Fabrication of Fe₃O₄@PVA-Cu Nanocomposite and Its Application for Facile and Selective Oxidation of Alcohols

Jamal Rahimi, Maryam Niksefat and Ali Maleki*

Fe₃O₄@PVA-Cu nanocomposite was introduced as an affordable catalyst for selective oxidation of alcohols into various aldehydes and ketones. The synthesized nanocomposite was characterized by applying essential analyses. The peaks that are appeared in FT-IR spectroscopy confirmed the production of the Fe₃O₄@PVA-Cu nanocomposite. In addition, EDX analysis proved the presence of oxygen, carbon, iron, and copper elements in the catalyst. Further, TGA analysis showed high thermal stability of the nanocomposite. VSM technique was applied to examine the magnetic property of the nanocomposite. The results demonstrated a high magnetic property in the catalyst, which enables easy separation of it from the reaction solution. TEM and SEM imaging showed the nanoscale size of the particles (∼20 nm) in the catalyst. Additionally, XRD data was compatible with that of Fe₃O₄ nanoparticles. The application of the nanocomposite has been studied in the selective oxidation of alcohols in the presence of acetonitrile as solvent, and hydrogen peroxide as a supplementary oxidizing agent. This technique is remarkably facile and inexpensive. Further, the products showed high yields.

Keywords: polyvinyl alcohol, magnetic nanocomposite, green chemistry, alcohol oxidation, copper catalyst

INTRODUCTION

In recent decades, introducing nanoscale materials has led to a remarkable change almost in all areas of science. Accordingly, specific and unique features of nanomaterials in the chemical reactions have attracted the attention of scientists in the field of chemistry. Nanomaterials are a class of compounds with at least one dimension in size ranging from 1 to 100 nm (Kreyling et al., 2010). Unlike bulk materials, nanoscale materials show distinct traits just because of their small size (Valenti et al., 2016). In general, nanoparticles can be categorized into two subclasses: Simple nanoparticles and nanocomposites or core/shells. The latter plays an important role in nanoscience. Core/shell nanoparticles are composed of a core that is placed in the inner part of shell material (Chaudhuri and Paria, 2012).

Some nanoparticles, like iron, nickel, and cobalt and their oxides such as Fe₃O₄ (Maleki et al., 2016), NiO (Tadic et al., 2015), and Co₃O₄ (Moro et al., 2013), have wide application in chemical, material, medicinal, and electronic sciences (Alivisatos, 2004; Kopelman et al., 2005).
Maleki et al., 2019). But they are extremely unstable, as their large surface area makes them highly active (Hutten et al., 2004). However, nanoparticles covered with a protection material show higher stability. Also, the protective shell can improve and develop the application of nanomaterials (Salama et al., 2018; Cheng et al., 2019). There are different types of materials that can be used as a shell to improve the stability of nanoparticles (including inorganic metals and polymers) (Zhu and Diao, 2011). Among various types of nanocomposites, researchers choose the shell material most suitable for their target reaction process.

Polyvinyl alcohol (PVA) ([CH₂CHOH]ₙ) is one of the most useful polymers that can be used in preparation of nanocomposites. PVA is produced from based-catalyzed hydrolysis of acetate groups in polyvinyl acetate (Rahimi et al., 2020b). It has special characteristics that enable it to act as a good substrate in the synthesis of nanocomposites. These characteristics include high solubility in water, resistance to chemicals, environmentally friendly, cheap, full of hydroxyl groups, etc. (Song et al., 2018). Despite of such precious characteristics, the rich hydroxyl groups make it unstable in aqueous solutions. One of the best ways to prevail over this limitation is to protect the –OH groups with a cover material such as hydrogen sulfate (Maleki et al., 2019b), clay (Kokabia et al., 2007), zinc acetate (Yang et al., 2004), TiO₂ (Yang, 2007), etc. Copper is an element that can be used as a useful protecting cover for improving and modifying PVA attributes (Khan et al., 2019). Copper element has singular properties, including propounded electrical conductivity and antibacterial activities (Lu et al., 2004; Kong et al., 2019). The copper chelated PVA can easily overcome the instability of polyvinyl alcohol by functionalizing hydroxyl groups (Hojo et al., 1978; Maleki et al., 2019a).

Selective oxidation of alcohols, which leads to the formation of aldehydes and ketones, considered among one of the most important processes in industry and scientific research (Su et al., 2010; Pereira et al., 2019; Rahimi et al., 2020a). Aldehydes and ketones are among the most important precursors for the synthesis of various compounds with precious properties (Fey et al., 2001). In past decades, numerous synthetic routes have been reported for the oxidation of alcohols. Most utilize hazardous and expensive oxidants, while others have strict conditions such as high pressure and temperature (Ghalavand et al., 2019; Lopes et al., 2019). Therefore, it is necessary to introduce a green and low-cost strategy based on an environmentally friendly and commercially available oxidant such as H₂O₂ (Kawamura et al., 2016), O₂ (Jiang et al., 2016), and air atmosphere (Noyori et al., 2003). This is to produce aldehydes and ketones through the oxidation reaction of alcohols (Ghalavand et al., 2019). Additionally, an appropriate catalyst in the oxidation reaction can significantly reduce the need for using detrimental oxidants (Dijskman et al., 2001; Rautiainen et al., 2014). During the past years, different strategies have been developed for the synthesis of aldehydes and ketones through the oxidation of alcohols with metal catalysts, especially Pd (Verma et al., 2017), Ru (Ray et al., 2016; Sarmah et al., 2018), Ag (Mir et al., 2019), Au (Zhan et al., 2018), and copper-based (Sasano et al., 2018) catalysts, which are limited in scope, have long reaction time, and in most cases low conversion rate (Table 1).

Herein, based on unique properties of nanocomposites and our previous research on the synthesis of nanomagnetic composites and their catalytic application in chemical reactions, we introduced the synthesis of the heterogeneous Fe₃O₄@PVA-Cu nanocomposite (Maleki and Rahimi, 2018; Maleki et al., 2019c). Moreover, we investigated the application of this nanocomposite for the selective oxidation of alcohols into aldehydes and ketones (Scheme 1).

**RESULTS AND DISCUSSION**

**Delineation of Fe₃O₄@PVA-Cu Nanoparticles**

**Fourier-Transform Infrared Spectroscopy (FT-IR)**

Figure 1 illustrates the FT-IR spectra of the synthesized catalyst, Fe₃O₄, PVA, and Fe₃O₄@PVA. The FT-IR spectrum of the recovered Fe₃O₄@PVA-Cu is also shown. According to Figure 1b, the observed intense peaks at wavelengths of ∼3,436 and ∼2,931 are related to OH groups and vibrational mode of C-H bonds of PVA, respectively. The FT-IR data indicated that, the intensity of hydroxyl groups signal at the wavelength of ∼3,430, which are corresponded to PVA, has been decreased (Figure 1d). This is due to the chelation of copper with oxygen atoms of PVA in the catalyst. The signal at ∼588 cm⁻¹ in Figure 1d demonstrates the formation of the covalent bond between Fe and O. The signals at  

| Entry | Catalyst | Reaction time (°C) | Yield (%) | References |
|-------|----------|-------------------|-----------|------------|
| 1     | Fe₃O₄@PVA-Cu | 5–30 min | 82 | 68–93 | This work |
| 2     | [Ru(H)(CO)Cl(PPh₃)₃] | 18–24 h | 90 | 40–95 | Ray et al., 2016 |
| 3     | RuO₂(3%)/Mn₃O₄ | 12–18 h | 90–110 | 30–99 | Sarmah et al., 2018 |
| 4     | Pd@TiC | 8 h | r.t. (vis. light) | 94–97 | Verma et al., 2017 |
| 5     | [Ru(CO)₂(CF₃CN)] | 4–8 h | r.t. | 84–94 | Mir et al., 2019 |
| 6     | Cu₂O@HKUST-1@Au | 10 h | 90 | 34–63 | Zhan et al., 2018 |
| 7     | AZADO, CuCl, bpy | 0.5–4 h | r.t. | 78–99 | Sasano et al., 2018 |
∼1,433 and ∼2,900 cm⁻¹ are related to vibrations of C-H bonds associated to PVA. As shown in Figure 1e, all signals of the recycled catalyst are compatible with the primary Fe₃O₄@PVA-Cu nanoparticles. In both spectra (Figures 1d,e), the signal corresponding to the Cu-O bond was occurred at ∼600 cm⁻¹ (Hajipour et al., 2015).

Energy-Dispersive X-Ray Spectroscopy (EDX)

For identifying the related elements in the catalyst, we employed the EDX spectroscopy technique. EDX analyses of Fe₃O₄@PVA (a), Fe₃O₄@PVA-Cu (b), and also EDX spectrum of recovered Fe₃O₄@PVA-Cu (c) were provided. As shown in Figure 2A, presence of carbon, oxygen, and iron elements are, respectively, confirmed by the recorded peaks at 0.29, 0.53, 6.44, and 7.1 KeV. Moreover, the signals that are located at 0.8, 8.1, and 9.0 KeV in Figures 2B,C, demonstrate the presence of copper in the nanocomposite. Therefore, the copper remained unchanged after recyclization of the catalyst. In addition, quantitative measurements indicated the chelation of copper elements with oxygen atoms of PVA (Table 2). The results showed that, 1.53 percent of the final product is associated with the chelated copper elements.
Rahimi et al. Fabrication of Fe$_3$O$_4$@PVA-Cu NC for Oxidation

**FIGURE 2** | EDX analyses of Fe$_3$O$_4$@PVA (A), Fe$_3$O$_4$@PVA-Cu (B), and recovered Fe$_3$O$_4$@PVA-Cu (C).

**TABLE 2** | Quantitative values of related elements by EDX measurements.

| Elements | Line | Atomic (%) | Weight (%) |
|----------|------|------------|------------|
| Cu       | La   | 0.46       | 1.53       |
| Fe       | Ka   | 10.50      | 30.59      |
| O        | Ka   | 58.14      | 48.52      |
| C        | Ka   | 30.89      | 19.35      |

**Thermogravimetric Analysis (TGA)**

We conducted the TGA analysis to evaluate the weight loss of the product in different thermal ranges. *Figure 3A* shows TGA analysis of Fe$_3$O$_4$@PVA-Cu in temperature ranged from 20 to 800°C in the surrounding atmosphere. TGA analyses of Fe$_3$O$_4$ and Fe$_3$O$_4$@PVA were provided for comparison in *Figure 1b* in the same conditions. The increase of weight observed at the beginning of the graph is due to adsorption of surrounding moisture. It was depleted by increasing the temperature ranged between 75 and 200°C. The approximate loss of 5% in weight was observed from 210 to 300°C. This corresponds to dehydration of H$_2$O groups that were trapped in the structure of the product. As indicated in *Figure 3A*, ~8% loss of weight occurred at the temperatures ranged between ~300 to ~700°C. Separation of copper and removal of hydroxyl groups in the form of water molecules from PVA is propounded in this thermal range. Eventually, the product was fully broke down at the elevated temperature, which is estimated at ~700°C. The results demonstrate the higher thermal stability of the nanocomposite compared with unfunctionalized PVA (Abdul Kareem and Anukali, 2011).

**Vibrating Sample Magnetometer (VSM)**

We used the VSM analysis to assess the magnetic property of the nanocomposite. The graph illustrates that, Fe$_3$O$_4$@PVA and Fe$_3$O$_4$@PVA-Cu nanoparticles show magnetization of ~29 and ~39 emu/g, respectively (*Figure 4*). Comparison of the curves in *Figure 4*, shows ~10 emu/g increase in the magnetic property of the Fe$_3$O$_4$@PVA-Cu nanoparticles. This is due to chelation of Cu$^{2+}$ with oxygen atoms of PVA. The high magnetic property of Fe$_3$O$_4$@PVA-Cu nanocomposite causes the catalyst to be smoothly isolated from the reaction solution by using an external magnet field.

**Electron Microscopy Techniques (SEM and TEM)**

We used microscopy-imaging techniques for identification of morphology and structure of the catalyst. *Figure 5* shows SEM (*Figure 5a*) and TEM (*Figure 5b*) images of the final product. In addition, size distribution of nanoparticles is provided in *Figure 5c*. The spherical morphology of the Fe$_3$O$_4$@PVA-Cu nanoparticles are clearly shown with an average diameter of ~20 nm in SEM image. The results in *Figure 5c* demonstrate that most of the particles have size ranged from 20 to 25 nm. Moreover, the TEM analysis confirmed the particles size. As illustrated in TEM image of the catalyst (*Figure 5b*), dark areas on the gray matrix clearly indicate the dispersion of nanoparticles on PVA.

**X-Ray Crystallography (XRD)**

XRD analysis was conducted to identify the crystalline structure of the catalyst. *Figure 6* indicates XRD patterns of copper Fe$_3$O$_4$@PVA catalyst (a) and Fe$_3$O$_4$ nanoparticles (b). The signal
around 20° confirms the presence of PVA in the product (Li et al., 2015). Furthermore, comparison of the appeared signals at 18.5°, 30.5°, 35°, 38.5°, 43°, 44.5°, 58°, 63°, and 78° (see Figure 6A) with the standard data of Fe₃O₄ (JCPDS: 19-0629) demonstrates the production of the nanocomposite (Todaka et al., 2003). Moreover, the Debye-Scherrer equation determined the mean size of ∼20 nm for particles, which is compatible with measurements in the electron microscopy analysis.

**Application of Fe₃O₄@PVA-Cu in Selective Oxidation of Alcohols**

**Optimization of Reaction Variables for the Selective Oxidation of Alcohols Using Fe₃O₄@PVA-Cu Nanoparticles**

We used the reaction of benzyl alcohol (0.5 mmol) in order to optimize the different variables in the selective oxidation reaction of alcohols in the presence of copper-functionalized Fe₃O₄@PVA. This reaction was implemented in the presence of several solvents with the different amount of the catalyst. In addition, we tested the oxidation effect of H₂O₂ on the model reaction. As presented in Table 3 (entries 1–9), the best performance occurred using acetonitrile as solvent in the trial of different solvents for the reaction (Table 3, entry 5). To obtain the best amount of Fe₃O₄@PVA-Cu for the reaction, we applied a diverse amount of the catalyst to the sample reaction. Further, the reaction was performed in the absence of the catalyst. As shown in Table 3 (entries 10–15), the best result was obtained using 20 mg of Fe₃O₄@PVA-Cu for the reaction. To evaluate the optimal amount and oxidation effect of H₂O₂ in the model reaction, we implemented the reaction in the different amounts of hydrogen peroxide. As mentioned in Table 3 (entries 12, 16–18), the optimal amount of H₂O₂ is 3 mol percent of H₂O₂ as the supplemental oxidizing agent. For optimizing the reaction temperature, the sample reaction was conducted at room temperature and at reflux (Table 3, entries 18–19). The best result was achieved at reflux condition. Moreover, the effect of Fe₃O₄, Fe₃O₄@PVA, and Fe₃O₄@Cu in the conversion of alcohols to...
FIGURE 4 | VSM graph of Fe$_3$O$_4$@PVA and Fe$_3$O$_4$@PVA-Cu nanoparticles at room temperature.

FIGURE 5 | SEM (a) and TEM (b) images of Fe$_3$O$_4$@PVA-Cu nanoparticles and size distribution of nanoparticles chart (c).
aldehydes and ketones was studied (Table 3, entries 20–22). The results have shown the ineffectiveness of these compounds to catalyze the selective oxidation reaction of alcohols.

Extending Catalytic Application of Fe₃O₄@PVA-Cu Nanoparticles to Selective Oxidation of Alcohols
In the interest of exerting catalytic application of Fe₃O₄@PVA-Cu in the selective oxidation of alcohols, we extended the optimized reaction conditions to various alcohols (Table 4). In this research, the oxidation reaction of alcohols was carried out in acetonitrile, as a solvent, in the presence of Fe₃O₄@PVA-Cu, as catalyst and oxidant. Additionally, hydrogen peroxide was used as the auxiliary oxidizing agent. The reaction solution was stirred under reflux condition until completion of the reaction. High values of calculated TONs and TOFs (see Table 4) show excellent efficiency of the catalyst for selective conversion of alcohols into desired products. According to Table 4 (entries 4–8, 12), maximum yields of products are shown by the alcohols with electron donation groups on ortho or meta position of the phenyl group. As electron donating groups in ortho and meta positions increase the negative charge on benzylic carbon, the removal of its hydrogen from intermediate complex would be easier.

Evaluation of Catalyst Reusability
Recyclability of the catalyst is a significant factor for the green synthesis of organic compounds. This feature also has a great impact on reducing the costs of the reaction. For this purpose, we tested the reusability of the Fe₃O₄@PVA-Cu nanoparticles for the selective oxidation reaction of alcohols. Figure 7 shows infinitesimal loss of catalytic activity after reusing the catalyst for five times in the oxidation reaction of benzyl alcohol as the model reaction under optimized conditions. In each trial, we separated the nanomagnetic catalyst by using an external magnetic field. Then, it was washed with acetone and deionized water for several times. The results demonstrated a high stability of Fe₃O₄@PVA-Cu magnetic nanocomposites in the reaction.

Suggested Mechanism for Selective Oxidation of Alcohols in the Presence of Fe₃O₄@PVA-Cu Nanocomposite
Scheme 2 shows a plausible mechanism for selective oxidation of alcohols in the presence of Fe₃O₄@PVA-Cu nanocomposite and hydrogen peroxide. The results implied that Cu(II) of nanocomposite acts as the active site in the selective oxidation reaction of alcohols in the presence of H₂O₂. In the first step, the chelated copper coordinated to the oxygen of hydrogen peroxide
TABLE 3 | Optimization of reaction conditions for the selective oxidation reaction of alcohols into aldehydes and ketones using Fe$_3$O$_4$@PVA-Cu nanoparticles.$^a$

| Entry | Solvent | Cat. (mg) | H$_2$O$_2$ (mol %) | Temperature ($^\circ$C) | Time (min) | Yield$^b$ (%) |
|-------|---------|-----------|-------------------|-------------------------|------------|---------------|
| 1     | Toluene | 20        | –                 | Reflux                  | 120        | –             |
| 2     | H$_2$O  | 20        | –                 | Reflux                  | 120        | 0             |
| 3     | MeOH    | 20        | –                 | Reflux                  | 120        | 35            |
| 4     | EtOH    | 20        | –                 | Reflux                  | 120        | 30            |
| 5     | CH$_3$CN| 20        | –                 | Reflux                  | 120        | 86            |
| 6     | Et$_2$O | 20        | –                 | Reflux                  | 120        | 10            |
| 7     | DMSO    | 20        | –                 | Reflux                  | 120        | 84            |
| 8     | CH$_3$Cl| 20        | –                 | Reflux                  | 120        | 40            |
| 9     | DMF     | 20        | –                 | Reflux                  | 120        | 83            |
| 10    | CH$_3$CN| –         | 5                 | Reflux                  | 300        | 0             |
| 11    | CH$_3$CN| 10        | 5                 | Reflux                  | 20         | 51            |
| 12    | CH$_3$CN| 20        | 5                 | Reflux                  | 20         | 87            |
| 13    | CH$_3$CN| 30        | 5                 | Reflux                  | 20         | 87            |
| 14    | CH$_3$CN| 40        | 5                 | Reflux                  | 20         | 72            |
| 15    | CH$_3$CN| 50        | 5                 | Reflux                  | 20         | 71            |
| 16    | CH$_3$CN| 20        | 1                 | Reflux                  | 20         | 65            |
| 17    | CH$_3$CN| 20        | 2                 | Reflux                  | 20         | 75            |
| 18    | CH$_3$CN| 20        | 3                 | Reflux                  | 20         | 88            |
| 19    | CH$_3$CN| 20        | 3                 | r.t.                    | 180        | 75            |
| 20    | CH$_3$CN| 20 mg Fe$_3$O$_4$ | 3             | Reflux                  | 20         | Trace         |
| 21    | CH$_3$CN| 20 mg Fe$_3$O$_4$@PVA | 3          | Reflux                  | 20         | Trace         |
| 22    | CH$_3$CN| 20 mg Fe$_3$O$_4$@Cu | 3          | Reflux                  | 20         | Trace         |

$^a$Reaction conditions: benzyl alcohol (0.5 mmol), Fe$_3$O$_4$@PVA-Cu as catalyst, solvent (2 mL), H$_2$O$_2$.

$^b$Isolated yield.

and creates intermediate complex A (Hojo et al., 1978). Then, the complex A reacted with corresponding alcohols to give the intermediate B. Further, the elimination of a water molecule from the complex resulted the intermediate complex C. In the next step, the removal of another water molecule provided the desired products (2a-2n), and regeneration of the catalyst completed the cycle (Narisawa et al., 1989; Yu et al., 2010).

EXPERIMENTAL

Substances and Instruments

All chemical substances such as H$_2$O$_2$, FeCl$_2$.4H$_2$O, FeCl$_3$.6H$_2$O, PVA 72000 MW, Cu(CH$_3$COO)$_2$, CH$_3$CN and other solvents were bought from Merck and Sigma Aldrich companies. A Shimadzu IR-470 spectrometer was used for obtaining FT-IR spectra of products by using KBr disk. TEM imaging was performed using Philips CM200 apparatus. SEM imaging was measured by a Sigma-Zeiss microscope with an attached camera. XRD analysis was assessed with a JEOL JDX-8030 (30 kV, 20 mA). EDX measurements were carried out by using a Numerix DXP-X1-P apparatus. TGA analysis was performed by an STA504. VSM evaluation was conducted with a Lakeshore 7407.

Synthetic Routes

**In-situ Synthesis of Fe$_3$O$_4$@PVA Nanoparticles**

In the first step, PVA 72000 MW (2.0 g) was added to a 250 mL round flask containing distilled water (40 mL) and was mixed on a magnetic stirrer at 80°C under the protection of inert gas (N$_2$). After the creation of a homogeneous and transparent mixture, ammonia (12 mL) was added to the mixture dropwise. We continued adding ammonia to the mixture until pH = 12 was acquired. Then, the prepared aqueous solutions of FeCl$_3$.6H$_2$O (2.5 g in 10 mL deionized water) and FeCl$_2$.4H$_2$O (1.0 g in 10 mL deionized water) were added to the mixture gradually. When the addition was finished, we left the flask to continue stirring for 2 consecutive hours at ambient temperature. After completion of the reaction, we separated the produced black magnetic nanoparticles by using an external magnetic field. Then we washed the nanoparticles with excessive amount of deionized water and acetone. In the next step, the nanoparticles were
TABLE 4 | Synthesis of aldehydes and ketones from selective oxidation of alcohols using Fe₃O₄@PVA-Cu as catalyst.

| Entry | Alcohol 1 | Product 2 | Time (min) | Yield (%) | TON | TOF (min⁻¹) |
|-------|-----------|------------|------------|-----------|-----|-------------|
| 1     | R<sub>1</sub>-OH | PhCHO (2a) | 5          | 88        | 2.3 × 10⁶ | 4.6 × 10⁵ |
| 2     | R<sub>2</sub>-OH | PhCHO (2a) | 15         | 68        | 1.8 × 10⁶ | 1.2 × 10⁵ |
| 3     | Cl-R<sub>2</sub>-OH | PhCHO (2c) | 5          | 82        | 2.1 × 10⁶ | 4.3 × 10⁵ |
| 4     | HO-R<sub>2</sub>-OH | PhCHO (2d) | 5          | 90        | 2.4 × 10⁶ | 4.7 × 10⁵ |
| 5     | HO-R<sub>2</sub>-OH | PhCHO (2e) | 5          | 92        | 2.4 × 10⁶ | 4.8 × 10⁵ |
| 6     | OMe-R<sub>2</sub>-OH | PhCHO (2f) | 5          | 86        | 2.3 × 10⁶ | 4.5 × 10⁵ |
| 7     | MeO-R<sub>2</sub>-OH | PhCHO (2g) | 5          | 92        | 2.4 × 10⁶ | 4.8 × 10⁵ |
| 8     | MeO-R<sub>2</sub>-OH | PhCHO (2h) | 5          | 92        | 2.4 × 10⁶ | 4.8 × 10⁵ |

(Continued)
TABLE 4 | Continued

| Entry | Alcohol 1 | Product 2 | Time (min) | Yield (%) | TON \(^c\) | TOF \(^d\) (min\(^{-1}\)) |
|-------|-----------|-----------|------------|-----------|-----------|-----------------|
| 9     | ![Methyl phenyl] | ![Formaldehyde] | 10 | 85 | \(2.2 \times 10^6\) | \(2.2 \times 10^6\) |
| 10    | ![Methyl phenyl nitro] | ![Formaldehyde] | 15 | 75 | \(1.9 \times 10^6\) | \(1.3 \times 10^6\) |
| 11    | ![Phenyl] | ![Formaldehyde] | 5 | 93 | \(2.4 \times 10^6\) | \(4.9 \times 10^5\) |
| 12    | ![Phenyl] | ![Formaldehyde] | 5 | 91 | \(2.4 \times 10^6\) | \(4.8 \times 10^5\) |
| 13    | ![Cyclohexyl] | ![Epoxy compound] | 30 | 88 | \(2.3 \times 10^6\) | \(7.7 \times 10^4\) |
| 14    | ![Cyclopentyl] | ![Epoxy compound] | 30 | 87 | \(2.3 \times 10^6\) | \(7.6 \times 10^4\) |

\(^a\)Reaction conditions: Alcohols 1 (0.5 mmol), Fe\(_3\)O\(_4\)@PVA-Cu (20 mg), H\(_2\)O\(_2\) (3 mol %), CH\(_3\)CN (2 mL) as solvent, reflux.

\(^b\)Isolated yield.

\(^c\)The turnover number [Yield/Amount of the catalyst (mol)].

\(^d\)The turnover frequency [TON/time (min)].

dried in a vacuum oven at 70°C. Then, the black powder of Fe\(_3\)O\(_4\)@PVA nanoparticles was provided by using a ball mill.

**Preparation of Fe\(_3\)O\(_4\)@PVA-Cu Nanoparticles**

Fe\(_3\)O\(_4\)@PVA nanoparticles (1.0 g) was added to a flask, which was containing distilled water (10 mL). The mixture was dispersed for about 10 min. Then, Cu(CH\(_3\)COO)\(_2\) (aq.) (5% wt.) was added to the dispersed aqueous mixture of Fe\(_3\)O\(_4\)@PVA nanoparticles dropwise. After 2 h stirring the mixture at room temperature, the produced mixture was filtered off and completely washed with water (50 mL) and ethanol (50 mL) for three times. Eventually, the yielded product was dried at room temperature.

**Synthesis of Aldehydes and Ketones (2a-2n) From the Selective Oxidation of Alcohols Using Fe\(_3\)O\(_4\)@PVA-Cu Nanoparticles**

Alcohol (0.5 mmol), of Fe\(_3\)O\(_4\)@PVA-Cu (20 mg), and hydrogen peroxide (3 mol %) were added to a flask, which was containing acetonitrile (2 mL) as solvent. The reaction solution was stirred until completion of the reaction. The reaction process was tracking with Thin Layer Chromatography (TLC) technique. After producing the target product, which was detected by TLC, the catalyst was removed from the container by using an external magnetic field. In the end, we purified the products with GC-MS technique.
CONCLUSION

In this study, we produced Fe$_3$O$_4$@PVA-Cu nanocomposite, which was characterized by employing TEM, SEM, EDX, XRD, TGA, VSM, and FT-IR techniques. Moreover, the application of the prepared nanocomposite was thoroughly examined for the selective oxidation of alcohols. Various aldehydes and ketones were synthesized in the presence of Fe$_3$O$_4$@PVA-Cu and hydrogen peroxide as the supplementary oxidant. Using the prepared heterogeneous nanocatalyst provided an environmentally friendly, economical, highly selective, and straightforward strategy for selective oxidation of alcohols. Moreover, simple isolation of the catalyst from the reaction solution with negligible loss of catalytic activity in further reactions is another advantage of this method.

DATA AVAILABILITY STATEMENT

All datasets presented in this study are included in the article/supplementary material.

AUTHOR CONTRIBUTIONS

JR, and MN as the students of AM’s research group carried out the analyses, characterization, and participated in discussing the results.
the results, prepared the draft of the manuscript, and revised the manuscript. AM designed the study, edited and revised the manuscript, and managed all steps of the project. All authors read and approved the final manuscript.

REFERENCES

Abdul Kareem, T., and Anu kaliani, A. (2011). Synthesis and thermal study of octahedral silver nano-plates in polyvinyl alcohol (PVA). Arab. J. Chem. 4, 325–331. doi: 10.1016/j.arabjc.2010.06.054

Alvisatos, P. (2004). The use of nanocrystals in biological detection. Nat. Biotechnol. 22, 47–52. doi: 10.1038/nbt927

Chaudhuri, R. G., and Paria, S. (2012). Core/shell nanoparticles: classes, properties, synthesis mechanisms, characterization, and applications. Chem. Rev. 112, 2373–2433. doi: 10.1021/cr100449n

Cheng, Y., Li, J., Deng, S., and Sun, F. (2019). AgNP@Ag(I)-AMTD metal-organic gel-nanocomposites act as a SERS probe for the detection of Hg^{2+}. Compos. Commun. 13, 75–79. doi: 10.1016/j.jcomcm.2019.03.005

Dijkstra, J., Daemen, J. J., and De Boer, P. (2010). Copper-containing polyvinyl alcohol composite systems: preparation, characterization and biological activity. J. Phys. Chem. Solids 63, 96–108. doi: 10.1016/j.jpcs.2013.05.030

Hojo, N., Shirai, H., Chuo, Y., and Hayashi, S. (1975). Catalytic activity of Cu(II)-poly(vinyl alcohol) complex for decomposition of hydrogen peroxide. Polym. Sci. Polym. Chem. Ed. 16, 447–455. doi: 10.1002/pol.19781060215

Hutter, A., Sudfeld, D., Ennen, L., Reiss, G., Hachmann, W., Heinzmann, U., et al. (2004). New magnetic nanoparticles for biotechnology. J. Biotechnol. 112, 47–63. doi: 10.1016/j.jbiotec.2004.04.019

Jiang, X., Zhang, J., and Ma, S. (2016). Iron catalysis for room-temperature aerobic enhancement and photodynamic therapy of a rat brain cancer. J. Magn. Mater. 293, 404–410. doi: 10.1016/j.jmmm.2005.02.061

Kreyling, W. G., Semmler-Behnke, M., and Chaudhry, Q. (2010). A complementary definition of nanomaterial. Nano Today 5, 165–168. doi: 10.1016/j.nantod.2010.03.004

Li, H.-Z., Chen, S.-C., and Wang, Y.-Z. (2015). Preparation and characterization of nanocomposites of polyvinyl alcohol/cellulose nanowhiskers/chitosan. Compos. Sci. Technol. 115, 60–65. doi: 10.1016/j.compscitech.2015.05.004

Lopes, J. C., Sampaio, M. J., Fernandes, R. A., Lima, M. J., Faria, J. L., and Silva, C. G. (2019). Recent strategies for hydrogen peroxide production by metal-free carbon nitride photocatalysts. Catalysts 9, 9990. doi: 10.3390/catal9120990

Lu, L., Shen, Y., Chen, X., Qian, L., and Lu, K. (2004). Ultrahigh strength and high electrical conductivity in copper. Science 304, 422–426. doi: 10.1126/science.1092905

Maleki, A., Azadegan, S., and Rahimi, J. (2019). Gallic acid grafted to amine-functionalized magnetic nanoparticles as a proficient catalyst for environmentally friendly synthesis of α-aminoalcohols. Appl. Organ. Chem. 33:4810. doi: 10.1002/aoc.4810

Maleki, A., Movahed, H., and Paydar, R. (2016). Design and development of a novel cellulose/γ-Fe2O3 Ag nanocomposite: a potential green catalyst and antibacterial agent. RSC Adv. 6, 13657–13665. doi: 10.1039/C5RA21550A

Maleki, A., Niksefat, M., Rahimi, J., and Hajizadeh, Z. (2019a). Design and preparation of Fe3O4@PVA polymer magnetic nanocomposite film and surface coating by sulfoxide via in situ methods and evaluation of its catalytic performance in the synthesis of dihydropyrimidines. BMC Chem. 13:19. doi: 10.1186/s13065-019-0538-2

Maleki, A., and Rahimi, J. (2018). Synthesis of dihydroxyquinozolinone and octahydroquinozolinone and benzimidazoloquinazolinone derivatives catalyzed by an efficiently magnetically recoverable GO-based nanocomposite. J. Porous Mater. 25, 1789–1796. doi: 10.1007/s10934-018-0592-5

Maleki, A., Rahimi, J., Hajizadeh, Z., and Niksefat, M. (2019c). Synthesis and characterization of an acidic nanostructure based on magnetic polyvinyl alcohol as an efficient heterogeneous nanocatalyst for the synthesis of α-aminoalcohols. J. Organomet. Chem. 881, 58–65. doi: 10.1016/j.jorganchem.2018.12.002

Maleki, A., Rahimi, J., and Valadi, K. (2019b). Sulfonated Fe3O4@PVA superparamagnetic nanostructure: design, in-situ preparation, characterization and application in the synthesis of imidazoles as a highly efficient organic-Inorganic Bronsted acid catalyst. Nano Struct. Nano Obj. 18:100264. doi: 10.1016/j.nanoso.2019.100264

Mir, R., Rowshanpour, R., Dempsey, K., Pilkington, M., and Dudding, T. (2019). Selective aerobic oxidation of benzylic alcohols catalyzed by a Dicyclopropenyldiene-Ag(I) complex. J. Org. Chem. 84, 5726–5731. doi: 10.1021/acs.joc.9b00624

Moroz, F., Tang, S. V. Y., Tuna, F., and Lester, E. (2013). Magnetic properties of cobalt oxide nanoparticles synthesised by a continuous hydrothermal method. J. Magn. Magn. Mater. 348, 1–7. doi: 10.1016/j.jmmm.2013.07.064

Narifumi, M., Ono, K., and Murakami, K. (1989). Interaction and structure of PVA-CuII complex: I. Binding of a hydrophobic dye toward PVA-Cu(II) complex. Polymers 30, 1540–1545. doi: 10.1016/0032-3861(89)90230-9

Nozori, R., Tani, A., and Sato, K. (2003). Green oxidation with aqueous hydrogen peroxide. Chem. Commun. 34, 1977–1986. doi: 10.1039/b303160b

Pereira, L. N. S., Ribeiro, C. E. S., Tofanello, A., Costa, J. C. S., de Moura, C. V. R., Garcia, M. A. S., et al. (2019). Gold supported on strontium surface-enriched CuFe2O4 nanoparticles: a strategy for the selective oxidation of benzyl alcohol. J. Braz. Chem. Soc. 30, 1317–1325. doi: 10.21577/1015-0303.20190030

Rahimi, J., Bahrami, N., Niksefat, M., Kamalzare, M., and Maleki, A. (2020a). A novel biodegradable magnetic bionanocomposite based on tannic acid as a biological molecule for selective oxidation of alcohols. Solid State Sci. 110:106284. doi: 10.1016/j.solidstatesciences.2020.106284

Rahimi, J., Tahteri-Ledari, R., Niksefat, M., and Maleki, A. (2020b). Enhanced reduction of nitrobenzene derivatives: Effective strategy executed by

ACKNOWLEDGMENTS

We thank the Research Council of Iran University of Science and Technology for their financial contribution to our study.
Fe$_3$O$_4$/PVA-10% Ag as a versatile hybrid nanocatalyst. Catalysis Commun. 134:105850. doi: 10.1016/j.catcom.2019.105850

Rautiainen, S., Simakova, O., Guo, H., Leino, A.-R., Kordás, K., Murzin, D., et al. (2014). Solvent controlled catalysis: synthesis of aldehyde, acid or ester by selective oxidation of benzyl alcohol with gold nanoparticles on alumina. Appl. Catal. A 485, 202–206. doi: 10.1016/j.apcata.2014.08.003

Ray, R., Chandra, S., Maiti, D., and Lahiri, G. K. (2016). Simple and efficient ruthenium-catalyzed oxidation of primary alcohols with molecular oxygen. Catal. Eur. J. 22, 8814–8822. doi: 10.1002/chem.201601800

Salama, A., Diab, M. A., Abou-Zeid, R. E., Aljohani, H. A., and Shoueir, K. R. (2018). Multifunctional hybrid nanomaterials for sustainable agri-food and ecosystems. Compos. Commun. 7, 7–11. doi: 10.1016/j.coco.2017.11.006

Sasano, Y., Kogure, N., Nagasawa, S., Kasabata, K., and Iwabuchi, Y. (2018). 2-Azaadamantane N-oxyl (AZADO)/Cu catalysis enables chemoselective aerobic oxidation of alcohols containing electron-rich divalent sulfur functionalities. Org. Lett. 20, 6104–6107. doi: 10.1021/acs.orglett.8b02528

Song, Y., Li, Y., Li, J., Li, Y., Niu, S., and Li, N. (2018). Ultrasonic-microwave assisted synthesis of three-dimensional Polyvinyl alcohol carbonate/graphene oxide sponge and studies of surface resistivity and thermal stability. Ultrason. Sonochem. 42, 665–671. doi: 10.1016/j.ultsonch.2017.12.037

Su, F., Mathew, S. C., Lipner, G., Fu, X., Antonietti, M., Blechert, S., et al. (2010). mpg-C3N4-catalyzed selective oxidation of alcohols using O$_2$ and visible light. J. Am. Chem. Soc. 132, 16299–16301. doi: 10.1021/ja102866p

Tadic, M., Nikolic, D., Panjan, M., and Blake, G. R. (2015). Magnetic properties of NiO (nickel oxide) nanoparticles: blocking temperature and neel temperature. J. Alloys Compd. 647, 1061–1068. doi: 10.1016/j.jallcom.2015.06.027

Todaka, Y., Nakamura, M., Hattori, S., Tsuchiya, K., and Umemoto, M. (2003). Synthesis of ferrite nanoparticles by mechanochemical processing using a ball mill. Mater. Trans. 44, 277–284. doi: 10.2320/matertrans.44.277

Valenti, G., Rampazzo, E., Bonacchi, S., Petrizza, L., Marcacci, M., Montalti, M., et al. (2016). Variable doping induces mechanism swapping in electrogenerated chemiluminescence of Ru(bpy)$_3^{2+}$ core–shell silica nanoparticles. J. Am. Chem. Soc. 138, 15935–15942. doi: 10.1021/jacs.6b08239

Verma, S., R., Baj, B. N., Nadagouda, M. N., and Varma, R. S. (2017). Aerobic oxidation of alcohols in visible light on Pd-grafted Ti cluster. Tetrahedron 73, 5577–5580. doi: 10.1016/j.tet.2016.07.070

Yang, C.-C. (2007). Synthesis and characterization of the cross-linked PVA/TiO$_2$ composite polymer membrane for alkaline DMFC. J. Membr. Sci. 288, 51–60. doi: 10.1016/j.memsci.2006.10.048

Yang, X., Shao, C., Guan, H., Li, X., and Gong, J. (2004). Preparation and characterization of ZnO nanofibers by electrosprun PVA/zinc acetate composite fiber as precursor. Inorg. Chem. Commun. 7, 176–178. doi: 10.1016/j.inoche.2003.10.035

Yu, Y., Lu, B., Wang, X., Zhao, J., Wang, X., and Cai, Q. (2010). Highly selective oxidation of benzyl alcohol to benzaldehyde with hydrogen peroxide by biphasic catalysis. Chem. Eng. J. 162, 738–742. doi: 10.1016/j.cej.2010.05.057

Zhan, G., Fan, L., Zhou, S., and Yang, X. (2018). Fabrication of integrated Cu$_2$O@HKUST-1@Au nanocatalysts via galvanic replacements toward alcohols oxidation application. ACS Appl. Mater. Interfaces 10, 35234–35243. doi: 10.1021/acsami.8b12380

Zhu, M., and Diao, G. (2011). Review on the progress in synthesis and application of magnetic carbon nanocomposites. Nanoscale 3, 2748–2767. doi: 10.1039/c1nr10165y

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Copyright © 2020 Rahimi, Niksefat and Maleki. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.