Environmentally-friendly synthesis of copper(I)-Tricine complex intercalated layered double hydroxide coated magnetite nanocomposites and its application in oxidative esterification by using ultrasonic irradiation

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Research Article

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Abstract

In this work, an approach described to successful intercalation of copper(I)-Tricine complex into layered double hydroxide (LDH) coated on magnetite nanocomposites by ultrasonic methods. The activity of this nanocatalyst was investigated for oxidative esterification of arylaldehydes under ultrasonic irradiation. The oxidative esterification reaction was performed in environmentally friendly condition, high yield, short reaction times and simple method with highly efficient catalyst system. In addition, this catalyst can be removed from the reaction medium simply by use of an external magnet.

1. Introduction

Green chemistry has developed in many fields to diminish the use of toxic reagents which impose a negative impact on the environment [1]. In this respect, various types of instrument-based methods based on green chemistry have emerged to recognize many chemical compounds and their effects on human health and the environment [2].

Notably, with reducing nonrenewable resources such as fossil fuel, many researches have been investigated for the production of chemicals with renewable sources [3]. The use of noble metals as a catalyst can be a route to reduce the restriction of the environment and nonrenewable resources. Nowadays, noble metal catalysts have been applied for green procedures that are essential to our daily life which are composed of cheap and earth-abundant elements and increase reaction efficiency and selectivity for renewable energy applications [4].

It is well known that the search for developing catalysts is essential to reach lessons from “mother nature” where earth-abundant and non-noble metal-based catalysts are always recognized as an important catalyst for several biological reactions for many years. Among these reactions in which non-noble metals have effective catalytic roles, oxidative esterification is indubitably considerable and prominent [4]. Thus, various alternative catalysts have been used to develop catalytic systems for oxidative esterification reaction.

Recently, Layered double hydroxide nanosheets have attained significant popularity due to their simple preparation, synthesis from earth-abundant elements, eco-friendly, well accessibility, being low cost simple tenability of the chemical material, good thermal stability, broad area, and high structural stability [5–9]. These are known as hydrotalcite like compounds or anionic clay with the common formula of LDH be defined by \([M_{1-x}^{2+}M_x^{3+}(OH)_2]x+[A_{x/n}]^{n-}.nH_2O\) which divalent and trivalent metals are \(M^{2+}\) and \(M^{3+}\) ions [8, 10]. Their catalytic properties are widely studied in various reactions [11]. In this regard, various routs have been used to preparation these compounds such as hydrothermal [6, 12], solvothermal [13], co-precipitation [14, 15], and ultrasonic method [16, 17]. These routes can be performed by various advantages and limitations. One of the suitable routs for the direct preparation of LDH is the ultrasonic assisted. This technique can be carried out by its energy-efficiency, mild, inexpensive, and
environmentally friendly synthetic. Moreover, LDH could be used as a sonocatalyst in sonochemical reactions because of the semiconductive properties of nanoparticles [18].

Specially, physical and chemical effects of ultrasonic irradiation were attended attention. The cavitation bubbles collapse in the ultrasonic irradiation that this condition employs severely strong pressure and provide big energy. Therefore, these high energy and pressure cause fast reaction of materials [2, 5, 19, 20].

Further, essential problems of consuming solvents are related to toxicity and high usage. Water due to its fascinating features such as low cost, being environmental, easy accessibility, and nontoxicity became appropriate for both scientific and industrial researches. The hydrophilicity of LDH provides any hosted oxidation catalyst, water compatible. On the basis of this property, in our present work, an efficient method envisioned for the oxidative esterification reaction of benzaldehyde derivatives under ultrasonic irradiation using copper(I)-Tricine complex intercalated LDH coated magnetite nanoparticles as a nanocatalyst in water. Applying the green solvent has a vital role in the eco-friendliness of the method [21]. Also, the ultrasonic technique for preparation of Fe₃O₄@LDH@Tricine–Cu(I) was a fast, easy, environmentally benign, low cost, and convenient way.

2. Experimental

2.1. Materials and Instrumentation

All the chemicals were commercial products. FeCl₃.6H₂O, FeCl₂.4H₂O, NH₄OH, Mg(NO₃)₂.6H₂O, Al(NO₃)₃.9H₂O, tricine, alcohol and aldehyde purchased from Merck Company. Ultrasonic irradiations were carried out in an ultrasonic bath DT 102H. Proton nuclear magnetic resonance (¹H NMR) (500 MHz) spectra were acquired on Bruker DRX-500 Advance spectrometers. A Philips X-Pert 1710 diffractometer was used for preparation of X-ray diffraction pattern (XRD) at room temperature. Fourier transform infrared spectroscopy (FT-IR) was carried out over the region 400–4,000 cm⁻¹ on a Shimadzu FT-IR-8400S spectrometer. The magnetic measurement experiments were tested on a vibrating magnetometer/alternating gradient force magnetometer (MD Co., Iran, www.mdk-magnetic.com). Energy-dispersive x-ray spectroscopy (EDX) were obtained by an Oxford Instrumental. Field Emission Scanning Electron Microscopy (FE-SEM) image was obtained for the catalyst morphology and size by on Zeiss-Sigma VP 500. N₂ adsorption–desorption analyses were carried out on an ASAP 2020 apparatus (Micromeritics, USA). The chromatography of products was accomplished by silica gel 60.

2.2 Preparation of Fe₃O₄

Ultrasonic-assisted reverse co-precipitation method (US-RP) used for the synthesis of Fe₃O₄ nanoparticles. 1.35 g of FeCl₃.6H₂O and 1.99 g of FeCl₂.4H₂O were dissolved in 15 mL deionized water. This solution was added dropwise into 10 wt% NaOH aqueous solution at 50°C under ultrasound irradiation. After 30 min, an external magnet was used for separation of final product then washed with
water and ethanol three times and was dried in an oven for 12 h at 50°C [22]. The mass of the isolated catalyst was 3 g.

### 2.3 Preparation of Fe$_3$O$_4$@LDH@Tricine

The Fe$_3$O$_4$@LDH@Tricine was synthesized by the ultrasonic method. 1.0 g of Fe$_3$O$_4$ nanoparticles and 0.003 mol of tricine were dispersed in 50 mL deionized water (solution A). For preparation solution B, Mg(NO$_3$)$_2$.6H$_2$O (0.009 mol) and Al(NO$_3$)$_3$.9H$_2$O (0.003 mol) were dissolved in deionized water (50 mL). Next, solution C was prepared by adding NaOH (0.005 mol) in 50 mL deionized water. After that, solutions B and C were added dropwise to the stirring solution A. The pH of final solution was obtained about 10. Then, sonication of this mixture was performed for 1 h. The separation of final precipitated Fe$_3$O$_4$@LDH@Tricine was carried out by external magnet. Finally, the product washed several times with water and ethanol, and dried in air at 60°C for 12 h [17, 23]. The mass of the isolated catalyst was 3.5 g.

### 2.4 Preparation of Fe$_3$O$_4$@LDH@Tricine–Cu(I)

The Fe$_3$O$_4$@LDH@Tricine–Cu(I) nanocomposites were synthesized by dissolving 1 g of Fe$_3$O$_4$@LDH@Tricine in tetrahydrofuran (THF) (50 ml) then dispersed in an ultrasonic bath for 15 minutes, then 0.007 mmol of CuI was dissolved in 20 mL THF. Then, the solution of CuI was added to Fe$_3$O$_4$@LDH@Tricine. After that, the mixture stirred at 25°C for 24 h. Finally, the Fe$_3$O$_4$@LDH@Tricine–Cu(I) nanocomposites were separated by an external magnet then the final product was dried in an oven at 65°C for 24 h (Fig. 1) [21, 24]. The mass of the isolated catalyst was 1 g.

### 2.5 Synthesis of esters from arylaldehydes and alcohols

A catalytic amount of Fe$_3$O$_4$@LDH@Tricine–Cu(I) (50 mg) was added to a mixture of arylaldehyde (1.0 mmol), alcohol (1.1 mmol), tert-Butyl hydroperoxide (TBHP) (1.5 mmol) and water (2 mL). The dispersion of mixture was performed by ultrasonic irradiations at 80°C. Next, the catalyst was separated using an external magnet and the resulting product was decanted and purified by silica gel chromatography.

### 3. Results And Discussion

#### 3.1 Characterization

Figure 2 compares FT-IR spectra of the sonochemically synthesized Fe$_3$O$_4$, sonochemically synthesized Fe$_3$O$_4$@LDH, sonochemically synthesized Fe$_3$O$_4$@LDH@Tricine, and sonochemically synthesized Fe$_3$O$_4$@LDH@Tricine–Cu(I). The characteristic absorption bands at around 3432 cm$^{-1}$ are attributed to the stretching vibration of O–H groups of the brucite layers of LDH, O—H stretching vibrations of Fe$_3$O$_4$ (black curve) and bending vibration modes of water molecules between interlayer of LDH [24].
The adsorption band at 1606 cm\(^{-1}\) is corresponding to water-bending vibrations of water and can be related to carbonyl of tricine. The sharp peak around 1380 cm\(^{-1}\) is ascribed to the stretching vibration of NO\(_3\) that these ions are between layers of LDH [3, 10]. The peaks from about 595 cm\(^{-1}\) are attributed to the stretching and bending vibrations of metal–oxygen bonds of lattice (Fe, Mg or Al) [25]. These observations can be used for demonstration of synthesis the Mg-Al LDH. The peaks around 1600 cm\(^{-1}\) and 2917 cm\(^{-1}\) are related to C = O and C-H of tricine. The characteristic bands for tricine at 1557 cm\(^{-1}\) and 1606 cm\(^{-1}\) that shifted to higher frequencies can confirm the formation of the complex.

The EDX analysis of sonochemically synthesized Fe\(_3\)O\(_4\)@LDH@Tricine–Cu(I) nanocomposites clearly confirms the presence of the constitutional elements and data is shown in Fig. 3 and Table 1, the EDX analysis shows that both Fe\(_3\)O\(_4\)@LDH@Tricine–Cu(I) nanocomposites contain Fe, Mg, Al, O, C, Cu, I, and N. Atomic ratio of Mg/Al is about 2.97, that is in correspondence with the nominal ratio (3:1) of Mg and Al.

![Table 1](image)

<table>
<thead>
<tr>
<th>Elt</th>
<th>W%</th>
<th>A%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>8.91</td>
<td>16.20</td>
</tr>
<tr>
<td>N</td>
<td>6.14</td>
<td>9.58</td>
</tr>
<tr>
<td>O</td>
<td>37.91</td>
<td>51.78</td>
</tr>
<tr>
<td>Mg</td>
<td>10.03</td>
<td>9.01</td>
</tr>
<tr>
<td>Al</td>
<td>3.74</td>
<td>3.03</td>
</tr>
<tr>
<td>Fe</td>
<td>17.84</td>
<td>6.98</td>
</tr>
<tr>
<td>Cu</td>
<td>4.45</td>
<td>1.53</td>
</tr>
<tr>
<td>I</td>
<td>10.99</td>
<td>1.89</td>
</tr>
<tr>
<td></td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

The size, morphology, and structure of the nanoparticles Fe\(_3\)O\(_4\)@LDH@Tricine–Cu(I) was investigated with SEM. SEM image (Fig. 4) of the synthesized Fe\(_3\)O\(_4\)@LDH@Tricine–Cu(I) shows spherical particles in a size of about 14 to 20 nm.
The presence of C, N, O, Fe, Mg, Al, I and Cu was indicated with elemental mapping images (Figure 5); that dispersion of Cu is confirmed uniformly on Fe$_3$O$_4$@LDH@Tricine–Cu(I) surface.

Thermogravimetric analysis (TGA) was performed for evaluating the percentage of moisture content, measurement of organic and inorganic ingredients in materials and degradation temperatures. Therefore, the TGA curve of the Fe$_3$O$_4$@LDH@Tricine–Cu(I) nanocomposites was investigated by at a range of 20–800°C under the N$_2$ atmosphere (Fig. 6). The initial weight loss near temperatures below 136°C (4%) is associated to water trapped on interlayers [24]. Two peaks within the temperature range around 136–450°C were associated with derivation curves (DTG) peak (Fig. 5). These peaks show weight loss of 14.39% in this range. The first peak is related to the partial decomposition of the tricine and the second peak at 384°C is related to the complete thermal decomposition of the complex. In addition, anions losse at temperature around 300–400°C [26]. Accordingly, Fe$_3$O$_4$@LDH@Tricine–Cu(I) is an effective nanocatalyst to perform the oxidative esterification reaction at 136°C without any decomposition.

The magnetic possession of Fe$_3$O$_4$ (black curve) and Fe$_3$O$_4$@LDH@Tricine–Cu(I) (red curve) nanocomposites were investigated with vibrating-sample magnetometer (VSM) (Figure. 7). The saturation magnetization of Fe$_3$O$_4$@LDH@Tricine–Cu(I) nanocomposite is approximately 47.55 emu/g which is lower that of Fe$_3$O$_4$ (63 emu/g). The magnetization curve exhibits that Fe$_3$O$_4$@LDH@Tricine–Cu(I) nanocomposites display magnetic characteristics. Therefore, Fe$_3$O$_4$@LDH@Tricine–Cu(I) could be separated comfortably from the media by using an external magnet.

In order to investigate the purity and crystallographic characteristics of the Fe$_3$O$_4$@LDH@Tricine–Cu(I) nanocomposites, XRD was carried out for the Fe$_3$O$_4$, Fe$_3$O$_4$@LDH, Fe$_3$O$_4$@LDH@Tricine and Fe$_3$O$_4$@LDH@Tricine–Cu(I) (Fig. 8). Five peaks of Fe$_3$O$_4$ could be observed for Fe$_3$O$_4$@LDH@Tricine–Cu(I) nanocatalyst (2θ = 32°, 32 °, 43°, 57°, and 67°). These peaks related to the (220), (311), (400), (422), and (511) lattice planes respectively (JCPDS19–629) [10, 21, 24, 27, 28]. These XRD peaks indicate the structure of Fe$_3$O$_4$ is not changed after the surface modification. Also, diffraction peaks at around 12°, 23°, and 39° are associated to Mg–Al LDH [29]. These facts show that Fe$_3$O$_4$@LDH@Tricine–Cu(I) has been successfully synthesized.

After synthesis and characterization of the Fe$_3$O$_4$@LDH@Tricine–Cu(I) nanocomposites, their catalytic activity was investigated in the oxidative esterification reaction. As a model system, the oxidative esterification reaction of benzaldehyde and methanol was used. On the basis of the optimized reaction conditions, the yield of model reaction was evaluated by various temperatures and the amount of catalyst. Firstly, the various amount of catalyst is assessed and the suitable yield of product was obtained with increasing the amount of catalyst to 50 mg (Table 2). The results revealed that more catalyst cannot acquire an obvious difference in the reaction progressive. Subsequently, to evaluate the effect of temperature, the model reaction was explored in various temperatures that the best result for oxidative esterification reaction was 80°C that can be shown in Table 2 entry 4. The progressive of reaction was performed smoothly in the without ultrasonic irradiation (Table 2 entry 8) but reaction
speeds up (15 minutes) in presence of ultrasonic irradiation. In order to increase reaction rate, we tried to use ultrasonic irradiation condition because the cavitation bubbles collapse in the ultrasonic irradiation that this condition employs severely strong pressure and provide big energy. Therefore, fast chemical reactions were performed in this condition.

Several catalysts were tested for oxidative esterification reaction, the poor result was produced when LDH, Fe₃O₄@LDH and Fe₃O₄@LDH@Tricine catalyzed reaction that can be in Table 3 entry 1, 3 and 4. Also, yield of Fe₃O₄@LDH@Tricine–Cu(I) better than Fe₃O₄@Tricine–Cu(I) because of more active sites of LDH linked to tricine (Table 3, entry 5 and 6). Without the use of catalyst, no product was observed in reaction.

Finally, the oxidative esterification reaction of various benzaldehydes and alcohols was explored in standard condition. With the optimal conditions, oxidative esterification of a wide range of structurally diverse electron-rich and electron-deficient benzaldehyde was explored using Fe₃O₄@LDH@Tricine–Cu(I) as catalyst and gave the corresponding esters in good to excellent yields. The summary of this protocol shows in Table 4. It was indicated in Table 4, entry 1 that best yields of the products were obtained in the oxidative esterification of benzaldehyde and methanol. Moreover, when 4-cholorobenzaldehyde with ethanol was reacted in this reaction, the related product was acquired in excellent yield (Table 4, entry 8). 4-chlorobenzaldehyde and 4-bromobenzaldehyde with methanol was reacted to produce the desired ester in the good yield (Table 4, entry 9 and 10).

### Table 2
Optimization of the reaction temperature and the catalyst amounts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amount of catalyst (mg)</th>
<th>Temperature (°C)</th>
<th>Time (minute)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20 a</td>
<td>80</td>
<td>15</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>30 a</td>
<td>80</td>
<td>15</td>
<td>55</td>
</tr>
<tr>
<td>3</td>
<td>40 a</td>
<td>80</td>
<td>15</td>
<td>84</td>
</tr>
<tr>
<td>4</td>
<td>50 a</td>
<td>80</td>
<td>15</td>
<td>97</td>
</tr>
<tr>
<td>5</td>
<td>60 a</td>
<td>80</td>
<td>15</td>
<td>97</td>
</tr>
<tr>
<td>6</td>
<td>50 a</td>
<td>50</td>
<td>15</td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>50 a</td>
<td>25</td>
<td>60</td>
<td>25</td>
</tr>
<tr>
<td>8</td>
<td>50 b</td>
<td>80</td>
<td>120</td>
<td>50</td>
</tr>
</tbody>
</table>

a Reaction conditions: The benzaldehyde (1.0 mmol), alcohol (1.1 mmol), and Fe₃O₄@LDH@Tricine–Cu(I) (50 mg) in the present ultrasound irradiation and in water as solvent.
b Reaction conditions: The benzaldehyde (1.0 mmol), alcohol (1.1 mmol), and Fe₃O₄@LDH@Tricine–Cu(I) (50 mg) in water as solvent in absente ultrasound irradiation

Table 3
Screening of the catalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>Yield (%)</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>LDH</td>
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</tr>
<tr>
<td>2</td>
<td>Fe₃O₄</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>Fe₃O₄@LDH@Tricine</td>
<td>trace</td>
</tr>
<tr>
<td>4</td>
<td>Fe₃O₄@LDH</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>Fe₃O₄@Tricine–Cu(I)</td>
<td>85</td>
</tr>
<tr>
<td>6</td>
<td>sonochemically synthesized Fe₃O₄@LDH@Tricine–Cu(I)</td>
<td>97</td>
</tr>
</tbody>
</table>

A suggested mechanism for the oxidative esterification reaction catalyzed with Fe₃O₄@LDH@Tricine–Cu(I) has been shown in Fig. 9. Initially, radical of tert-Butyl hydroperoxide radical (T-BuOO.) was produced by Fe₃O₄@LDH@Tricine–Cu(I) and this radical reacted with benzaldehyde to produce the radical of benzaldehyde. Whereafter, TBHP reacted with radical of benzaldehyde to produce acid. Methoxide produced in reaction with NO₃⁻ (NO₃⁻ located between layers of LDH) and attacked to acid to produce ester [30, 31].

One of the special advantages of a heterogeneous catalyst is reusability. Therefore, the recyclability of the Fe₃O₄@LDH@Tricine–Cu(I) nanocomposites was assessed in the oxidative esterification reaction of 4-chlorobenzaldehyde with methanol (Fig. 11a). It is found that these nanoparticles did not show any significant loss of catalytic activity after 5 times of reaction. The structure and morphology of the nanocomposites also remained intact after 5 times of reaction, as evident from their SEM image and FT-IR spectra (Fig. 10b and c). As can be seen in Fig. 10b, SEM of Fe₃O₄@LDH@Tricine–Cu(I) nanoparticles has a rough surface that plate-like shape particles attached to their surface. In Fig. 11c, the bands at around 3434 cm⁻¹ (stretching of O–H groups of LDH, O―H stretching vibrations of Fe₃O₄), 1610 cm⁻¹ (water-bending vibrations of water), the sharp peak around 1381 cm⁻¹ (stretching vibration of NO₃) and the adsorption bands from about 596 cm⁻¹ (metal–oxygen bonds of lattice) can be seen.

Finally, the stability of the catalyst during the catalytic reaction was investigated by the leaching test (Fig. 11). After 7 minutes, the Fe₃O₄@LDH@Tricine–Cu(I) nanocomposites were separated from the solution of the reaction. Next, the solution of reaction was stirred for 8 minutes. Then, no progress of reaction indicates that had no leached active species during the course of the catalytic reaction.
The comparison of acquired results of this work with previously published was performed and listed in the Table 5. The Fe₃O₄@LDH@Tricine–Cu(I) nanocomposites showed excellent catalytic activity due to efficient, safe, durable, the reusability of catalyst, terms of price and easy preparation of the heterogeneous catalyst. In addition, this work is comparable in low-toxicity, speed of reaction, commercially available materials.

<table>
<thead>
<tr>
<th>Entries</th>
<th>Catalyst</th>
<th>Reaction conditions</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>KI</td>
<td>Benzaldehyde (1.0 mmol), methanol (4ml), TBHP at 65°C for 10h</td>
<td>97[32]</td>
</tr>
<tr>
<td>2</td>
<td>N-bromosuccinimide (NBS)-pyridine</td>
<td>Benzaldehyde (3.311 mmol), methanol (10 ml), pyridine (3.311 mmol) for 6h</td>
<td>83[33]</td>
</tr>
<tr>
<td>3</td>
<td>B(C₆F₅)₃ (1 mol %)</td>
<td>Benzaldehyde (1 mmol), methanol, TBHP (3 equiv), reflux for 18h</td>
<td>86[34]</td>
</tr>
<tr>
<td>4</td>
<td>CaCl₂ (10 mol %)</td>
<td>Benzaldehyde (1 mmol), methanol (4 ml), H₂O₂ (4 equiv), 65 °C, 48 h.</td>
<td>55[35]</td>
</tr>
<tr>
<td>5</td>
<td>Pd²⁺/Fe/FeO/graphene</td>
<td>Benzaldehyde (1 mmol), methanol (3 ml), K₂CO₃ (1.2 mmol) at 60 °C for 6h.</td>
<td>88[36]</td>
</tr>
<tr>
<td>6</td>
<td>Fe–Au magnetic nanoparticles</td>
<td>Benzaldehyde (1 mmol), methanol (3 ml), K₂CO₃ (10 mol %), O₂, 80 °C for 7h.</td>
<td>94[37]</td>
</tr>
<tr>
<td>7</td>
<td>Fe₃O₄@LDH@Tricine–Cu(I)</td>
<td>Benzaldehyde (1.0 mmol), methanol (1.1 mmol), TBHP (1.5 mmol) in ultrasound bath in water at 80°C for 15 minute.</td>
<td>97</td>
</tr>
</tbody>
</table>

4. Conclusion

In conclusion, we developed an environmentally friendly, inexpensive, easy and fast way for oxidative esterification reaction of benzaldehydes with alcohols through the synthesis of a highly efficient and sustainable catalytic system of a sonochemically synthesized Fe₃O₄@LDH@Tricine–Cu(I) in the ultrasound bath. The modification of LDH nanoparticles with active copper with fabrication with sonochemical method on magnetic nanoparticles surface increased the efficiency and activity of Fe₃O₄@LDH@Tricine–Cu(I) catalyst that the catalyst activity was suitable for oxidative esterification reaction under green condition with applied water as a green solvent. This rout shows the application of the sonochemistry approach with the environmental method, short reaction time, easy separation catalyst, efficient, and durable catalyst for oxidative esterification of arylaldehydes.
Declarations

Acknowledgements

The authors are grateful for supporting this work from Tarbiat Modares University and University of Oulu.

Ethics Approval

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Authors Contributions

Farzane Pazoki designed and performed the experiments and was involved in planning the work. Sepideh Bagheri helped to analyzed the data. Elahe Yazdani to write the paper. Fatemeh Mohsenzadeh helped to edit the paper. Akbar Heydari was involved in planning and supervised the work.

Data availability

The datasets used or analyzed during the current study are available from the corresponding author on reasonable request.

References


Table

Table 4 is available in the Supplementary Files section
**Figures**

**Figure 1**

Preparation of Fe$_3$O$_4$@LDH@Tricine–Cu(l)

**Figure 2**

FT-IR spectra of the Fe$_3$O$_4$ (black curve), Fe$_3$O$_4$@LDH (yellow curve), Fe$_3$O$_4$@LDH@Tricine (orange curve), Fe$_3$O$_4$@LDH@Tricine–Cu(l) (red curve)
Figure 3

EDX spectrum of sonochemically synthesized Fe₃O₄@LDH@Tricine–Cu(I) nanocomposites

Table 1 The weight percent of the various elements on the surface of Fe₃O₄@LDH@Tricine–Cu(I) from EDX analysis (W% = Weight percentage, A% = Atomic percentage)
Figure 4

SEM of Fe₃O₄@LDH@Tricine-Cu(I)
Figure 5

Elemental mapping of the Fe₃O₄@LDH@Tricine–Cu(I)
Figure 6
Thermogravimetric analysis and derivation curves (DTG) of Fe$_3$O$_4$@LDH@Tricine–Cu(I).

Figure 7
Magnetization curves of Fe$_3$O$_4$ (black curve) and Fe$_3$O$_4$@LDH@Tricine–Cu(I) (red curve).
Figure 8

XRD of the Fe$_3$O$_4$@LDH@Tricine–Cu(I)
Figure 9

Proposed mechanism

Figure 10
a) Recyclability study of the catalyst  
b) SEM image of catalyst after reaction  
c) FT-IR of catalyst after reaction

Figure 11

Leaching test for catalyst.

Supplementary Files

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- Table4SynthesisofestersfromarylaldehydesandalcoholsusingFe3O4.docx
- SUPPORTINGINFORMATION12.docx