Catalysis Communications 43 (2014) 164–168

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Palladium nanoparticles supported on Fe_3O_4/amino acid nanocomposite: Highly active magnetic catalyst for solvent-free aerobic oxidation of alcohols

Farzad Zamani [a,b,*], Seyed Mohsen Hosseini [a]

[a] Department of Chemistry, Shahreza Branch, Islamic Azad University, Shahreza 31186145, Isfahan, Iran
[b] Laboratory of Applied Chemistry, Central Laboratory Complex, Isfahan Science and Technology Town, Isfahan University of Technology, Isfahan 8415683111, Iran

ARTICLE INFO

Article history:
Received 17 August 2013
Received in revised form 26 September 2013
Accepted 27 September 2013
Available online 12 October 2013

Keywords:
Heterogeneous magnetic catalyst
Palladium nanoparticle
Cysteine amino acid
Solvent-free aerobic oxidation of alcohol
High selectivity

ABSTRACT

In this paper, Fe_3O_4 nanoparticles were coated by a number of amino acids, e.g. cysteine, serine, glycine and β-alanine, via a simple method. Because of the surface modification of the magnetic nanoparticles with amino acid, the obtained magnetic nanocomposite is able to trap palladium nanoparticles through a strong interaction between the metal nanoparticles and the functional groups of amino acids. Among the synthesized nanocomposites, Fe_3O_4/cysteine-Pd exhibited the highest catalytic performance and excellent selectivity in the solvent-free aerobic oxidation of various alcohols, along with high level of reusability.

1. Introduction

The selective oxidation of alcohols to the corresponding carbonyl compounds is a fundamental organic transformation in both laboratory and industrial synthetic chemistry because the resulting carbonyl compounds are widely used in the preparation of pharmaceutical, agricultural and fragrance chemicals [1]. In general, the oxidation process based on the use of traditional stoichiometric or excess amount of oxidants has caused serious environmental problems [2]. Therefore, the development of efficient catalysts for selective oxidation of alcohols using molecular oxygen or air to replace the stoichiometric oxidizing reagents has become urgent from the demand for establishing both environmentally benign and economically practical synthetic routes. In this regard, the solvent-free aerobic oxidation of alcohols using molecular oxygen or air as the oxidant has drawn much attention recently [3–5], due to positive effects in terms of cost, safety and environmental impact. In this study, it is highly attractive to develop the efficient catalytic system for the aerobic oxidation of various alcohols under solvent-free condition.

Over the last decade, organic–inorganic magnetic nanocomposites have become interesting as magnetic catalysts in both academic and industrial fields. The use of these magnetic nanoparticle catalysts can address the isolation and recycling problem encountered in many heterogeneous and homogenous catalytic reactions. Most importantly, the magnetic-supported catalysts show not only high catalytic activity but also high degree of chemical stability and they do not swell in organic solvents [6–8]. They can also be recovered with an external magnetic field and their catalytic efficiency remains after many repeated reactions [9]. In recent years, several heterogeneous noble metal catalysts based on magnetic nanoparticles have been applied for the aerobic oxidation of alcohols [10–12]. However, the application of noble metal nanoparticle catalysts based on organic–inorganic magnetic nanocomposites as heterogeneous catalysts in the oxidation reaction of alcohols has received no considerable attention.

In recent years, modified magnetic nanoparticles have received a lot of attention as support for preparation of noble metal nanoparticles. However, most of these techniques require many reaction steps to introduce functional groups to the magnetic surface and they use organosilica precursors as organic shell in order to prepare a suitable support for trapping metal nanoparticles [13–18]. The organosilane precursors not only involve complicated synthesis and purification method, but also are very expensive and toxic. Therefore, from both environmental and economic points of view, preparation of the modified magnetic nanoparticles via a simple method and without using organoalkoxysilane compounds is highly desirable. In this study, amino acids, which are inexpensive and nontoxic materials, were used as good candidates for incorporation of palladium nanoparticles.

In continuing our efforts towards the development of efficient and environmentally benign heterogeneous catalysts [19,20], herein, we will report a simple preparation of palladium nanoparticles incorporated

---

* Corresponding author. Tel.: +98 311 3865355; fax: +98 311 3869714.
E-mail address: fzamani@iaush.ac.ir (F. Zamani).

1566-7367/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.catcom.2013.09.029

into Fe_3O_4/amino acid nanocomposite as a new magnetically recoverable heterogeneous catalyst. The catalytic activity of this magnetic catalyst was tested in the aerobic oxidation reaction of different alcohols under solvent-free condition.

2. Experimental

2.1. Catalyst preparation

Fe_3O_4/amino acid-Pd magnetic nanocomposite was synthesized via a simple and in-situ method as the following:

> In the first step, magnetic nanoparticles were prepared in the presence of several amino acids, e.g. L-cysteine (Cys), β-alanine (Ala), serine (Ser) and glycine (Gly), via a co-precipitation route in an early study [21]. $FeCl_3 \cdot 6H_2O$ (13 g, 0.048 mol), $FeCl_2 \cdot 4H_2O$ (4.8 g, 0.024 mol) and amino acid (Cys, Ala, Ser or Gly, 0.096 mol) were dissolved in 100 mL deionized water. Then, the solution pH was adjusted to 11 with NaOH solution (2 M) to form a black suspension. Afterwards, the suspension was reflux for 12 h under vigorous stirring and Ar atmosphere. Finally, the obtained nanocomposite was separated from the aqueous solution by magnetic decantation, washed several times with deionized water and dried in an oven overnight. The resulting powders were denoted as Fe_3O_4/Cys, Fe_3O_4/Ala, Fe_3O_4/Ser and Fe_3O_4/Gly.
>
> In the second step, Pd nanoparticles were immobilized on Fe_3O_4/amino acid through the reduction of $PdCl_2$ by hydrazine hydrate in ethanol. Briefly, the as-synthesized Fe_3O_4/amino acid (1.0 g) and $PdCl_2$ (0.1 g) were dispersed in an ethanol solution (30 mL) and reflux for 10 h. Then, the reaction mixture was cooled to room temperature and hydrazine hydrate solution (catalyst: hydrazine hydrate = 1:5) was slowly dropped into the mixture and refluxed further for 2 h. The resultant product was collected by an external magnetic field, washed several times with ethanol and deionized water and dried in a vacuum oven at 60 °C. The as-synthesized magnetic nanocomposites were denoted as Fe_3O_4/Cys-Pd, Fe_3O_4/Ala-Pd, Fe_3O_4/Ser-Pd and Fe_3O_4/Gly-Pd. The amount of Pd in the obtained catalysts, based on ICP analysis, was found to be 6.27, 3.62, 5.28 and 3.14 wt.% for Fe_3O_4/Cys-Pd, Fe_3O_4/Ala-Pd, Fe_3O_4/Ser-Pd and Fe_3O_4/Gly-Pd respectively.

2.2. General procedure for solvent-free aerobic oxidation of alcohols

In a typical reaction, benzyl alcohol (0.2 mL, 2 mmol) and magnetic catalyst (0.06 g) were loaded in a two-neck round bottom flask. The mixture was then immersed in a 50 °C oil bath and the oxygen flow was bubbled into the mixture to initiate the reaction. The reaction mixture was then stirred under solvent-free condition. The progress of reaction was monitored by thin layer chromatography (TLC). On completion of the reaction, the catalyst was removed by an external magnet and the liquid organic product was analyzed by an Agilent gas chromatograph 6890 equipped with a HP-5 capillary column. Dodecane was the internal standard to calculate benzyl alcohol conversion and benzaldehyde selectivity.

3. Results and discussion

3.1. Catalyst characterization

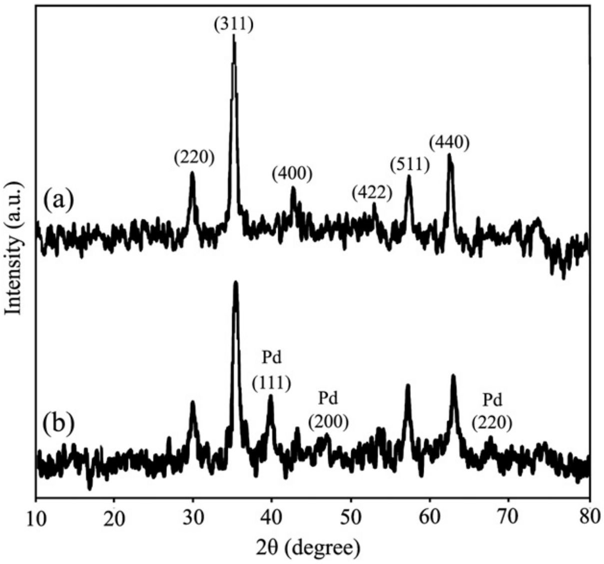

Fig. 1. X-ray powder diffraction patterns of (a) Fe_3O_4/Cys and (b) Fe_3O_4/Cys-Pd nanocomposite.

The high angle XRD patterns of the Fe_3O_4/Cys and Fe_3O_4/Cys-Pd nanocomposites were shown in Fig. 1 (evaluated by Bruker D8 Advance diffractometer). It could be seen that the strong characteristic diffraction peaks at 2θ of 30.1°, 35.4°, 43.2°, 53.7°, 56.9° and 62.9° belong to the diffraction of (220), (311), (400), (422), (511) and (440) of the Fe_3O_4 (JCPDS 89-3854), which were found in both samples (Fig. 1a,b). This result means that the nanocomposite has been successfully synthesized without damaging the crystal structure of Fe_3O_4 core. Moreover, apart from the original peaks related to Fe_3O_4, the new peaks at 2θ of 40°, 46.7° and 67.9° were observed, which correspond to (111), (200) and (220) crystalline planes of Pd, indicating that Pd element exists in the form of Pd(0) (Fig. 1b). The crystallite size of Pd nanoparticles was evaluated using Scherrer equation for the (111) peak and was found to be approximately 4 nm in size. The average grain size of the Pd nanoparticles is approximately the same as the average particle size of the Pd nanoparticles determined by the TEM observations, which indicates that the Pd nanoparticles are single crystals. It seems that the size of the metal nanoparticles, determined by TEM analysis, is more reliable than using Scherrer formula in XRD analysis.

The FT-IR spectra of Fe_3O_4/Cys and Fe_3O_4/Cys-Pd nanocomposites were recorded to confirm the modification of the magnetite surface with the amino acid and Pd nanoparticles (Fig. 1) (measured with a Perkin Elmer 65 spectrometer). The presence of magnetite nanoparticles is observable by the strong adsorption band at 587 cm^{-1}, corresponding to the Fe – O vibrations (Fig. 2a,b). As can be seen, the adsorption peaks at 1586, 1418 and 3286 cm^{-1} are due to asymmetric and symmetric

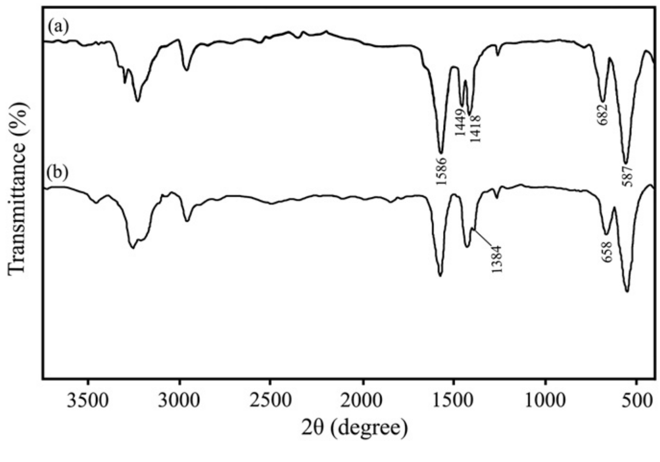

Fig. 2. FT-IR spectra of (a) Fe_3O_4/Cys and (b) Fe_3O_4/Cys-Pd nanocomposite.