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Short Communication

Fibrous nano-silica supported palladium nanoparticles: An efficient catalyst for the reduction of 4-nitrophenol and hydrodechlorination of 4-chlorophenol under mild conditions

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ABSTRACT

In this study, a fibrous nano-silica supported palladium nanocatalyst (Pd/KCC-1), which features with easy accessibility of active sites and high catalytic activity, was synthesized by a simple, cost-effective procedure. The Pd/KCC-1 nanocatalyst exhibited excellent catalytic activity in the reduction of 4-nitrophenol and hydrodechlorination of 4-chlorophenol in aqueous solution under mild condition. The unique dendritic fibrous morphology of the support led to the poor aggregation of the Pd nanoparticles and dramatically increased its accessibility. The easy accessibility and excellent catalytic activity demonstrated by the Pd/KCC-1 nanocatalyst make it a promising candidate for various Pd-based catalytic applications.

1. Introduction

Recently, the transformation of harmful organic wastes into reusable compounds with low toxicity in aqueous solutions under mild conditions has become an extremely important area of study for chemists. In this aspect, the disposal of nitrophenol and chlorophenol is one area of intensive research. As is well known, 4-nitrophenol (4-NP) and 4-chlorophenol (4-CP) are among the most used chemicals in the chemical industry today. 4-NP and 4-CP can be used for the synthesis of pharmaceutical products, dyes, and explosives [1]. However, a significant drawback associated with the use of 4-NP and 4-CP is the tendency of these chemicals to cause both soil and water pollution due to their high toxicity [2]. Because of this, the disposal of 4-NP and 4-CP has become a major environmental concern. The handling methods for 4-NP and 4-CP contamination mainly include: adsorption [3], microbial degradation [4], incineration [5], photocatalytic degradation [6], catalytic chemical oxidation [7], nitro group reduction [8], and catalytic hydrodechlorination (HDC) [9]. Among these methods mentioned above, the reduction of the nitro group was commonly used for 4-NP, while HDC was often used for 4-CP. These methods have the following advantages: mild reaction conditions, simple reaction treatment, and environment-friendly characteristics [10]. Furthermore, the reduction product (aminophenol) and the HDC product (phenol) can be reused. Therefore, it is extremely important to develop effective catalysts for both the reduction of 4-NP and the HDC of 4-CP and to transfer them into reusable products.

Previously, palladium-based catalysts has been confirmed the most effective catalysts for both the reduction of 4-NP and the HDC of 4-CP [11,12]. Palladium nanoparticles (Pd NPs) are of particular importance among the noble metals, owing to their superior catalytic performances [13]. Pd NP nanocatalysts are now receiving more and more attention for their catalytic activity in the treatment of wastewaters containing 4-NP or 4-CP pollutants [14,15]. However, the surface energy of NPs increases as their particle size decreases, which makes them unstable and increases the tendency for inter-particle aggregation [16]. Thus, various support materials have been employed to prevent Pd NP aggregation, including SBA-15 [17], PPy nanocapsules [18], activated carbon [19], and Al_2O_3 [20]. However, none of these supported catalysts were ideal for mass transport. Therefore, in order to enhance mass transfer effects and avoid Pd NP aggregation, catalytic supports with high surface areas and easy accessibility are required.

Fibrous nano-silica (KCC-1), which features a high surface area and easy accessibility through its fibers (as opposed to the traditional use of pores), is reported by Polshettiwar et al. [21]. This would be an ideal catalyst support candidate for the fabrication of noble metal-based catalysts that exhibit high accessibility of active sites and excellent catalytic activity.

Inspired by the abovementioned considerations, in this study, the fibrous nano-silica supported palladium nanocatalyst (Pd/KCC-1) was synthesized (Scheme 1) and used for the reduction of 4-NP and HDC of 4-CP. This catalytic system has three major advantages: first, the

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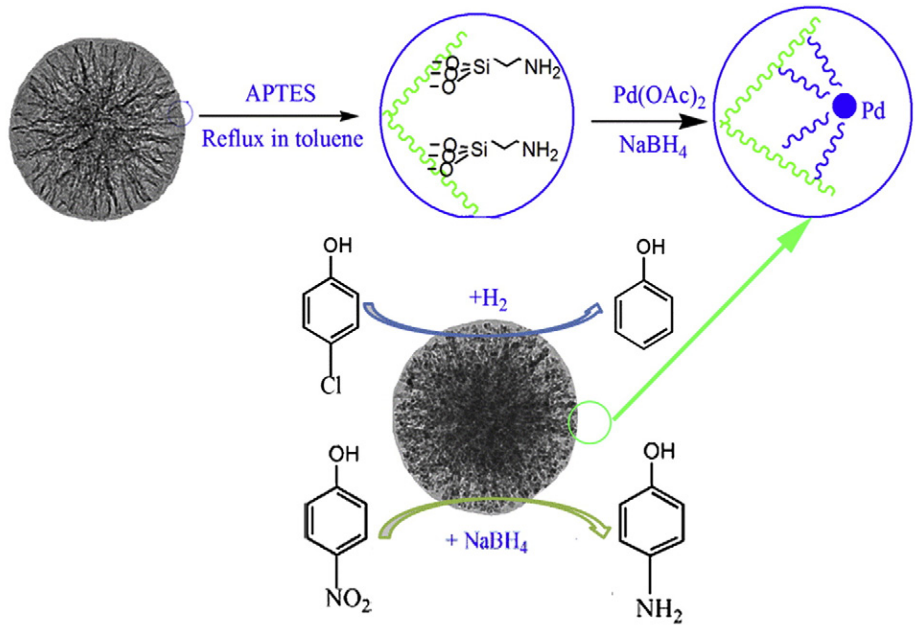

Scheme 1. Preparation of the Pd/KCC-1 catalyst.

preparation of the Pd/KCC-1 nanocatalyst is simple and cost effective; second, the Pd/KCC-1 nanocatalyst exhibits high accessibility and excellent catalytic activity; and third, the as-prepared catalyst exhibits long-life and high reusability in the reduction of 4-NP and HDC of 4-CP. The Pd/KCC-1 nanocatalyst is a promising candidate for various Pd-based catalytic applications.

2. Experimental section

2.1. Material

Tetraethoxysilane (TOES), 3-aminopropyltriethoxysilane (APTES) and Pd(II) acetate were purchased from Aladdin Chemical Co., Ltd. 4-CP, 4-NP, 1-pentanol and urea were purchased from Lanzhou Aihua Chemical Company. Organic solvents used were of analytical grade and did not require further purification.

2.2. Synthesis of KCC-1

In this study, KCC-1 was successfully synthesized by a traditional hydrothermal method [22]. TEOS (2.5 g) was dissolved in a solution of cyclohexane (30 mL) and 1-pentanol (1.5 mL). A stirred solution of cetylpyridinium bromide (CPB 1 g) and urea (0.6 g) in water (30 mL) was then added. The resulting mixture was continually stirred for 45 min at room temperature and then placed in a teflon-sealed hydrothermal reactor and heated 120 °C for 5 h. The silica formed was isolated by centrifugation, washed with deionized water and acetone, and dried in a drying oven. This material was then calcined at 550 °C for 5 h in air.

2.3. Preparation of Pd/KCC-1 nanocatalyst

KCC-1 supported palladium catalyst was reported by Fihri et al. [23]. In this work, we used a simple and energy saving method (Scheme 1). Firstly, KCC-1 was functionalized with APTES to obtain KCC-1-NH_2 nanocomposite. Secondly, a 100 mL round-bottom flask was charged with 0.5 g of KCC-1-NH_2 nanocomposite, 0.1 g of $Pd(OAc)_2$ and 50 mL of acetonitrile, after which it was ultrasonically dispersed for 30 min. Subsequently, the fresh $NaBH_4$ solution (0.2 M, 10 mL) was added dropwise into the abovementioned suspension. The product was isolated by centrifugation, washed repeatedly with deionized water and ethanol, and dried in a vacuum.

2.4. Characterization, reduction of 4-NP and HDC of 4-CP

The characterization of the samples and the detailed experimental procedures for the reduction of 4-NP and HDC of 4-CP could be found in the supporting information.

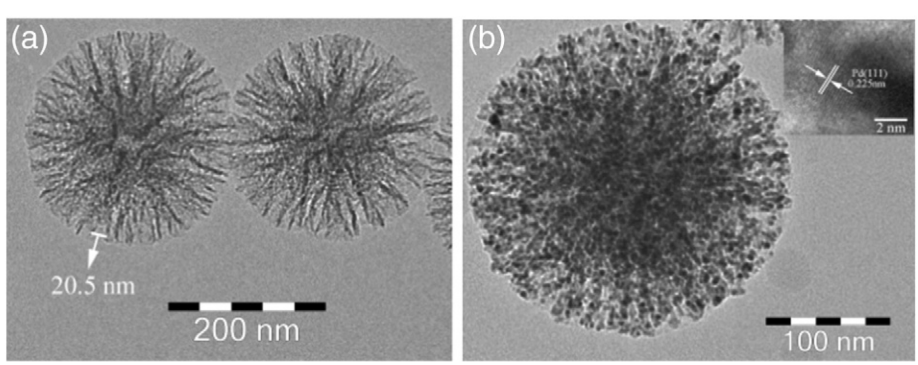

Fig. 1. TEM images of (a) KCC-1, (b) Pd/KCC-1, inset pictures HRTEM image of the Pd NPs crystal structure in detail on KCC-1.