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Research paper

Composite of Au-Pd nanoalloys/reduced graphene oxide toward catalytic selective organic transformation to fine chemicals

Yanhui Zhang [a,b,*], Fei Gao [a], Ming-Lai Fu [b]

[a] College of Chemistry and Environment, Fujian Province Key Laboratory of Morden Analytical Science and Separation Technology, Minnan Normal University, Zhangzhou 363000, People's Republic of China
[b] CAS Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Science, Xiamen 361021, People's Republic of China

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ABSTRACT

A facile, stabilizing-molecules-free strategy has been utilized for anchoring Au-Pd alloy nanoparticles onto the flat surface of two-dimensional (2D) reduced graphene oxide (RGO) nanosheets. Formation of Au-Pd nanoalloys and loading onto the RGO are accomplished simultaneously. The Au-Pd/reduced graphene oxide (Au-Pd/RGO) exhibits higher catalytic activity than both Au/RGO and Pd/RGO, prepared by the same approach toward selective oxidation of benzyl alcohol and selective reduction of nitroaromatics, the catalytic activity order can be in good agreement with the noble metal particles size distribution of the Au, Pd and Au-Pd/RGO.

1. Introduction

Over the past few decades, the group of Hutchings has demonstrated that Au catalysts or bimetallic Au-Pd catalysts support on various materials (such as carbon, TiO_2) can be applied to catalysis reaction in many fields, such as CO oxidation, ethyne hydrochlorination, alcohol oxidation, alkene epoxidation, and selective hydrogenation of α,β-unsaturated nitro-compounds [1–6]. Among catalytic reactions, selective oxidation of benzylic alcohols is a fundamental transformation for the synthesis of fine chemicals, because aldehyde derivatives are widely utilized in the flavor, confectionary, and beverage industries [6–10]. Besides selective oxidation processes, selective reduction of nitroaromatics to the corresponding amines is a significant chemical transformation in synthetic organic chemistry, because amino group can serve as a site for further derivatization towards final products, and aromatic amines are widely used as important intermediates in the preparation of a number of valuable chemicals, such as pharmaceuticals, agricultural chemicals, photographic and rubber chemicals [11–14].

For catalyst supports, carbon materials including carbon black, activated carbon, fullerenes, carbon nanotubes, graphene, graphdiyne, and carbon nanofibers are still the most widely studied as catalyst supports [15–18]. In addition, it is known that the catalytic activity of dispersed metal catalysts depends strongly on both the preparation method and the characteristics of the support [19–22]. However, synthetic techniques for bimetallic materials supported on carbonaceous nanomaterials are not yet well developed [23–30]. In particular, graphene (GR, GR is also called RGO in the literature), with the unique two-dimensional (2D) structure and electronic properties [31–37]. Nevertheless, it should be noted that studies regarding Au-Pd/RGO in literature are mainly focused on the photocatalytic degradation of organic pollutants, electrochemical detection, and electrocatalytic properties [23–26,38–41]. In the long run, one of the challenges as well as opportunities faced by the researchers is to develop highly selective Au-Pd/RGO catalysts used for selective oxidation of benzyl alcohol in solvent-free and selective reduction of nitroaromatics in water. Water is a desirable green solvent for organic reactions because of its features of environmental concerns, safety, and low cost [42].

In this present work, we have prepared the Au-Pd/RGO nanocomposites *via* a simple wet chemistry approach during which no additional dendrimers, ligands, polyelectrolytes, surfactants, or polymers are required, the extra protecting agents, would be incorporated into the resultant product, which might further affect the catalytic activity of the Au-Pd/RGO nanohybrids. Obviously, these Au, Pd, Au-Pd/RGO exhibit a highly catalytic activity toward selective oxidation benzyl alcohol to benzaldehyde in solvent-free and selective reduction of nitroaromatics to corresponding amines in water, and the rates of oxidation and reduction follow the sequence, Au-Pd/RGO > Pd/RGO > Au/RGO. The possible

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* Corresponding author at: College of Chemistry and Environment, Fujian Province Key Laboratory of Morden Analytical Science and Separation Technology, Minnan Normal University, Zhangzhou 363000, People's Republic of China.

E-mail address: zhangyh@mnnu.edu.cn (Y. Zhang).

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reasons accounting for the differences in the catalytic activities among the Au, Pd and Au-Pd/RGO nanocomposites have been discussed.

2. Experimental

2.1. Materials

Graphite powder, sulfuric acid (H_2SO_4), potassium persulfate ($K_2S_2O_8$), phosphorus pentoxide (P_2O_5), nitric acid (HNO_3), potassium permanganate ($KMnO_4$), hydrochloric acid (HCl), hydrogen peroxide, 30% (H_2O_2), chloroauric acid tetrahydrate ($AuCl_3{\cdot}HCl{\cdot}4H_2O$), palladium chloride ($PdCl_2$), sodium borohydride ($NaBH_4$), benzyl alcohol ($C_6H_5CH_2OH$), benzaldehyde ($C_6H_5CHO$), 4-nitroaniline ($O_2NC_6H_4NH_2$), 4-nitrophenol ($O_2NC_6H_4OH$), 1-bromo-4-nitrobenzene ($O_2NC_6H_4Br$), 1-chloro-4-nitrobenzene ($O_2NC_6H_4Cl$), 4-nitrotoluene ($O_2NC_6H_4CH_3$), 4-nitroanisole ($O_2NC_6H_4OCH_3$), *p*-phenylenediamine ($H_2NC_6H_4NH_2$), 4-aminophenol ($H_2NC_6H_4OH$), 4-bromoaniline ($H_2NC_6H_4Br$), 4-chloroaniline ($H_2NC_6H_4Cl$), *p*-toluidine ($H_2NC_6H_4CH_3$), 4-methoxyaniline ($H_2NC_6H_4OCH_3$), and ethanol (C_2H_5OH) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All materials (analytic grade) were used as received without further purification. Deionized water used in the synthesis was from local sources.

2.2. Preparation of catalysts

Graphene oxide (GO), the precursor of reduced graphene oxide (RGO), was prepared *via* a modified Hummers method, which was also used in our previous studies [43]. The precursor of Au was dissolved in deionized water to produce the corresponding solution with the requisite concentration of 0.01 M directly but on the account of slight solubility of $PdCl_2$ in water. HCl was employed to dissolve it. The resulting H_2PdCl_4 solution had the same concentration of 0.01 M as the precursor solution of Au. The fabrication of Au-Pd/RGO catalyst was typically performed as follows, as outlined in Scheme 1. 95 mg of GO was ultrasonicated in 100 mL of deionized water to make it disperse well; then 1.27 mL of $HAuCl_4$ and 2.35 mL of H_2PdCl_4 solution were added drop by drop and aged with stirring for 30 min. Subsequently, 50 mL of 0.15 M $NaBH_4$ solution was added drop by drop for 30 min, and the mixing solution was heated to 373 K in an oil bath with a cooling condenser with stirring for 24 h. Afterward, the solution was cooled down to room temperature. The products were separated by filtration, washed by deionized water, and fully dried at 333 K in an oven to get the final Au-Pd/RGO catalyst. For Au/RGO and Pd/RGO catalysts, the synthesis procedures are similar except that the noble metal precursor of $HAuCl_4$ or H_2PdCl_4 is 2.54 or 4.70 mL, respectively.

2.3. Characterization of catalysts

The crystalline structure of the samples was determined by the powder X-ray diffraction (XRD, Rigaku Ultima Ⅳ) with Cu Kα_1 radiation (40 kV, 40 mA, λ = 1.5406 Å) in a 2θ ranging from 5° to 80° at the scan rate of 8° per minute. The transmission electron microscopy (TEM) images, high-resolution TEM images, and energy-dispersive X-ray spectra (EDS) of elements, and element mapping were obtained using a JEOL model JEM 2010 EX instrument at an accelerating voltage of 200 kV. The particles size distribution was performed using *Nano measurer* software.

2.4. Tests of catalytic activity

(a) Catalytic selective oxidation of benzyl alcohol

A mixture of 50 mg catalyst and 20 mL benzyl alcohol was transferred into Parr autoclave reactor and stirred for 30 min to ensure an even blend of catalyst in solution. The autoclave was then purged 3 times with oxygen leaving the vessel at the desired pressure of 3 × 10^5 Pa. The stirrer speed was set at 1500 r min^{-1} and the reaction mixture was heated to 373 K. After reaction, samples were analyzed by Agilent Gas Chromatograph. Conversion of benzyl alcohol (BA) and selectivity for benzaldehyde (BAD) were defined as:

$$\%\ \text{conversion} = [(C_0 - C_{BA})/C_0] \times 100$$

$$\%\ \text{selectivity} = [C_{BAD}/(C_0 - C_{BA})] \times 100$$

where C_0 is the initial concentration of benzyl alcohol, C_{BA} and C_{BAD} are the concentration of benzyl alcohol and benzaldehyde, respectively, at a certain time after the catalytic reaction.

(b) Catalytic selective reduction of nitroaromatics

The catalytic reactions were carried out in a beaker. 80 mg $NaBH_4$ was dissolved into 160 mL of 10 mg L^{-1} nitroaromatic aqueous solution. This mixture was stirred vigorously at room temperature for 3 min to generate uniform aqueous solution. Subsequently, 5 mg of the catalyst was added into the above solution. During the process of the reaction, 3 mL of the solution was withdrawn by a syringe and filtered by 0.45 μm Millpore film at each time interval for UV–vis spectroscopy analysis. Conversion of nitroaromatic and selectivity for amine were defined as:

$$\%\ \text{conversion} = [(C_0 - C_{nitro})/C_0] \times 100$$

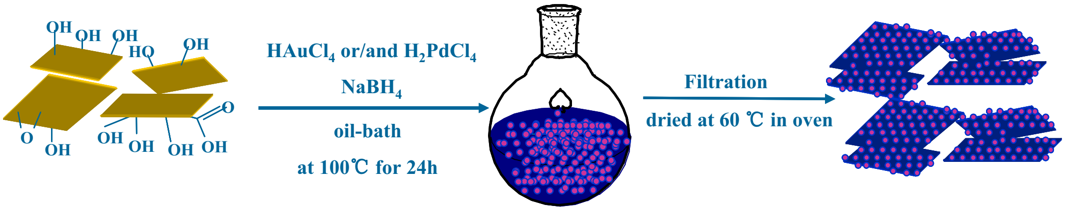
$$\%\ \text{selectivity} = [C_{amine}/(C_0 - C_{nitro})] \times 100$$

where C_0 is the initial concentration of nitroaromatic, C_{nitro} and C_{amine} are the concentration of nitroaromatic and amine, respectively, at a certain time after the catalytic reaction.

3. Results and discussion

3.1. Characterization of as-prepared catalysts

Shown in Fig. S1 (Supplementary Materials) are the characterization data of X-ray diffraction (XRD) of the GO sample. The XRD pattern of GO shows a sharp diffraction peak at 2θ values of *ca.* 10.2°. For the Au-Pd/RGO obtained from the $NaBH_4$ reduction and reflux, *ca.* 10.2° diffraction peak disappeared and a very broad diffraction peak at 2θ values of *ca.* 24.6° appeared, this is means that GO sheets have been effectively exfoliated from the raw



Scheme 1. Illustration for fabrication of Au-Pd/RGO catalyst by a simple reflux method.