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# Short Communication

# Palladium nanoparticles supported on Fe<sub>3</sub>O<sub>4</sub>/amino acid nanocomposite: Highly active magnetic catalyst for solvent-free aerobic oxidation of alcohols

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### ABSTRACT

In this paper,  $Fe_3O_4$  nanoparticles were coated by a number of amino acids, e.g. cysteine, serine, glycine and  $\beta$ -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.

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#### 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







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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<sub>3</sub>O<sub>4</sub>/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),  $\beta$ -alanine (Ala), serine (Ser) and glycine (Gly), via a co-precipitation route in an early study [21]. FeCl<sub>3</sub>·6H<sub>2</sub>O (13 g, 0.048 mol), FeCl<sub>2</sub>·4H<sub>2</sub>O (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<sub>3</sub>O<sub>4</sub>/Cys, Fe<sub>3</sub>O<sub>4</sub>/Ala, Fe<sub>3</sub>O<sub>4</sub>/Ser and Fe<sub>3</sub>O<sub>4</sub>/Gly.

In the second step, Pd nanoparticles were immobilized on Fe<sub>3</sub>O<sub>4</sub>/ amino acid through the reduction of PdCl<sub>2</sub> by hydrazine hydrate in ethanol. Briefly, the as-synthesized Fe<sub>3</sub>O<sub>4</sub>/amino acid (1.0 g) and PdCl<sub>2</sub> (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<sub>3</sub>O<sub>4</sub>/Cys-Pd, Fe<sub>3</sub>O<sub>4</sub>/ Ala-Pd, Fe<sub>3</sub>O<sub>4</sub>/Ser-Pd and Fe<sub>3</sub>O<sub>4</sub>/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<sub>3</sub>O<sub>4</sub>/Cys-Pd, Fe<sub>3</sub>O<sub>4</sub>/Ala-Pd, Fe<sub>3</sub>O<sub>4</sub>/Ser-Pd and Fe<sub>3</sub>O<sub>4</sub>/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

The high angle XRD patterns of the Fe<sub>3</sub>O<sub>4</sub>/Cys and Fe<sub>3</sub>O<sub>4</sub>/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 20 of 30.1°, 35.4°, 43.2°, 53.7°, 56.9° and 62.9° belong to the



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

diffraction of (220), (311), (400), (422), (511) and (440) of the Fe<sub>3</sub>O<sub>4</sub> (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<sub>3</sub>O<sub>4</sub> core. Moreover, apart from the original peaks related to Fe<sub>3</sub>O<sub>4</sub>, the new peaks at 20 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 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<sub>3</sub>O<sub>4</sub>/Cys and Fe<sub>3</sub>O<sub>4</sub>/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<sup>-1</sup>, corresponding to the Fe – O vibrations (Fig. 2a,b). As can be seen, the adsorption peaks at 1586, 1418 and 3286 cm<sup>-1</sup> are due to asymmetric and symmetric



Fig. 2. FT-IR spectra of (a) Fe<sub>3</sub>O<sub>4</sub>/Cys and (b) Fe<sub>3</sub>O<sub>4</sub>/Cys-Pd nanocomposite.

stretching of the COO<sup>-</sup> and N-H stretching, respectively, which indicate the presence of bound amino acid on the magnetite nanoparticle surface (Fig. 2a,b). Furthermore, it has been reported that the wavenumber separation between the  $COO_{as}^{-}$  and  $COO_{s}^{-}$  IR bands can be used to distinguish the type of the interaction between the carboxylate head and the metal atom [22]. Since the wavenumber separation between the  $COO_{as}^{-}$  and  $COO_{s}^{-}$  bands is 168 cm<sup>-1</sup> (1586–  $1418 = 168 \text{ cm}^{-1}$ ) (Fig. 2a,b), it can be concluded that the interaction between the COO<sup>-</sup> group and the Fe atom was covalent and bridging bidentate [22]. In addition, the bands in the 2900–3000  $\text{cm}^{-1}$  are attributed to the stretching of C-H bonds of the amino acid (Fig. 2a,b). Moreover, the band at around  $682 \text{ cm}^{-1}$ , which corresponds to C-S bond of the supported cysteine (Fig. 2a), is shifted to lower wavenumbers (658  $\text{cm}^{-1}$ ) (Fig 2.b), suggesting a strong interaction between sulfur group and metal particles [23]. The bending vibration absorption band of N-H at 1449 cm<sup>-1</sup> (Fig. 2a) is also shifted to lower wavenumbers (1449  $\rightarrow$  1384), which is possibly due to the interaction of amine group with metal particles (Fig. 2b) [24]. Taking the above observations into consideration, it can be concluded that the Fe<sub>3</sub>O<sub>4</sub>/Cys-Pd nanocomposite was successfully obtained along with a strong interaction between sulfur and amine groups of the supported cysteine and the Pd nanoparticles.

The morphology of the nanocomposite was observed on transmission electron microscopy (Phillips CM10 microscope). Fig. 3 shows TEM image of the Fe<sub>3</sub>O<sub>4</sub>/Cys-Pd nanocomposite catalyst. It can be seen that the particle diameter of the catalyst is about 20 nm and they are nearly uniform in size. Moreover, the Pd nanoparticles were found to be highly dispersed on the surface of the Fe<sub>3</sub>O<sub>4</sub>/Cys nanoparticles with the average diameter size of ~3 nm. Li et al. have reported that the metal nanoparticle catalysts with a medium mean size of about 3 nm exhibit the highest conversion and selectivity for the oxidation of alcohols, compared with those with larger or smaller metal particles [25]. As a result, it could be expected that the synthesized magnetic catalyst has high activity/selectivity performance, which will be investigated in further steps.

In order to obtain information on the structural features of the nanocomposite, the XPS study was carried out on the  $Fe_3O_4/Cys$ -Pd catalyst (recorded by Shimadzu ESCA SSX-100). The XPS result of Pd nanoparticles dispersed in the  $Fe_3O_4/Cys$  nanocomposite for Pd 3d spectrum with the binding energies of Pd  $3d_{5/2}$  and Pd  $3d_{3/2}$  lying at about 332.5 and 337.8 eV, respectively (Fig. 4). It means that Pd nanoparticles are stable as metallic state in the  $Fe_3O_4/Cys$ 



Fig. 3. TEM micrograph of Fe<sub>3</sub>O<sub>4</sub>/Cys-Pd nanocomposite.



Fig. 4. XPS spectrum of Pd 3d of Fe<sub>3</sub>O<sub>4</sub>/Cys-Pd nanocomposite.

nanocomposite structure. In comparison to the standard binding energy of Pd<sup>0</sup>, with Pd  $3d_{5/2}$  of about 335 eV and Pd<sub>3/2</sub> of about 340 eV [26], it can be concluded that the Pd peaks in the Fe<sub>3</sub>O<sub>4</sub>/Cys-Pd shifted to lower binding energy than Pd<sup>0</sup> standard binding energy. It has been reported that the position of Pd 3d peak is usually influenced by the local chemical/physical environment around Pd species besides the formal oxidation state, and shifts to lower binding energy when the charge density around it increases [26]. Therefore, the peaks at 332.5 and 337.8 could be due to Pd<sup>0</sup> species bound directly to oxygen and sulfur groups in the Fe<sub>3</sub>O<sub>4</sub>/Cys, which is in agreement with IR results.

#### 3.2. Catalytic activity

In order to evaluate catalytic activity of the  $Fe_3O_4/amino$  acid-Pd nanocomposites and to optimize the reaction conditions, the aerobic oxidation of benzyl alcohol was chosen as a model reaction. Before optimizing the reaction conditions, the catalytic activity of synthesized nanocomposites was compared in the solvent-free aerobic oxidation of benzyl alcohol. Then, after choosing the best nanocomposite as catalyst, the aerobic oxidation reaction was conducted in different reaction parameters such as solvent and amount of catalyst.

In an effort to compare the catalytic activity of synthesized magnetic nanocomposites for the oxidation of benzyl alcohol under  $O_2$  atmosphere and solvent-free condition, it was found that these nanocomposites demonstrated the different activity for the alcohol oxidation. As displayed in Table 1, Fe<sub>3</sub>O<sub>4</sub>/Gly-Pd catalyst afforded the lowest reaction yield, while the Fe<sub>3</sub>O<sub>4</sub>/Cys-Pd catalyst exhibited the highest catalytic performance in

#### Table 1

Solvent-free aerobic oxidation of benzyl alcohol catalyzed by different synthesized magnetic nanocomposites.<sup>a</sup>

Catalyst	Selectivity to benzaldehyde $(\%)^{\rm b}$	Yield (%) <sup>c</sup>
Fe <sub>3</sub> O <sub>4</sub> /Cys-Pd	>99	48
Fe <sub>3</sub> O <sub>4</sub> /Ala-Pd	>99	23
Fe <sub>3</sub> O <sub>4</sub> /Ser-Pd	>99	35
Fe <sub>3</sub> O <sub>4</sub> /Gly-Pd	>99	16

 $^a\,$  Reaction conditions: benzyl alcohol (2 mmol), catalyst (0.03 g), reaction time =1.5 h, temperature  $=50\,^\circ\text{C},$  O\_2 bubbling.

<sup>b</sup> Determined by GC using dodecane as internal standard.

<sup>c</sup> GC yield.



Scheme 1. Structures of the amino acids used in the preparation of Fe<sub>3</sub>O<sub>4</sub>/amino acid-Pd nanocomposite.

the solvent-free aerobic oxidation of benzyl alcohol. These results indicate that the ligand structure could play an important role in the catalytic activity of nanocomposites. It has been reported that sulfurcontaining ligands are highly efficient stabilizers for the preparation of palladium nanoparticles [27]. Among the used amino acids, sulfur groups in the structure of cysteine make it the best candidate for the preparation of metal nanoparticles, which is in agreement with the metal content of the catalysts (determined by ICP in the experimental section). The structures of used amino acids were represented in Scheme 1.

As far as the effect of solvent is concerned, the model reaction was carried out in several solvents as well as solvent-free condition to investigate the efficiency of the catalyst (Fe<sub>3</sub>O<sub>4</sub>/Cys-Pd). As can be seen in Table 2, the best yields were obtained when the reactions were performed in water and solvent-free condition at 50 °C (52% and 48% respectively). Since the solvent-free condition is more environmentally benign, it was chosen as the best reaction medium for the aerobic oxidation of benzyl alcohol in the presence of Fe<sub>3</sub>O<sub>4</sub>/Cys-Pd. Moreover, the effect of catalyst amount on the alcohol reaction was also carried out by different amounts of the catalyst (Table 2). It was observed that while the amount of catalyst increased from 0.03 to 0.06 g, the product vield raised significantly from 48% to 85% with excellent selectivity to benzaldehyde (>99%). Since then, the percentage of yield remained stable and selectivity to benzaldehyde decreased by 6% between 0.06 g and 0.08 g. According to the data, 0.06 g was chosen as the best amount of catalyst for further steps.

It should be mentioned that the oxidation of benzyl alcohol was performed under air instead of oxygen, based on the optimized reaction conditions. It was observed that when the solvent-free oxidation of benzyl alcohol was carried out under air, the product yield was not satisfying (55% in 235 min).

In the view of industrial purposes, reusability of the catalyst was tested by carrying out repeated runs of the reaction on the same batch of the catalyst in the case of the model reaction (Table 3). In order to regenerate the catalyst, after each cycle, it was separated by a magnet, and washed several times with deionized water and ethanol. Then, it was dried in oven at 60 °C and used in the next run. The results show

that this catalyst can be reused seven times without any significant loss in activity/selectivity performance in the solvent-free aerobic oxidation of benzyl alcohol. This high catalytic activity can be possibly related to the strong interaction of Pd nanoparticles with active sites of cysteine, because sulfur-containing ligands are highly efficient stabilizers for the metal nanoparticles [27].

The Fe<sub>3</sub>O<sub>4</sub>/Cys-Pd catalyst also represented a good activity and selectivity in the solvent-free aerobic oxidation of different aromatic and aliphatic alcohols (Table 4). All the investigated alcohols were converted to the corresponding aldehydes in high yields with excellent selectivity.

## 4. Conclusion

In conclusion,  $F_3O_4$  nanoparticles were coated with several amino acids as organic shell via a co-precipitation method. The  $Fe_3O_4/amino$ acid nanocomposites were effectively employed as scaffold for in-situ generation of Pd nanoparticles. This new heterogeneous catalyst showed the following advantages: (a) simple preparation; (b) easy separation after reaction by an external magnet; and (c) reusability for several times without any significant loss in the yield and selectivity of the products in the solvent-free aerobic oxidation of alcohols. Interestingly,  $Fe_3O_4/cysteine-Pd$  nanoparticles ( $Fe_3O_4/Cys-Pd$ ) exhibited the highest activity in the oxidation reaction among the other synthesized nanocomposites, which is possibly due to the existence of sulfur groups in the cysteine structure. These unique results open new perspectives for the application of these types of magnetic catalysts in other organic reactions.

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Table 2
Effects of different solvents and amount of catalyst on the oxidation of benzyl alcohol in
the presence of Fe <sub>3</sub> O <sub>4</sub> /Cys-Pd. <sup>a</sup>

Solvent	Catalyst (g)	Selectivity to benzaldehyde $(\%)^{\rm b}$	Yield (%) <sup>d</sup>
Water	0.03	>99	52
Acetonitrile	0.03	>99	42
n-Hexane	0.03	>99	32
Toluene	0.03	>99	36
Solvent-free	0.03	>99	48
Solvent-free	0.06	>99	85
Solvent-free	0.08	94 <sup>c</sup>	85

 $^a\,$  Reaction conditions: benzyl alcohol (2 mmol), reaction time = 1.5 h, temperature = 50 °C, O\_2 bubbling.

<sup>b</sup> Determined by GC using dodecane as internal standard.

<sup>c</sup> The main by-product was toluene.

<sup>d</sup> GC yield.

 Table 3

 The catalyst reusability for the solvent-free aerobic oxidation of benzyl alcohol.<sup>a</sup>

Yield (%) <sup>c</sup>	Selectivity to benzaldehyde $(\%)^{\rm b}$	Cycle
85	>99	Fresh
85	>99	1
85	>99	2
83	>99	3
83	>99	4
82	>99	5
80	>99	6
80	>99	7

<sup>a</sup> Reaction conditions: benzyl alcohol (2 mmol), catalyst (0.06 g, Fe<sub>3</sub>O<sub>4</sub>/Cys-Pd), reaction time = 1.5 h, temperature = 50 °C, O<sub>2</sub> bubbling.

<sup>b</sup> Determined by GC using dodecane as internal standard.

<sup>c</sup> GC yield.

#### Table 4

Solvent-free aerobic oxidation of various aromatic and aliphatic alcohols over Fe<sub>3</sub>O<sub>4</sub>/Cys-Pd.<sup>a</sup>

Entry	Substrate	Product	Time (h)	Yield (%) <sup>b</sup>
1	CH <sub>2</sub> OH	СНО	1.5	85
2	Br CH <sub>2</sub> OH	Br CHO	1	83
3	сі Сн <sub>2</sub> он	СІ СНО	1	82
4	О2N СН2ОН	02N СНО	3	58
5	HO CH <sub>2</sub> OH	но	1.5	70
6	МеО СН2ОН	МеО	1.5	82
7	СН₂ОН	СНО	1	87
8		СНО	4	74
9	ОП	СНО	4	75

<sup>a</sup> Reaction conditions: benzyl alcohol (2 mmol), catalyst (0.06 g, Fe<sub>3</sub>O<sub>4</sub>/Cys-Pd), temperature = 50 °C, O<sub>2</sub> bubbling, selectivity = >99.

<sup>b</sup> GC yield

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