ORIGINAL PAPER



Pd(II) anchored to modified Fe₃O₄ nanoparticles as a new magnetically recoverable catalyst for epoxidation of styrene

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Received: 20 December 2015 / Accepted: 13 June 2016 © Iranian Chemical Society 2016

Abstract A new support for Pd(II) was synthesized via the functionalization of Fe_3O_4 nanoparticles with *N*-(2-aminoethyl)acetamide. PdCl₂ was anchored to the support for obtaining a heterogeneous magnetically recoverable catalyst for Pd(II). High yield and excellent selectivity were obtained for the green epoxidation of styrene derivatives using H_2O_2 as a green oxidant in H_2O as the solvent at 100 °C. Also, the recovered catalyst is applicable for four times without significant decrease in yield.

Keywords Magnetic nanoparticles · Epoxidation · Styrene · Styrene oxide · Heterogeneous catalyst

Introduction

In recent years, a remarkable increase was observed in the importance of nanomaterials in fundamental research and technological applications. Among many of known nanomaterials, the special position belongs to magnetic nanoparticles (MNPs). MNPs fundamentally differ from the classic magnetic materials with their domain structure. As a result of recent investigations, the new physics of magnetic phenomena—nanomagnetism—was developed. These nanomaterials have broad applications in biotechnology,

Electronic supplementary material The online version of this article (doi:10.1007/s13738-016-0914-y) contains supplementary material, which is available to authorized users.

Sajjad Keshipour s.keshipour@urmia.ac.ir biomedical, material science, engineering and environmental areas [1-3]. Various modified MNPs were introduced in the drug delivery with unique features [4-6]. Modified MNPs also widely have been studied in the catalyst designing [7-9].

The epoxidation of olefins as an important chemical processes gives epoxides [10, 11] which widely used as the starting materials or intermediates for the production of epoxy resins, paints, surfactants and medicines. Excellent selectivity can be obtained for the epoxidation of olefins using a heterogeneous silver catalyst [12], but typically chlorinated hydrocarbons and nitrogen oxides have to be added to quench unfavorable by-product formation, and this makes the process nongreen in this respect. Propene can be epoxidized using hydrogen peroxide in the presence of the titanium silicalite TS-1 as the catalyst [13]. Supported gold is a potent catalyst for the epoxidation of propene with oxygen in the presence of H₂ as a sacrificial reductant that permits the activation of O₂ at relatively low temperatures [14–16]. In this route, it was considered that a hydroperoxy species was formed in situ and this led to the selective oxidation chemistry. Au/TiO2, prepared using deposition precipitation, oxidized propene to propene oxide. Initially, selectivity was low but promising; improvements were made by using different titanium-containing supports including TS-1, Ti-zeolite b, Ti-MCM-41 and Ti-MCM-48 [17–24]. Recently, a selective oxidation of alkenes was performed using graphite-supported gold-palladium catalysts with *t*-butyl hydroperoxide in high yields [25]. Palladium especially is an efficient catalyst for epoxidation of allylic alcohols. There are numerous reports for epoxidation of allylic alcohols with Pd [26].

In continuation of our efforts to the development of the new heterogeneous catalytic system [27–30], herein a new efficient catalytic system was introduced for the

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Ph
$$\xrightarrow{Pd(II)@AEA-Fe_3O_4NP, DMA}$$
 Ph \xrightarrow{O}
1 $\xrightarrow{H_2O_2, H_2O}$ 2

Scheme 1 Epoxidation of styrene with Pd(II)@AEA-Fe₃O₄NP

epoxidation of styrene to styrene oxide by Pd(II) supported on *N*-(2-aminoethyl)acetamide functionalized Fe₃O₄ nanoparticles (Pd(II)@AEA-Fe₃O₄NP) as a heterogeneous recoverable catalyst with H₂O₂ as a green oxidant and *N*,*N'*-dimethylformamide (DMA) as the Pd activator ligand in H₂O as a green solvent (Scheme 1).

Amines specially diamines are efficient groups for the grafting of metal cations such as Pd(II) which widely used as the catalyst [28]. So, modification of the supports with amine ligands can be assisted to grafting of metal cations with the support. Fe₃O₄ NPs is one of the interesting supports especially due to the magnetic properties. This material has many hydroxyl groups with the ability to react with the organic functional groups. Herein, we use this ability of Fe₃O₄ NPs to functionalization of the magnetic NPs with ethylenediamine.

Materials and methods

All reagents were purchased from Aldrich or Merck and used without further purification. Transmission electron microscopy (TEM) was performed by LEO 912AB electron microscope. Energy-dispersive X-ray spectroscopy (EDS) was made with scanning electron microscope of TSCAN company. X-ray powder diffraction (XRD) data were collected on an XD-3A diffractometer using Cu K_{α} radiation. Thermal gravimetric analysis (TGA) was performed with Linseis STA PT1000. Pd(0) determination was carried out on an FAAS (Shimadzu model AA-680 atomic absorption spectrometer) with a Pd hollow cathode lamp at 242.8 nm, using an air–acetylene flame.

Preparation of Pd(II)@AEA-Fe₃O₄NP

In a typical procedure, a mixture of FeCl₂·4H₂O (0.25 g) and FeCl₃·6H₂O (0.67 g) in 20 mL of H₂O was treated with 20 mL ammonia solution with vigorous stirring at 60 °C. After 2 h, chloroacetic acid (0.5 g) was added to the mixture and stirring continued at 60 °C for 24 h. Acetic acid functionalized Fe₃O₄ NPs was separated with a magnet, washed with ethanol (2 × 5 mL) and dried at 70 °C. Ethylenediamine (2 mL) was added to the vessel containing acetic acid functionalized Fe₃O₄ NPs (2.00 g) and 2-propanol



Scheme 2 Preparation of Pd(II)@AEA-Fe₃O₄NP

(10 mL), and the mixture stirred at room temperature. After 24 h, compound (5) was separated with a magnet, washed with ethanol (2 × 5 mL) and dried at 70 °C. The obtained support (2.00 g) was added to a two-necked flask containing PdCl₂ (0.10 g) and H₂O (30 mL), and after 24 h stirring at room temperature, the catalyst was separated with a magnet. The catalyst was washed with H₂O (2 × 10 mL) and dried at 70 °C. All of the steps were performed under N₂ atmosphere.



Fig. 1 FTIR spectra of compounds 1-4



Fig. 2 XRD patterns of the Pd(II)@AEA-Fe₃O₄NP

Materials and methods for determination of Pd(II) on Pd(II)@AEA-Fe₃O₄NP using FAAS

Pd(II)@AEA-Fe₃O₄NP (0.05 g) was added to a mixture of HCl/HNO₃ (1:3) (10 mL) and sonicated for 3 h. Then, the mixture filtered off and the total volume of the filtrate was made up to about 30 mL with distilled water. The final solution was aspirated into the flame of the AAS against the blank prepared with AEA-Fe₃O₄NP. The Pd concentration obtained 0.02 g Pd per 1 g catalyst (0.19 mmol Pd/1 g catalyst), using calibration curve prepared with palladium solution standards.

Typical procedure for the epoxidation of styrene

Styrene (0.10 g, 1.00 mmol) was added to a round-bottomed flask containing colloidal of Pd(II)@AEA-Fe₃O₄NP (0.1 g) and DMA (0.02 mmol) in H₂O (5 mL) and temperature raise up to 100 °C. H₂O₂ (3 mmol) was added dropwise to the reaction vessel during 0.5 h. After 1.5 h, the reaction mixture was cooled to room temperature, and Pd(II)@AEA-Fe₃O₄NP was separated by a magnet and washed with acetone (2 × 5 mL). The filtrate solvent was evaporated under vacuum, and the product purified with column chromatography with *n*-hexane/ethylacetate (5:1).

Results and discussion

For the preparation of the catalyst (Scheme 2), Fe_3O_4 NPs was prepared from $FeCl_2$ and $FeCl_3$ in basic moiety under



Fig. 3 EDS analysis of the catalyst



Fig. 4 TEM image of Pd(II)@AEA-Fe₃O₄NP sample

Fig. 5 TGA of the catalyst



inert atmosphere. Chloroacetic acid was selected for making a connection between hydroxyl groups of Fe₃O₄ NPs and amines of ethylenediamine. Chloroacetic acid has two active sites including Cl-CH₂ and COOH for the reaction with a hydroxyl group and an amine, respectively. Fe₃O₄ NPs reacted with chloroacetic acid to give acetic acid functionalized Fe_3O_4 NPs (4). FTIR spectra of 4 indicate a new absorption band at 1650 cm^{-1} for the C=O band (Fig. 1). The resulted nanocompound reacted with ethylenediamine to give N-(2-aminoethyl)acetamide functionalized Fe_3O_4 NPs (5). Absorption band at 1650 cm^{-1} for compound 4 was shifted to 1630 cm^{-1} for compound 5 due to amidation of carboxylic acid group. Finally, Pd(II) was complexed with the diamine groups of the support during 24 h to yield the catalyst (6). The carbonyl absorption band of the catalyst was shifted to 1620 cm⁻¹ due to complexation of Pd(II) with the moiety. The catalyst was characterized with FTIR spectrum, EDS, TGA, XRD pattern and TEM image.

The structure of Pd(II)@AEA-Fe₃O₄NP was determined by powder XRD. There are various diffraction peaks which indicate existence of Pd and Fe₃O₄. The details of the peaks are shown in Fig. 2 [31].

The presence of Pd and Fe was also confirmed with EDS. EDS obviously shows that Pd is loaded on the catalyst (Fig. 3).

The TEM image of catalyst indicates existence of Fe_3O_4 NPs (Fig. 4). The Pd concentration obtained 0.10 mmol Pd per 1 g catalyst (0.011 g Pd per 1 g catalyst) using FAAS analysis.

For the study of thermal behavior of the catalyst, TGA was performed. TGA showed that the catalyst starts to decomposition above 232 °C which indicates good thermal stability for the catalyst (Fig. 5).

The catalytic activity of Pd(II)@AEA-Fe₃O₄NP was evaluated in the oxidation of styrene. The ¹H NMR study showed styrene oxide as the product. So, the oxidation of styrene (1) with H_2O_2 was investigated for the optimization of the reaction conditions. It was found that 2 mol% Pd (Table 1, entries 1–3) and 4 mol% DMA (Table 1, entries 4-7) in H₂O (Table 1, entries 8-12) with three equivalents of H₂O₂ at 100 °C (Table 1, entries 13-15) are the best reaction conditions for the oxidation of styrene. Oxidation of styrene proceeded to give styrene oxide (2) as the sole product in 91 % yield in short reaction duration (2 h) without isomerization or chlorination of styrene. The reaction needs long time for high yields in the absence of DMA. However, performing the reaction in the absence of DMA shows that the epoxidation reaction can be carried out with anchored amines to the support, but in long time and low efficiency. 3 mmol H_2O_2 is necessary for obtaining high yield which may be attributed to the decomposition of some H₂O₂ at 100 °C (Table 1, entry 8). After screening a variety of solvents, H₂O was determined to be the best solvent (Table 1, entries 9–13). Temperature is an important factor for this reaction, and the yield was decreased in low temperatures (Table 1, entries 14–16).

The reaction was examined under an oxygen atmosphere created with a balloon instead of H_2O_2 which the reaction was performed in long duration (24 h) with 64 % yield.

For investigation of the scope and limitations of the method, the catalyst activity was evaluated for the oxidation of various styrene derivatives. The reaction was performed for styrene derivatives with electron-withdrawing and electron-donating substitutes successfully in high yields (Table 2).

Potential Pd leaching into the reaction mixture was also analyzed with FAAS analysis. For this purpose, samples were taken through a syringe filter during the heterogeneous oxidation reaction of styrene, the solvent was evaporated, and the residue was dissolved in HNO₃. The analysis of these samples with FAAS showed that the Pd concentration in the reaction solution was less than the detection limit.

 Table 1
 Optimization of the reaction conditions for epoxidation of styrene

Entry	Catalyst amount (Pd mol%)	Solvent	Temp. (°C)	Time (h)	Yield (%)
1	1	H ₂ O	100	2	58
2	2	H_2O	100	2	91
3	3	H_2O	100	2	91
4 ^b	2	H_2O	100	2	33
5 ^b	2	H_2O	100	4	41
6 ^b	2	H_2O	100	12	68
7 ^c	2	H_2O	100	2	76
8 ^d	2	H_2O	100	2	73
9	2	DMA	100	2	48
10	2	MeCN	Ref.	3	83
11	2	EtOH	Ref.	2	80
12	2	CH_2Cl_2	Ref.	2	67
13	2	MeOH	Ref.	2	90
14	2	H_2O	80	4	72
15	2	H_2O	90	2	87
16	2	H_2O	r.t.	24	37

Reaction conditions: styrene (1 mmol), DMA (4 mol%), $\rm H_2O_2$ (3 mmol), solvent (5 mL)

^a Isolated yield, ^b without DMA, ^c DMA (3 mol%), ^d H₂O₂ (2 mmol)

Table 2 Epoxidation of styrene derivatives in the presence of $Pd(II)@AEA-Fe_3O_4NP$

Entry	Olefine	Yield (%) ^a
1	Styrene	91
2	2-Methylstyrene	90
3	4-Methoxystyrene	88
4	4-Chlorostyrene	90
5	3-Nitrostyrene	93

Reaction conditions: olefine (1 mmol), DMA (4 mol%), H_2O_2 (3 mmol), H_2O_2 (5 mL), 100 $^{\circ}C$, 2 h

^a Isolated yield

Table 3 Successive trials by using recoverable $Pd(II)@AEA-Fe_3O_4NP$ for the epoxidation of styrene

Trial	Catalyst amount (g)	Yield (%) ^a
1	0.10	91
2	0.99	91
3	0.99	90
4	0.99	90

Styrene (1 mmol), DMA (4 mol%), $\rm H_2O_2$ (3 mmol), $\rm H_2O$ (5 mL), 100 °C, 2 h

^a Isolated yield

Recyclability of the Pd(II)@AEA-Fe₃O₄NP was examined in the oxidation reaction of styrene. After carrying out the reaction, the catalyst was separated with a magnet as a dark solid, washed with EtOH (2×5 mL) and reused. Only minor decreases in the reaction yield were observed after four repetitive cycles for the reaction (Table 3).

The durability of catalyst was investigated with FTIR which any changes were observed in FTIR after recycling of the catalyst in every steps (see supporting information).

Conclusions

In conclusion, we have demonstrated the Pd(II)@AEA-Fe₃O₄NP-assisted epoxidation of styrene into styrene oxide. High yield of styrene oxide was obtained selectively in short reaction duration. H₂O as a green solvent, H₂O₂ as a green oxidant and development of an organic solvent-free approach are other advantages of this report. Separation of the catalyst with a magnet and recyclability of the catalyst are characteristics of this reaction.

Acknowledgments We gratefully acknowledge financial support from the Research Council of Urmia University.

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