

Pd and Fe₃O₄ Nanoparticles Supported on N-(2-Aminoethyl)Acetamide Functionalized Cellulose as an Efficient Catalyst for Epoxidation of Styrene

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Abstract

A new efficient heterogeneous catalyst was introduced for the epoxidation of styrene. The catalyst was obtained from functionalization of cellulose with N-(2-aminoethyl)acetamide, and then deposition of nanoparticles and Pd(0) nanoparticles on the modified cellulose. The Fe₃O₄ nanoparticles were deposited via chemical oxidation in basic media and Pd(0) nanoparticles were deposited with chemical reduction using NaBH₄. The catalyst was characterized with various characterization methods including FT-IR (for study of structure modifications), XRD (for study of nanoparticles), TGA (for thermal stability), EDX (for elemental analysis), CHN (for elemental analysis of organic compounds), FAAS (for Pd and Fe concentrations) and TEM (for study of nanoparticles). High yield and excellent selectivity was achieved for the epoxidation of styrene. The reaction was performed in H₂O as the green solvent at 100 °C using H₂O₂ as a green oxidant. The reaction has some advantages such as green solvent, high yield, excellent selectivity and green oxidant. Also, the catalyst easily was recovered with a magnet. The magnetically recovered catalyst is applicable for 4 times without decrease in the yield.

Keywords: Cellulose, Epoxidation, Styrene oxide, Magnetic catalyst, Heterogeneous catalyst.

1. INTRODUCTION

Cellulose is a carbohydrate polymer made up of repeating β-D-glucopyranose units and consists of many hydroxyl groups giving the cellulose molecule a high degree of functionality. This most abundant natural biopolymer has the characteristic properties such as hydrophilicity, chirality, biodegradability and high functionality. A great deal of attention has been attracted in recent years for cellulose and its derivatives focusing on their biological, chemical, as well as mechanical properties. Cellulose and its derivatives can be used as a support since they are renewable, biodegradable and non-toxic [1]. There are some reports about cellulose derivatives as support for some important catalysts such as Cu(0) [2],

Pd(0) [3,4], Cu(I)/Pd(0) [5] and Co(II) [6,7].

Epoxidation of olefins or substituted olefins is a necessary step in a number of important organic transformation reactions. Epoxides are industrially interesting compounds due to applications such as synthesis of several perfume materials, anthelmintic preparations, epoxy resins, plasticizers, drugs, sweeteners, etc. [8]. One of the most interesting epoxides is the styrene oxide which largely is produced from the epoxidation of styrene. Styrene oxide can be used for producing of epoxy resin diluting agent, ultraviolet absorbent, flavoring agent, etc., and is also an important intermediate in organic synthesis and pharmaceutical compounds synthesis such as Fluoxetine and Norfluoxetine [9].

Therefore the synthesis of styrene oxide by an easier method and a low cost route is of great interest to researchers working in this field.

Various styrene epoxidation reactions were reported and for most of them hydrogen peroxide is an ideal oxidant both from environmental and economic viewpoints. Hydrogen peroxide is a relatively less expensive and environmentally safe, and forms innocuous water as the only by-product. The epoxidation of styrene can be conducted under strongly alkaline conditions with H_2O_2 as the oxidant [10]. However, the use of strong bases is highly undesirable due to the production of large amounts of industrial waste. For solving this problem the reaction was performed with hydrogen peroxide in the presence of hydrotalcites such as $\text{Mg}_{10}\text{Al}_2(\text{OH})_{24}\text{CO}_3$ as a heterogeneous base catalyst [11-14]. The epoxidation reaction using hydrotalcites can be accelerated using microwave-heating [12]. Al_2O_3 is an active catalyst for epoxidation of styrene with anhydrous hydrogen peroxide as oxidant in the absence of nitrile. Forming an active oxidant resulted from alumina and H_2O_2 interaction (alumina-OOH) can catalyzed the epoxidation of olefin and the desirable products can be obtained in low to modest yields at ambient temperature [15]. MgO and CaO are other efficient metal oxide for the epoxidation of styrene with hydrogen peroxide as the oxidant in the presence of acetonitrile [10, 16].

Recently, we reported the copper free Wacker oxidation reaction of styrene with $\text{PdCl}_2/\text{Fe}_3\text{O}_4$ nanoparticles (Fe_3O_4 NPs)/dimethylacetamide (DMA) catalytic system [17]. In continuation of our efforts to develop of new catalytic systems with cellulose as the support [4-8], herein a new efficient catalytic system was introduced for the oxidation of styrene by $\text{Pd}(0)/\text{Fe}_3\text{O}_4$ nanoparticles (Fe_3O_4 NPs) supported on *N*-(2-aminoethyl)acetamide functionalized cellulose (AEAC) as a heterogeneous recoverable catalyst ($\text{Pd}/\text{Fe}_3\text{O}_4\text{NP@AEAC}$) with H_2O_2 as a

green oxidant in H_2O as a green solvent. While the oxidation reaction of styrene using $\text{Pd}(\text{II})/\text{Fe}_3\text{O}_4$ gave acetophenone [17], we expected acetophenone as the product for oxidation of styrene using $\text{Pd}(0)$ and Fe_3O_4 supported on AEAC but interestingly styrene oxide obtained as the sole product. Also, the magnetic property of the catalyst assisted to easy separation of the catalyst with a magnet [18-20].

2. EXPERIMENTAL

2.1. Materials and Methods

All reagents were purchased from Aldrich or Merck and used without further purification. Cellulose was purchased from Merck with particle size: $\leq 20\%$ less than $20\ \mu\text{m}$, $\leq 2\%$ greater than $160\ \mu\text{m}$ and $\geq 80\%$ between $20\text{-}160\ \mu\text{m}$. Transmission electron microscopy (TEM) was performed by LEO 912AB electron microscope. X-ray powder diffraction (XRD) data were collected on an XD-3A diffractometer using Cu K_α radiation. The elemental analyses (CHN) were performed with an Elementar Analysensysteme GmbH VarioEL. Pd and Fe determination was carried out on an FAAS (Shimadzu model AA-680 atomic absorption spectrometer) with Pd and iron hollow cathode lamps at $242.8\ \text{nm}$ and $248.3\ \text{nm}$, respectively.

2.2. Preparation of $\text{Pd}/\text{Fe}_3\text{O}_4\text{NP@AEAC}$

In a typical procedure, a mixture of cellulose (2.00 g) and NaOH (0.05 g) in 20 mL of H_2O was stirred at $60\ ^\circ\text{C}$ for 2 h to yield a yellow solid. Chloroacetic acid (0.5 g) was added during 0.5 h to the mixture and stirring continued for 3.5 h at $60\ ^\circ\text{C}$ to afford cellulose acetic acid. After filtration and drying of the product in oven at $70\ ^\circ\text{C}$, ethylene diamine (2 mL) was added to the vessel containing cellulose acetic acid (2.00 g, white powder) and 2-propanol (10 mL), and the mixture stirred at room temperature. After 24 h, the white participate filtered off as the *N*-(2-aminoethyl)acetamide functionalized cellulose (**3**) and dried in oven at $50\ ^\circ\text{C}$. Then, a mixture containing compound (**3**) (2.00 g), $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ (0.25 g), $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$

(0.67 g) and H₂O (30 mL) after 2 h stirring under N₂ atmosphere, was heated to 70 °C and treated with drop wise addition of 30 mL NH₃ during 0.5 h under N₂ atmosphere. After addition of ammonia, the mixture was stirred for 0.5 h, and then the grey solid was separated with a magnet from the mixture and dried in 50 °C under N₂ atmosphere. The support containing Fe₃O₄ (2.00 g) was added to a vessel containing PdCl₂ (0.12 g) and H₂O (30 mL) under N₂ atmosphere, and after 24 h stirring at room temperature, a solution of NaBH₄ (30 mL of 1 g/L) was added drop wise during 0.5 h. The catalyst after 3 h stirring was separated with a magnet as a dark solid and dried in oven at 50 °C under N₂ atmosphere.

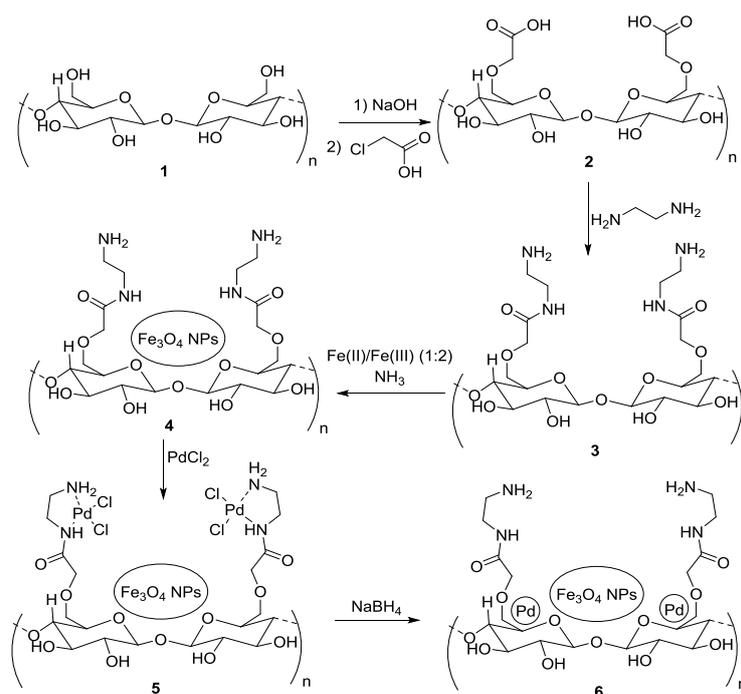
2.3. Typical Procedure for the Epoxidation of Styrene

Styrene (0.10 g, 1.00 mmol) was added to a round-bottomed flask containing colloidal of Pd/Fe₃O₄NP@AEAC (0.015 g) and DMA (0.02 mmol) in H₂O (5 mL) and the temperature raise up to 100 °C. H₂O₂ (3 mmol) was added drop wise to the reaction vessel during 0.5 h. After 2 h, the reaction mixture was cooled to room

temperature, Pd/Fe₃O₄NP@AEAC 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).

3. RESULTS AND DISCUSSION

For the preparation of the catalyst (Scheme 1), cellulose was converted to cellulose acetic acid in two steps. The first step is the activation of cellulose with NaOH solution to yield a yellow mixture. The resulted compound is active space for nucleophilic attack. In the second step, chloroacetic acid was added to the reaction mixture to give cellulose acetic acid. The reaction of cellulose acetic acid with ethylenediamine in 2-propanol led to the formation of *N*-(2-aminoethyl)acetamide functionalized cellulose (**3**). The amine moiety such as diamine assisted to homogeneous distribution of metal nanoparticles on the support particularly for nanoparticles which are made up in situ from the corresponding cations [4].



Scheme 1. Preparation of Pd/Fe₃O₄NP@AEAC.

Fe₃O₄ NPs were deposited on the support via in situ precipitation of Fe(II) and Fe(III) with ammonia. Finally, Pd(II) was complexed with the amine groups of the support during 24 h and reduced to Pd NPs with NaBH₄.

All of these transformations are confirmed with FT-IR spectra and the catalyst was characterized with FT-IR, XRD, TGA, FAAS, EDX, CHN and TEM. FT-IR spectra gave good evidence about the performing of compounds **1-5**. For example the formation of compound **2** was confirmed via a new absorption band in FT-IR spectrum at 1608 cm⁻¹ for acetic acid group of compound **2**. This peak was shifted to 1593 cm⁻¹ in compound **3** which indicates formation of amide groups (Fig. 1). Compound **4** has new absorption peak for Fe-O band at 553 cm⁻¹. All of the compounds 1-6 show some absorption peaks related to OH (about 3400 cm⁻¹) and aliphatic CH (about 2850 cm⁻¹).

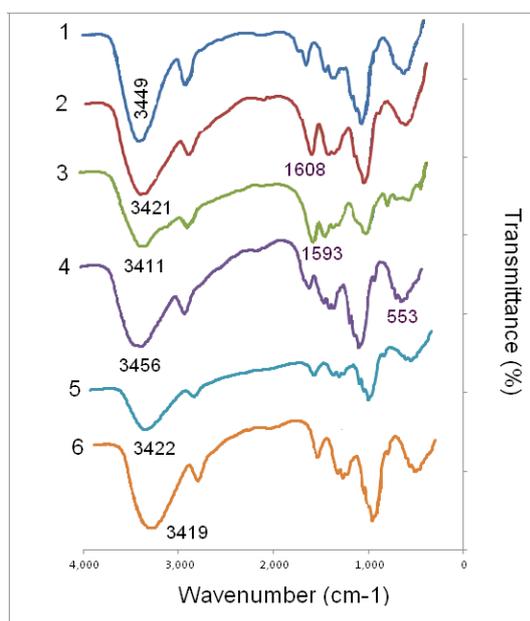


Figure 1. FT-IR spectra for compounds 1-6.

Ethylenediamine deposition also was confirmed with calculating of nitrogen content of the catalyst about 0.78% obtained by CHN analysis (Table 1).

Table 1. CHN analysis of Pd/Fe₃O₄NP@AEAC

Element	C	H	N
(%)	41.86	6.01	0.37

The structure of Pd/Fe₃O₄NP@AEAC was determined by powder XRD. The XRD patterns of the catalyst, cellulose, Fe₃O₄ NPs and Pd NPs are shown in the Figure 2. The catalyst has characteristic diffraction peaks which observed in the XRD patterns of cellulose, Fe₃O₄ NPs and Pd NPs.

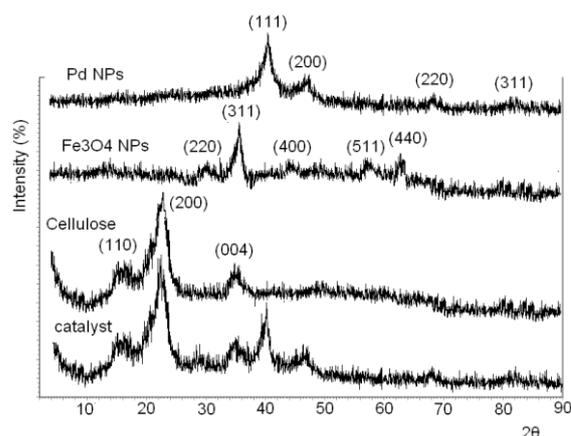


Figure 2. XRD pattern of the catalyst.

TEM image of the catalyst indicates deposition of Fe₃O₄ NPs on the support. Also, Pd NPs deposited on the Fe₃O₄ NPs (Fig. 3).

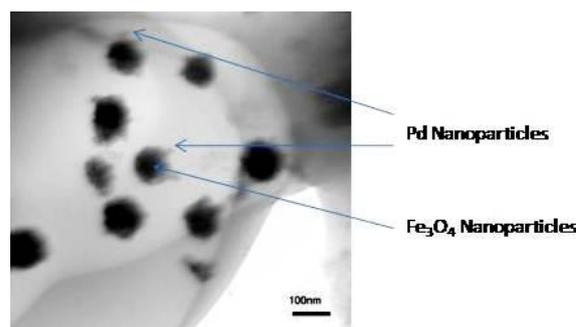


Figure 3. TEM image of Pd/Fe₃O₄NP@AEAC sample.

The catalyst surface was analyzed with EDX microanalyses which indicated the presence both of the Pd and Fe (Fig. 4). The Pd and Fe concentrations obtained were 0.66 mmol Pd per 1 g catalyst (0.07 g Pd per 1 g catalyst) and 1.83 mmol Fe per 1 g catalyst (0.1 g Fe per 1 g catalyst)

using calibration curve prepared with palladium and iron solution standards in FAAS analysis.

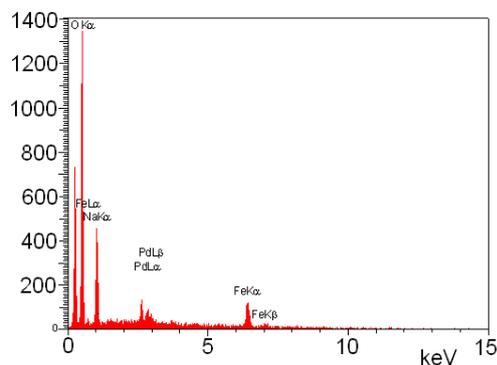


Figure 4. EDX microanalysis of Pd/Fe₃O₄NP@AEAC.

Thermogravimetric analysis (TGA) of the catalyst showed that the catalyst has good thermal stability (dec>243 °C) in air (Fig. 5). The mass loss in the TGA diagram was performed in a step with 100% weight loss.

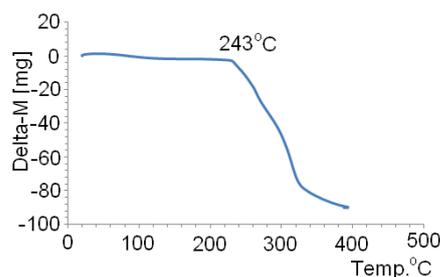


Figure 5. TGA spectra of Pd/Fe₃O₄NP@AEAC.

The catalytic activity of Pd/Fe₃O₄NP@AEAC was investigated in the oxidation of styrene. So, the oxidation of styrene (**1**) with H₂O₂ was studied for the optimization of reaction conditions. It was found that 1 mol% Pd (Table 2, entries 1-3) and 2 mol% DMA (Table 2, entries 4-7) in H₂O (Table 2, entries 8-12) with 3 equivalents of H₂O₂ at 100 °C (Table 2, entries 13-15) is the best reaction conditions for the oxidation of styrene. Oxidation of styrene proceeded to give styrene oxide (**2**) as the sole product with 93% yield in short reaction duration (2 h) without any byproduct such as acetophenone or acetaldehyde. This is a selective oxidation reaction of styrene

since the formation of acetophenone or acetaldehyde is probable in the oxidation of styrene. The reaction needs long time for high yields in the absence of DMA (Table 2, entries 4-8), since DMA as a ligand for Pd(II) in the catalytic oxidation cycle can be improve the yield. However, performing of the reaction in the absence of DMA shows that the oxidation reaction can be carried out with anchored amines to the support, but in long time and low efficiency. After screening a variety of solvents, H₂O was determined to be the best solvent (Table 2, entries 8-12). Temperature is an important factor for this reaction and the yield was decreased in low temperatures (Table 2, entries 13-15).

The reaction was examined using oxygen as an oxidant instead of H₂O₂. For this propose, the reaction was performed with an oxygen balloon which 71% yield was obtained in long duration (24 h). Also, the reaction was investigated with Fe₃O₄ NPs which any product did not obtained.

Turn Over Number (TON) and Turn Over Frequency (TOF) of the catalyst were determined. For this propose, styrene (10 mmol), catalyst (0.015 g or 0.01 mmol Pd), DMA (0.02 g), H₂O₂ (30 mmol) in H₂O (5 mL) was stirred at 100 °C. After 2 h, the catalyst was separated with a magnet and the solvent was evaporated. GC study of the product was shown 39% conversion. So, TON (mol of product per mol of the catalyst) was calculated about 390. Regarding that TOF is the TON per time, TOF was obtained 3.25 S⁻¹.

For the investigation of Fe₃O₄NPs effect on the reaction, the oxidation reaction was studied using Pd@AEAC as the catalyst instead of Pd/Fe₃O₄NP@AEAC. The reaction gave the styrene oxide with 82% yield in 2 h. So, Fe₃O₄NPs assisted to oxidation reaction of styrene and also, give the magnetic property to the catalyst. It is interesting to note, the reaction in the presence of Pd(II) and Fe₃O₄NPs (without support) gave acetophenone as the sole product [17].

Table 2. Optimization of the reaction conditions for oxidation of styrene^a.

Entry	Catalyst amount (Pd mol%)	Solvent	Temp. (°C)	Time (h)	Yield (%) ^b
1	0.5	H ₂ O	100	2	67
2	1	H ₂ O	100	2	93
3	1.5	H ₂ O	100	2	94
4 ^c	1	H ₂ O	100	2	53
5 ^c	1	H ₂ O	100	4	62
6 ^c	1	H ₂ O	100	12	88
7 ^d	1	H ₂ O	100	2	91
8	1	DMA	100	2	39
9	1	MeCN	Ref.	3	41
10	1	EtOH	Ref.	2	81
11	1	CH ₂ Cl ₂	Ref.	2	87
12	1	EtOH:H ₂ O (1:3)	100	2	90
13	1	H ₂ O	80	4	52
14	1	H ₂ O	90	2	87
15	1	H ₂ O	r.t.	24	43

^a Reaction conditions: styrene (1 mmol), DMA (2 mol%), H₂O₂ (3 mmol), solvent (5 mL); ^b Isolated yield; ^c Without DMA; ^d DMA (1 mol%).

Potential Pd and Fe leaching into the reaction mixture were studied with FAAS analysis. For this purpose, sample was taken through a syringe filter during the 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 and Fe concentrations in the reaction solution were less than the detection limit. This result indicates that virtually no Pd and Fe leach from the surface into the solution.

The hot filtration test was carried out to investigate heterogeneous nature of the catalyst, and to make sure no leaching of Pd during the course of catalytic oxidation reaction. In this test, a mixture of Pd/Fe₃O₄NP@AEAC (0.015 g), styrene (1 mmol), DMA (0.02 g), H₂O₂ (3 mmol) in H₂O (5 mL) was heated at 100 °C for 1 h. The Pd/Fe₃O₄NP@AEAC catalyst was separated from the hot reaction mixture after 1 h using magnetic separation technique. Then, it was observed by using GC that only 59% conversion was achieved. The reaction was continued with the filtrate for another 1 h at the same

reaction temperature. But, no increase in the oxidation product conversion was observed after 1 h confirmed by GC analysis. This test also confirms no leaching of Pd was performed during the reaction.

Also, did not observe any change in IR spectrum for the catalyst recovered from the reaction (Fig. 6).

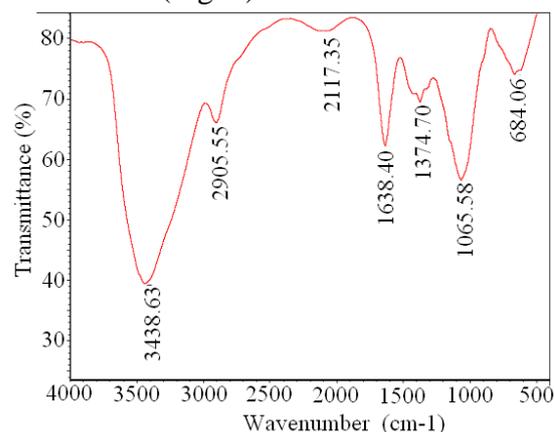


Figure 6. FT-IR spectra of the catalyst after reaction.

The XRD pattern of the recovered catalyst did not show any changes from original catalyst that approved the catalyst has good chemical stability in the reaction mixture.

Recyclability of the Pd/Fe₃O₄NP@AEAC was examined in the epoxidation of styrene.

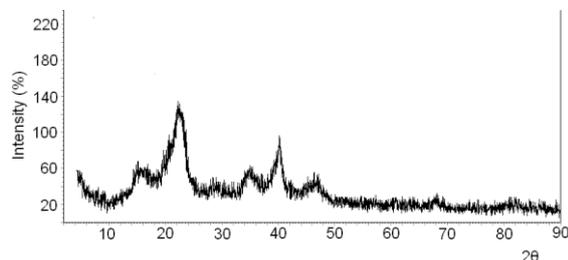


Figure 7. XRD pattern of the recovered catalyst.

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 this reaction (Table 3).

Table 3. Successive trials by using recoverable Pd/Fe₃O₄NP@AEAC for epoxidation of styrene.

Trial	Catalyst amount (g)	Yield (%) ^b
1	0.015	93
2	0.014	92
3	0.014	92
4	0.014	92

^a Reaction conditions: styrene (1 mmol), DMA (2 mol%), H₂O₂ (3 mmol), H₂O (5 mL), 100 °C, 2 h; ^b Isolated yield.

The results of our catalyst are compared with previously reports about epoxidation

of styrene with respect to their recyclability, solvent, reaction duration, temperature, yield and selectivity (Table 4). The present work has some disadvantages compared to some recent work performed with Fe₃O₄-CuO supported on mesoporous silica [21], gold nanoparticles supported on silica [22] and Ag supported on Fe₃O₄ [23] such as high temperature and lower yield, but recyclability, green solvent, short reaction duration and high selectivity are advantages of this work compared to most of reports.

4. CONCLUSION

In conclusion, Pd/Fe₃O₄NP@AEAC was demonstrated as an efficient catalyst for styrene epoxidation. High yield of styrene oxide was selectively obtained in short reaction duration due to a controlled oxidation reaction. Avoiding from strong basic moieties and self-controlling catalytic system which prevent from transformation of styrene oxide to acetophenone and acetaldehyde were characteristic features of this approach. H₂O as a green solvent, H₂O₂ as a green oxidant were other advantages of this report.

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Table 4. Comparison of the result with previous reports.

Entry	Catalytic system	Recyclable	Solvent	Time (h)	Temp. (°C)	Isolated yield (%) (I) or GC yield (%) (G)	Selectivity
1	Fe ₃ O ₄ -CuO@meso-SiO ₂	yes	CH ₃ CN	7.5	80	100 (G)	93
2	Au@silica	no	CH ₃ CN	14	80	98.5 (G)	82.8
3	Ag@Fe ₃ O ₄	yes	Toluene	0.25	Reflux	86.4 (G)	95.1
4	Pd/Fe ₃ O ₄ NP@AEAC	yes	H ₂ O	2	100	93 (I)	100

REFERENCES

- Habibi, Y., Lucia, L. A., Rojas, O. J. (2010). "Cellulose nanocrystals: chemistry, self-assembly, and applications", *Chemical Review*, 110: 3479-3500.
- Reddy, K. R., Kumar, N. S. (2006). "Cellulose-supported copper(0) catalyst for aza-michael addition", *Synlett*, 2246-2250.

3. Cirtiu, C. M., Dunlop-Brière, A. F., Moores, A. (2011). "Cellulose nanocrystallites as an efficient support for nanoparticles of palladium: application for catalytic hydrogenation and Heck coupling under mild conditions", *Green Chemistry*, 13: 288-291.
4. Keshipour, S., Shojaei, S., Shaabani, A. (2013). "Palladium nano-particles supported on ethylenediamine-functionalized cellulose as a novel and efficient catalyst for the Heck and Sonogashira couplings in water", *Cellulose*, 20: 973-980.
5. Keshipour, S., Shaabani, A. (2014). "Copper(I) and palladium nanoparticles supported on ethylenediamine-functionalized cellulose as an efficient catalyst for the 1,3-dipolar cycloaddition/direct arylation sequence", *Applied Organometallic Chemistry*, 28: 116-119.
6. Shaabani, A., Keshipour, S., Hamidzad, M., Seyyedhamzeh, M. (2014). "Cobalt(II) supported on ethylenediamine-functionalized nanocellulose as an efficient catalyst for room temperature aerobic oxidation of alcohols", *Journal of Chemical Sciences*, 126: 111-115.
7. Shaabani, A., Keshipour, S., Hamidzad, M., Shaabani, S. (2014). "Cobalt(II) phthalocyanine covalently anchored to cellulose as a recoverable and efficient catalyst for the aerobic oxidation of alkyl arenes and alcohols", *Journal of Molecular Catalysis A: Chemical*, 395: 494-499.
8. Laha, S. C., Kumar, R. (2001). "Selective epoxidation of styrene to styrene oxide over TS-1 using urea hydrogen peroxide as oxidizing agent", *Journal of Catalysis*, 204: 64-70.
9. Mitchell, D., Koenig, T. M. (1995). "Synthesis of *R*- and *S*- Fluoxetine, Norfluoxetine and related compounds from Styrene Oxide", *Synthetic Communications*, 25: 1231-1238.
10. Gu, Q., Han, D., Shi, L., Sun, Q. (2012). "Styrene epoxidation with hydrogen peroxide over calcium oxide catalysts prepared from various precursors", *Journal of Natural Gas Chemistry* 21: 452-459.
11. Ueno, S., Yoshida, K., Ebitani, K., Kaneda, K. (1998). "Hydrotalcite catalysis: heterogeneous epoxidation of olefins using hydrogen peroxide in the presence of nitriles", *Chemical Communications*, 295-296.
12. Pillai, U. R., Sahle-Demessie, E., Varma, R. S. (2002). "Microwave-expedited olefin epoxidation over hydrotalcites using hydrogen peroxide and acetonitrile", *Tetrahedron Letters*, 43: 2909-2911.
13. Kirm, I., Medina, F., Rodriguez, X., Cesteros, Y., Salagre, P., Sueiras, J. (2004). "Epoxidation of styrene with hydrogen peroxide using hydrotalcites as heterogeneous catalysts", *Applied Catalysis A: General*, 272: 175-185.
14. Ionescu, R., Pavel, O. D., Birjega, R., Zavoianu, R., Angelescu, E. (2010). "Epoxidation of cyclohexene with H₂O₂ and acetonitrile catalyzed by Mg–Al hydrotalcite and cobalt modified hydrotalcites", *Catalysis Letters*, 134: 309-317.
15. Mandelli, D., Avan Vliet, M. C., Sheldon, R. A., Schuchardt, U. (2001). "Alumina- catalyzed alkene epoxidation with hydrogen peroxide", *Applied Catalysis A: General*, 219: 209-213.
16. Bian, X. L., Gu, Q. M., Shi, L., Sun, Q. (2011). "Epoxidation of styrene with hydrogen peroxide over MgO catalyst", *Chinese Journal of Catalysis*, 32: 682-687.
17. Keshipour, S., Nadervand, S. (2015). "Fe₃O₄ nanoparticles as a new efficient co-catalyst for Pd(II) in Wacker oxidation of styrene using H₂O₂ as an oxidant", *RSC Advances*, 5: 47617-47620.
18. Maleki, A., Aghaei, M., Ghamari N., Kamalzare, M (2016). "Efficient synthesis of 2,3-dihydroquinazolin-4(1H)-ones in the presence of ferrite/chitosan as a green and reusable nanocatalyst", *International Journal of Nanoscience and Nanotechnology*, 12: 215-222.
19. Khorshidi, A., Shariati, S (2016). "-OSO₃H functionalized mesoporous MCM-41 coated on Fe₃O₄ nanoparticles: an efficient and recyclable nano-catalyst for preparation of 3,2'-bisindoles", *International Journal of Nanoscience and Nanotechnology*, 12: 139-147.
20. Ghasemi, E., Ghahari, M (2015). "Synthesis of silica coated nanoparticles" *International Journal of Nanoscience and Nanotechnology*, 11: 133-137.
21. Zhang, X., Wang, G., Yang, M., Luan, Y., Dong, W., Dang, R. (2014). "Synthesis of a Fe₃O₄–CuO@meso-SiO₂ nanostructure as a magnetically recyclable and efficient catalyst for styrene epoxidation", *Catalysis Science and Technology*, 4: 3082-3089.
22. Liu, J., Wang, F., Qi, S., Gu, Z., Wu, G. (2013). "Highly selective epoxidation of styrene over gold–silica catalysts via one-pot synthesis: synthesis, characterization, and catalytic application", *New Journal of Chemistry*, 37: 769-774.
23. Zhang, D. H., Li, H. B., Li, G. D., Chen, J. S. (2009). "Magnetically recyclable Ag-ferrite catalysts: general synthesis and support effects in the epoxidation of styrene", *Dalton Transactions*, 10527-10533.