Pd and Fe$_3$O$_4$ Nanoparticles Supported on N-(2-Aminoethyl)Acetamide Functionalized Cellulose as an Efficient Catalyst for Epoxidation of Styrene

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(Received: 21 June 2016 and Accepted: 08 February 2017)

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 Fe$_3$O$_4$ nanoparticles were deposited via chemical oxidation in basic media and Pd(0) nanoparticles were deposited with chemical reduction using NaBH$_4$. 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 H$_2$O as the green solvent at 100 °C using H$_2$O$_2$ 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 Flouxetine and Norflouxetine [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 H₂O₂ 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 Mg₁₀Al₂(OH)₂₄CO₃ as a heterogeneous base catalyst [11-14]. The epoxidation reaction using hydrotalcites can be accelerated using microwave-heating [12]. Al₂O₃ 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 H₂O₂ 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 PdCl₂/Fe₃O₄ nanoparticles (Fe₃O₄ 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 Pd(0)/Fe₃O₄ nanoparticles (Fe₃O₄ NPs) supported on N-(2-aminoethyl)acetamide functionalized cellulose (AEAC) as a heterogeneous recoverable catalyst (Pd/Fe₃O₄NP@AEAC) with H₂O₂ as a green oxidant in H₂O as a green solvent. While the oxidation reaction of styrene using Pd(II)/Fe₃O₄ gave aceto phenone [17], we expected aceto phenone as the product for oxidation of styrene using Pd(0) and Fe₃O₄ 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: ≤ 20% less than 20 μm, ≤ 2% greater than 160 μm and ≥ 80% between 20-160 μm. 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 Kα 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 nm and 248.3 nm, respectively.

2.2. Preparation of Pd/Fe₃O₄NP@AEAC
In a typical procedure, a mixture of cellulose (2.00 g) and NaOH (0.05 g) in 20 mL of H₂O was stirred at 60 °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 °C to afford cellulose acetic acid. After filtration and drying of the product in oven at 70 °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 °C. Then, a mixture containing compound (3) (2.00 g), FeCl₂.4H₂O (0.25 g), FeCl₃.6H₂O (2.50 g), and...
(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.
Fe$_3$O$_4$ 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 NaBH$_4$. 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$^{-1}$).

**Table 1. CHN analysis of Pd/Fe$_3$O$_4$NP@AEAC**

<table>
<thead>
<tr>
<th>Element</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd NPs</td>
<td>41.86</td>
<td>6.01</td>
<td>0.37</td>
</tr>
</tbody>
</table>

The structure of Pd/Fe$_3$O$_4$NP@AEAC was determined by powder XRD. The XRD patterns of the catalyst, cellulose, Fe$_3$O$_4$ NPs and Pd NPs are shown in the Figure 2. The catalyst has characteristic diffraction peaks which observed in the XRD patterns of cellulose, Fe$_3$O$_4$ NPs and Pd NPs.

**Figure 2. XRD pattern of the catalyst.**

TEM image of the catalyst indicates deposition of Fe$_3$O$_4$ NPs on the support. Also, Pd NPs deposited on the Fe$_3$O$_4$ NPs (Fig. 3).

**Figure 3. TEM image of Pd/Fe$_3$O$_4$NP@AEAC sample.**

Ethylenediamine deposition also was confirmed with calculating of nitrogen content of the catalyst about 0.78% obtained by CHN analysis (Table 1). 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/Fe$_3$O$_4$NP@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/Fe$_3$O$_4$NP@AEAC.**

The catalytic activity of Pd/Fe$_3$O$_4$NP@AEAC was investigated in the oxidation of styrene. So, the oxidation of styrene (1) with H$_2$O$_2$ 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 H$_2$O (Table 2, entries 8-12) with 3 equivalents of H$_2$O$_2$ 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 reaction reaction can be carried out with anchored amines to the support, but in long time and low efficiency. After screening a variety of solvents, H$_2$O 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 H$_2$O$_2$. 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 Fe$_3$O$_4$ 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), H$_2$O$_2$ (30 mmol) in H$_2$O (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 Fe$_3$O$_4$NPs effect on the reaction, the oxidation reaction was studied using Pd@AEAC as the catalyst instead of Pd/Fe$_3$O$_4$NP@AEAC. The reaction gave the styrene oxide with 82% yield in 2 h. So, Fe$_3$O$_4$NPs 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 Fe$_3$O$_4$NPs (without support) gave acetophenone as the sole product [17].
Table 2. Optimization of the reaction conditions for oxidation of styrene\textsuperscript{a}.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst amount (Pd mol%)</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Yield (%)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>H\textsubscript{2}O</td>
<td>100</td>
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<td>67</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
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<td>2</td>
<td>93</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>H\textsubscript{2}O</td>
<td>100</td>
<td>2</td>
<td>94</td>
</tr>
<tr>
<td>4\textsuperscript{c}</td>
<td>1</td>
<td>H\textsubscript{2}O</td>
<td>100</td>
<td>2</td>
<td>53</td>
</tr>
<tr>
<td>5\textsuperscript{c}</td>
<td>1</td>
<td>H\textsubscript{2}O</td>
<td>100</td>
<td>4</td>
<td>62</td>
</tr>
<tr>
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<td>H\textsubscript{2}O</td>
<td>100</td>
<td>12</td>
<td>88</td>
</tr>
<tr>
<td>7\textsuperscript{d}</td>
<td>1</td>
<td>H\textsubscript{2}O</td>
<td>100</td>
<td>2</td>
<td>91</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>DMA</td>
<td>100</td>
<td>2</td>
<td>39</td>
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<tr>
<td>9</td>
<td>1</td>
<td>MeCN</td>
<td>Ref.</td>
<td>3</td>
<td>41</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>EtOH</td>
<td>Ref.</td>
<td>2</td>
<td>81</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>Ref.</td>
<td>2</td>
<td>87</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>EtOH:H\textsubscript{2}O (1:3)</td>
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<td>90</td>
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<tr>
<td>13</td>
<td>1</td>
<td>H\textsubscript{2}O</td>
<td>80</td>
<td>4</td>
<td>52</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>H\textsubscript{2}O</td>
<td>90</td>
<td>2</td>
<td>87</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>H\textsubscript{2}O</td>
<td>r.t.</td>
<td></td>
<td>24</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: styrene (1 mmol), DMA (2 mol%), H\textsubscript{2}O\textsubscript{2} (3 mmol), solvent (5 mL); \textsuperscript{b} Isolated yield; \textsuperscript{c} Without DMA; \textsuperscript{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 HNO\textsubscript{3}. 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/Fe\textsubscript{3}O\textsubscript{4}NP@AEAC (0.015 g), styrene (1 mmol), DMA (0.02 g), H\textsubscript{2}O\textsubscript{2} (3 mmol) in H\textsubscript{2}O (5 mL) was heated at 100 °C for 1 h. The Pd/Fe\textsubscript{3}O\textsubscript{4}NP@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.](image)

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/Fe$_3$O$_4$NP@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 ($2 \times 5$ 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/Fe$_3$O$_4$NP@AEAC for epoxidation of styrene

<table>
<thead>
<tr>
<th>Trial</th>
<th>Catalyst amount (g)</th>
<th>Yield (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.015</td>
<td>93</td>
</tr>
<tr>
<td>2</td>
<td>0.014</td>
<td>92</td>
</tr>
<tr>
<td>3</td>
<td>0.014</td>
<td>92</td>
</tr>
<tr>
<td>4</td>
<td>0.014</td>
<td>92</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: styrene (1 mmol), DMA (2 mol%), H$_2$O$_2$ (3 mmol), H$_2$O (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 Fe$_3$O$_4$-CuO supported on mesoporous silica [21], gold nanoparticles supported on silica [22] and Ag supported on Fe$_3$O$_4$ [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/Fe$_3$O$_4$NP@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 moietyes and self-controlling catalytic system which prevent from transformation of styrene oxide to acetophenone and acetaldehyde were characteristic features of this approach. H$_2$O as a green solvent, H$_2$O$_2$ as a green oxidant were other advantages of this report.

ACKNOWLEDGMENTS

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

Table 4. Comparison of the result with previous reports.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalytic system</th>
<th>Recyclable</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Temp. (°C)</th>
<th>Isolated yield (%) (I) or GC yield (%) (G)</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe$_3$O$_4$-CuO@meso-SiO$_2$</td>
<td>yes</td>
<td>CH$_3$CN</td>
<td>7.5</td>
<td>80</td>
<td>100 (G)</td>
<td>93</td>
</tr>
<tr>
<td>2</td>
<td>Au@silica</td>
<td>no</td>
<td>CH$_3$CN</td>
<td>14</td>
<td>80</td>
<td>98.5 (G)</td>
<td>82.8</td>
</tr>
<tr>
<td>3</td>
<td>Ag@Fe$_3$O$_4$</td>
<td>yes</td>
<td>Toluene</td>
<td>0.25</td>
<td>Reflux</td>
<td>86.4 (G)</td>
<td>95.1</td>
</tr>
<tr>
<td>4</td>
<td>Pd/Fe$_3$O$_4$NP@AEAC</td>
<td>yes</td>
<td>H$_2$O</td>
<td>2</td>
<td>100</td>
<td>93 (I)</td>
<td>100</td>
</tr>
</tbody>
</table>

REFERENCES


