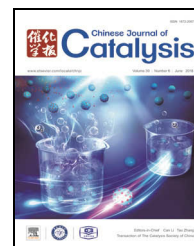


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Article

Facile *in-situ* synthesis and deposition of monodisperse palladium nanoparticles on polydopamine-functionalized silica gel as a heterogeneous and recyclable nanocatalyst for aerobic oxidation of alcohols



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ABSTRACT

This paper describes a facile *in-situ* synthesis of palladium nanoparticles (Pd NPs) on silica gel/polydopamine composite (SiO₂/PDA) without any stabilizer or reducing agent. In this approach, palladium ions were adsorbed on SiO₂/PDA surfaces by immersing the PDA-coated SiO₂ particles in a palladium plating bath. Then, they were reduced *in situ* to Pd nanoclusters by the reducing ability of PDA's N-containing groups. The structure, morphology, and physicochemical properties of the synthesized nanocomposites were characterized by different analytical techniques such as high-resolution transmission electron microscopy, field-emission scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction analysis, X-ray photoelectron spectroscopy, inductively coupled plasma and Fourier-transform infrared spectroscopy. The Pd NPs capped by the PDA groups had a strikingly small size (30–40 nm). SiO₂/PDA/Pd NPs exhibited high catalytic activity as a recyclable nanocatalyst in the aerobic oxidation of alcohols. Furthermore, recovery and multiple reuse of the catalyst revealed no detectable activity loss.

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1. Introduction

One of the most important transformations in synthetic organic chemistry is oxidation of alcohols to their corresponding carbonyl compounds [1,2]. Researchers have attempted to use transition-metal-catalyzed aerobic oxidation reactions as an economic and environmentally friendly approach to carry out this transformation [3,4]. Oxygen utilized in aerobic oxidation has considerable advantages in that molecular oxygen is inexpensive and its only byproduct is water. Therefore, extensive catalytic studies on finding efficient active metals for aerobic homo- and heterogeneous catalytic oxidation, e.g. Fe [5], Ru [6], Co [7], Cu [8], Mn [9], Os [10] and Pd [11], have been reported. Furthermore, solid-supported transition metal nanoparticles

(NPs) have gained some interest in development of new catalysts because they are active and reusable catalysts [12–14]. With this purpose in mind, a few researchers have reported that heterogeneous palladium NPs can catalyze aerobic oxidation of aromatic alcohols [15,16].

It is also worth noting that the applications of Pd-based catalysts are not limited to alcohol oxidation. They play important roles in organic synthesis, pharmaceutical chemistry, and polymer science [17,18]. Furthermore, they are not limited to heterogeneous catalysis; Pd complexes with various ligands have been synthesized and applied as homogeneous catalysts to obtain high selectivity and efficiency. However, homogeneous Pd catalysts suffer from several problems including difficulty in separation, recovery, and regeneration of the particles and

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resulting pollution of the environment and the products [19]. Heterogeneous Pd catalysts can overcome these limitations efficiently, though they are not as active as homogeneous catalysts due to the disfavored kinetics of biphasic catalytic systems. Therefore, Pd species are usually anchored on a solid support matrix with high specific surface area to increase the number of collisions between Pd particles and the substrates [20–24]. Leaching of Pd during catalysis is another disadvantage of Pd heterogeneous catalysis. To reduce leaching and increase catalytic activity of supported Pd catalysts, solid matrices can be modified chemically with different chelating ligands to improve the interaction of the solid support with Pd particles [25–27]. Unfortunately, leaching of Pd species from catalyst supports cannot be completely avoided because the interaction between the supports and Pd species weakens under harsh reaction conditions, e.g. high reaction temperature.

This study is an attempt to continue our previous research [28–36] and to develop a new hybrid nanocomposite, which can act as both a reducing agent and a stabilizing agent for immobilization of Pd NPs. For this purpose, SiO₂ particles were modified in situ with polydopamine by polymerization of dopamine in tris-buffer solution (pH 8.5) under constant stirring. Then, the generated SiO₂/PDA NPs were used to adsorb Pd ions on the PDA layers. Pd ions were immediately reduced to metallic Pd nanoparticles in situ by active catechol and amine groups. The synthesis of the catalyst SiO₂/PDA/Pd NPs is depicted in Scheme 1. The synthesized NPs were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDS), high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), and inductively coupled plasma (ICP) techniques. Furthermore, catalytic performance, recyclability

and convenience of separation of SiO₂/PDA/Pd NPCs were examined by carrying out aerobic oxidation of alcohols to their corresponding carbonyl compounds (Scheme 1).

2. Experimental

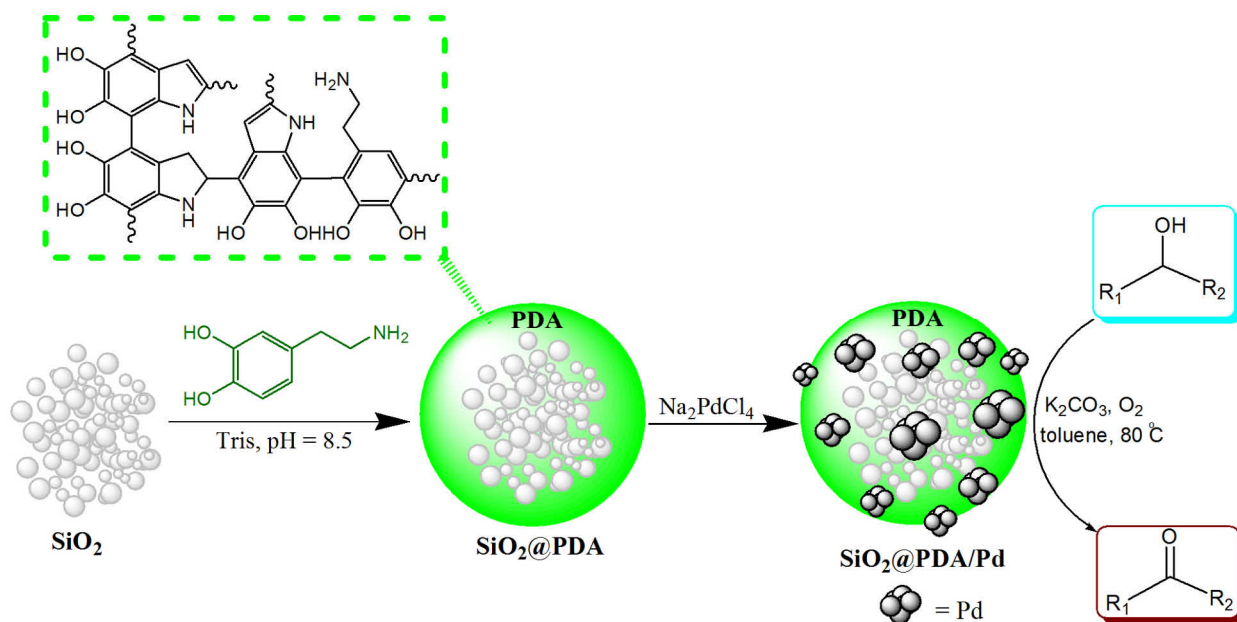
2.1. Preparation of SiO₂/PDA/Pd NPs

Silica gel (1 g) was dispersed in 500 mL Tris buffer (10 mmol/L, pH 8.5), then dopamine (1 g) was added, and the mixture was mechanically stirred for 24 h at room temperature. After reaction, the SiO₂/PDA nanoparticles were filtered and washed with deionized water and anhydrous ethanol and dried at 40 °C to give SiO₂/PDA.

In the next step, the SiO₂/PDA composite (0.5 g) was dispersed in H₂O (100 mL) by ultrasonic bath for 20 min. Subsequently, a solution of Na₂PdCl₄ (0.02 g) in 20 mL water was added to the reaction mixture and stirred for 24 h under reflux conditions. Then, the SiO₂/PDA/Pd NPs was separated by centrifuge and washed with H₂O and acetone respectively to remove the unattached substrates. Scheme 1 depicts the synthetic procedure of SiO₂/PDA/Pd NPs. The final nanocatalyst was dried in vacuum at 40 °C. The concentration of palladium was 1.89 wt% (0.18 mmol/g), as determined by ICP-AES.

2.2. Aerobic oxidation of alcohols

A mixture of K₂CO₃ (1 mmol) and the SiO₂/PDA/Pd NPs (80 mg, 0.5 mol% Pd) in toluene (5 mL) was prepared in a two-necked flask. The flask was evacuated and refilled with pure oxygen. To this solution, the alcohol (1 mmol, in 1 mL toluene) was injected and the resulting mixture was stirred at 80 °C in an oxygen atmosphere. After completion of the reac-



Scheme 1. Preparation of SiO₂/PDA/Pd NPs and its application as a novel heterogeneous nanocatalyst for aerobic oxidation of alcohols.

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