AgCl wire and Pt foil (3.0 mol L^{-1} KCl, 0.201 V vs SHE at 25 °C) were used as the reference and counter electrode, respectively. The whole cell was immersed in a thermostatic bath to maintain the EHDC reaction at a constant temperature of 25 °C. For each test, 100 mL of N_2 -saturated Na_2SO_4 solution (50 mmol L^{-1}) was added into each compartment, then 1.0 mL of the 2,4-DCP stock solution was added into the cathode compartment to obtain a con-

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