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**REGULAR ARTICLE**

# Green and selective oxidation of alcohols by immobilized Pd onto triazole functionalized $Fe_3O_4$ magnetic nanoparticles

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**Abstract**
Carbonyl compounds were prepared by selective oxidation of alcohols in the presence of recoverable $Fe_3O_4@SiO_2@Pd$ magnetic nanocatalyst in aqueous media as a green solvent. Molecular oxygen served as an oxidant. The catalyst was removed from the reaction media by external magnetic field, washed with methanol, and reused for six more times without any considerable reduction in its reactivity. The chemoselectivity and regioselectivity of the catalyst can serve for selective oxidation of primary alcohols in the presence of secondary ones, and for oxidation of unhindered alcohols in the presence of hindered ones.

**Keywords.** Alcohol oxidation; magnetic nanocatalyst; recyclability; selectivity.

## 1. Introduction

Carbonyl compounds are excellent precursors for the synthesis of molecules with versatile applications in industry, pharmacology and other research work.[1] So, their synthesis from the corresponding alcohols is of paramount importance.[2] Many different ways and reagents such as oxalyl chloride-dimethyl sulfoxide (Swern oxidation),[3] hypervalent iodine[4] and stoichiometric amounts of Cr(VI) salts[5] have been previously reported, but they suffer from many drawbacks such as toxic and hazardous reagents, nonselective alcohol oxidation, noncompliance of atom economy, low yield and high price, as well as serious environmental damages. They also produce a lot of waste, which is not acceptable from the green chemistry point of view. Consequently, the selective oxidation of alcohols to their corresponding carbonyl compounds with molecular oxygen, instead of stoichiometric toxic oxidants in the green medium, has attracted attention of researchers.[6] Catalysts speed up the reactions by reducing the activation energy without being consumed. They are divided into two general groups, heterogeneous and homogenous.[7] Among them, homogenous ones are generally more effective, but the time-consuming separation and expensive recyclability limit their application, especially in industry. Moreover, the final products can be polluted by the homogeneous catalysts. On the contrary, heterogeneous catalysts are non-soluble in reaction media and can be easily removed from the reaction and reused for several times. The heterogeneous catalysts suffer from low yield, which can be attributed to their poorly defined active sites. Therefore, the quality of the surface area of a heterogeneous catalyst determines the availability of catalytic active sites for reactants. To increase the effectiveness of a heterogeneous catalyst, its surface area should be increased, which is possible by using it in nanoscale.[8] Although the collision number increases by using nanoparticles, they have generally high surface energy and are thermodynamically unstable and susceptible to form agglomeration. By using magnetic nanoparticles and coating them with an organic linker, not only this deficiency is obviated, but also the long, tedious filtration or centrifugation removal of nanocatalyst becomes easier by just applying an external magnetic field.[9]

Not all metals are magnetic, but it is possible to couple them with those with magnetic properties directly or through a ligand. Metal leaching is the problem of directly attached metals to magnetic nanoparticles, which is solved by coating the core by organic linkers and anchoring active metals to them.[10] Moreover, it has been shown that the reactivity of a nanomagnetic

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catalyst can be even better than a corresponding homogeneous catalyst.[11]

For oxidation reactions, different metals like Fe,[12] Cu,[13] Co,[14] Bi,[15] and Au[16] have been used as a catalyst, but among them, palladium-based catalysts (both homogeneous and heterogeneous) have shown better activity.[17] For green and selective alcohol oxidation, different metals, oxidants, heterogeneous and homogeneous catalysts have been reported in literature up to now. Among them, the heterogeneous ones have exceeded the homogeneous ones.[18]

In this work, we combined the advantages of eco-friendly molecular oxygen as a green oxidation source, Pd nanomagnetic particles as an efficient catalyst, and water as a green solvent for the selective oxidation of alcohols in mild reaction conditions without any environmentally unfriendly mediator, like 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO).[19]

## 2. Experimental

### 2.1 *General procedure for catalyst preparation*

2.1a *General procedure for preparation of* $Fe_3O_4@SiO_2$: $FeCl_3$ (66.58 mmol) and $FeCl_2$ (31.56 mmol) were dissolved in 40 mL deionized water in an inert atmosphere of argon. Ammonium hydroxide 28% (v/v) was added to the solution to adjust pH=10. The solution was mechanically stirred at room temperature for 20 min until a black suspension was formed. The prepared $Fe_3O_4$ magnetic nanoparticles were filtered, washed, and dried. The powder was then dispersed ultrasonically in ethanol for 20 min. 3 mL of tetraethylorthosilicate (TEOS) was slowly added to the solution. Ammonium hydroxide (3 mL) was added to the solution within 15 min and stirred for 12 h at 40 °C. The silica coated $Fe_3O_4$ magnetic nanoparticles ($Fe_3O_4@SiO_2$) were collected by external magnetic field, washed with methanol and dried under vacuum in a rotary evaporator.[20]

2.1b *Preparation of* $Fe_3O_4@SiO_2@3$*-glycidoxypropyltrimethoxysilane*: 2 g of silica-coated $Fe_3O_4$ was sonicated in toluene for 30 min, and then 11.32 mmol 3-glycidoxypropyltrimethoxy-silane was added and refluxed for 48 h. The prepared catalyst was washed with methanol and dried under vacuum.[20]

2.1c *Preparation of* $Fe_3O_4@SiO_2@triazole@Cu$: $Fe_3O_4@SiO_2@$3-glycidoxypropyltrimethoxysilane (1 g) and 18.2 mmol phenylacetylene were added to the solution of sodium azide (22.7 mmol), copper(II) chloride (0.74 mmol) and sodium ascorbate (0.76 mmol) in THF/water (80/20) for 10 h at 60 °C. The catalyst was removed, washed and dried.[21]

2.1d *Preparation of* $Fe_3O_4@SiO_2@triazole$: To remove Cu from catalyst structure, 1.5 g potassium cyanide was dissolved in $H_2O$/methanol (1/1, 10 mL) and the solution was added to $Fe_3O_4@SiO_2@$triazole@Cu which was synthesized in the previous step and stirred for 5 h at room temperature. The catalyst was then removed by an external magnetic field, washed, and dried in air at room temperature.[21]

2.1e *Preparation of* $Fe_3O_4@SiO_2@triazole@Pd$: Potassium chloride (0.3 g) was dissolved in methanol/water (50/50, 10 mL), and 0.1 g palladium chloride was added to the solution and stirred for 4 h at room temperature. The transparent and clear reddish solution was [$K_2PdCl_4$]. The prepared $Fe_3O_4@SiO_2@$triazole was dispersed and sonicated for 15 min in 10 mL methanol. The [$K_2PdCl_4$] solution was added to that and stirred for 24 h at room temperature. Then, the catalyst was removed by an external magnetic field, washed 2 times with methanol and dried in air at room temperature.[22]

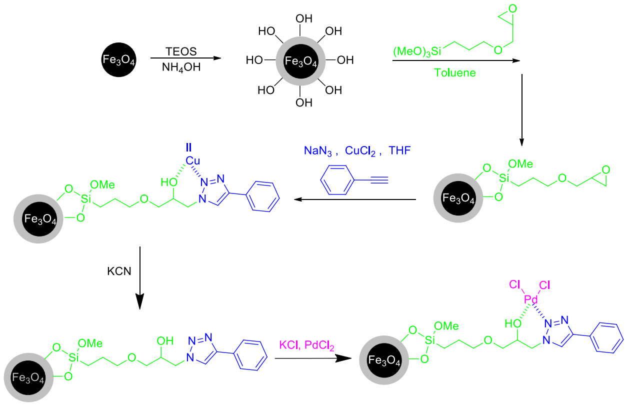
### 2.2 *General procedure for alcohol oxidation*

A mixture of alcohol (1 mmol), $K_2CO_3$ (1 mmol), and catalyst (1 mmol%) in $H_2O$ (5 mL) was prepared in a flask equipped with a condenser. The flask was then filled with pure oxygen and equipped with an oxygen balloon. The mixture was stirred at 80 °C. The progress of the reaction was monitored by thin layer chromatography (TLC) and gas chromatography (GC). After completion of the reaction, the catalyst was separated by an external magnetic field from the reaction media and corresponding carbonyl compounds were extracted with ethyl acetate. To have a complete extraction of products, sodium chloride was added to the mixture and after separation of the aqueous layer, the organic solvent was evaporated by rotary evaporator under reduced pressure. The products were purified by column chromatography or re-crystallization method. The separated catalyst was washed two times with methanol, and dried overnight at room temperature and then used directly for subsequent reaction runs.

## 3. Results and Discussion

### 3.1 *Catalyst synthesis and characterization*

The catalyst $Fe_3O_4@SiO_2@$triazole@Pd was synthesized according to the previously described procedure by the authors (Scheme 1),[19] and its structure was re-characterized by field emission scanning electron microscope (FESEM) (Figure 1), thermal gravimetric analysis (TGA) (Figure 2), Fourier transform infrared spectroscopy (FTIR) (Figure 3), CHN analysis, vibrating sample magnetometery (VSM) (Figure 4) and inductively coupled plasma optical electron spectrometry (ICP-OES).



**Scheme 1.** Catalyst preparation.

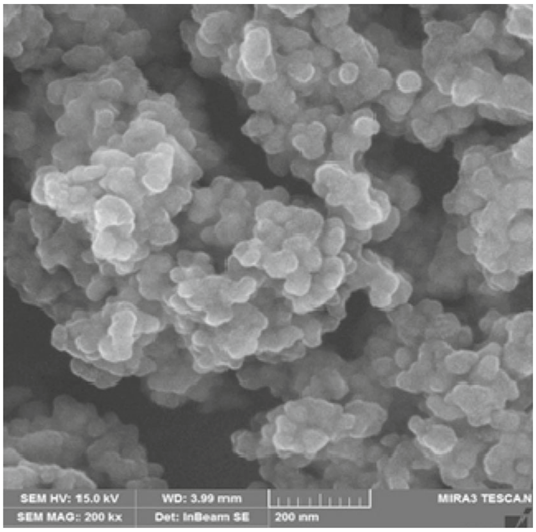


**Figure 1.** FESEM image of the catalyst.

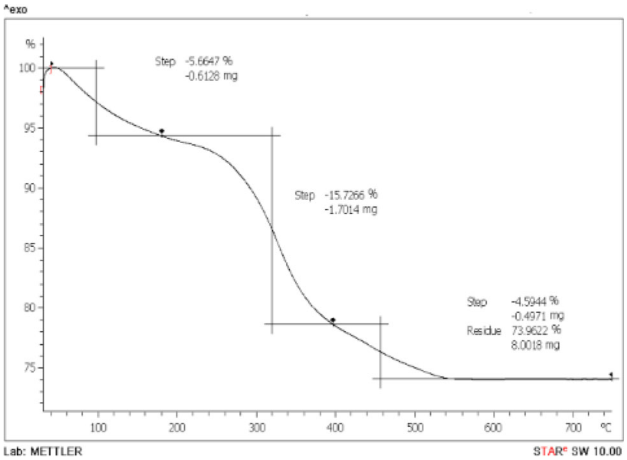


**Figure 2.** TGA of the catalyst.

The catalyst shape and size was confirmed by FESEM. The diameter of the nanoparticles is about 50 nm, and they are approximately spherical (Figure 1).

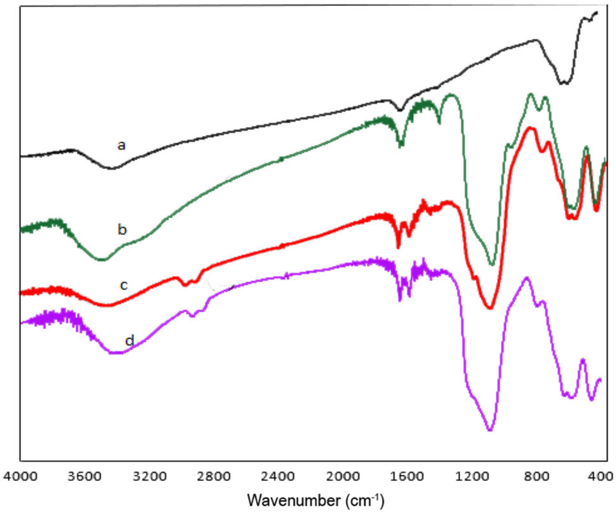


**Figure 3.** FT-IR spectra of the catalyst, (a) $Fe_3O_4$; (b) $Fe_3O_4$@$SiO_2$; (c) $Fe_3O_4$@$SiO_2$@triazole; (d) $Fe_3O_4$@$SiO_2$@triazole@Pd.

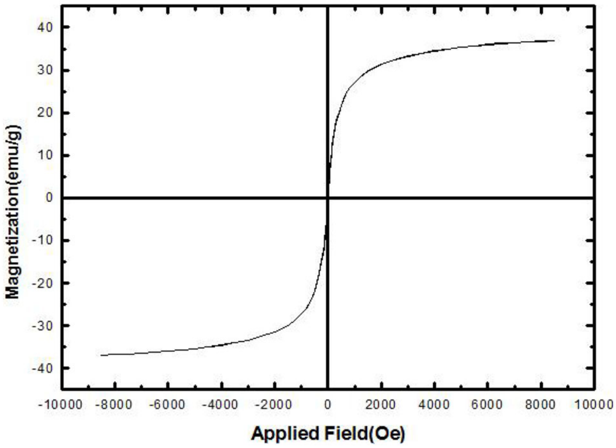
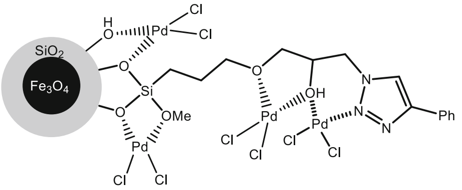


**Figure 4.** VSM of the catalyst.

According to the TGA analysis in Figure 2, adsorbed water in catalyst structure is removed before 200 °C. The catalyst decomposition occurs between about 190 °C and 540 °C, which is equal to *ca*. 21% of the weight of the catalyst and certified the immobilization of organic groups onto the magnetic core. As the catalyst is stable up to *ca*. 200 °C, it can be also used for high-temperature organic reactions.

The FT-IR spectra of the catalyst shows strong absorption bands at 1150 $cm^{-1}$ and 600 $cm^{-1}$, which refer to the Si-O and Fe-O vibrations, respectively (Figure 3). The peaks at 2930 and 2910 $cm^{-1}$ are attributed to C-H stretching vibrations, which confirm the presence of the alkylsilane groups on $Fe_3O_4$@$SiO_2$.

The palladium loading on the catalyst surface was determined by ICP-OES as 1.24 $mmol.g^{-1}$, while the nitrogen content was determined by CHN analysis as



**Scheme 2.** Various possibilities for coordination of Pd atoms.

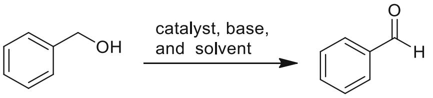
3.00 wt%. This amount of nitrogen corresponds to *ca.* 0.71 mmol.g$^{-1}$$N_3$ moiety. This means that not all the Pd atoms are exclusively coordinated by the nitrogen atoms in the $N_3$ group, as shown in Scheme 1. There are also some other possibilities as shown in Scheme 2. As shown, Pd atoms can also be chelated by oxygen atoms present in the structure. It is also possible that a Pd atom has been coordinated by a nitrogen atom of a particle chain along with a nitrogen or an oxygen atom of another chain.

Anyway, owing to the strong coordination of nitrogen and oxygen groups to palladium, metal loading was relatively high, and leaching during reactions was negligible. Furthermore, palladium black formation, which is generally resulted from palladium nanoparticles agglomeration, was not formed here; so the activity of palladium did not diminish. The magnetic property of the catalyst was measured by a vibrating sample magnetometer (VSM) at room temperature. According to Figure 4, the saturation magnetization of the catalyst is about 38 emu/g with a magnetic field within the range of −9000 to 9000 Oe. This magnetization value is enough for separating the magnetic catalyst from reaction media by an external magnetic field.

### 3.2 *Catalytic experiments*

To find the optimized reaction conditions, oxidation of 1.0 mmol benzyl alcohol was chosen as the model reaction. An oxygen balloon was chosen as an oxidant source. The effect of the catalyst, base and solvent has been investigated (Table 1). As it is shown in Table 1 (Entries 1–3), in the absence of the catalyst, no product was formed after 4 h in 3 different solvents. The addition of the catalyst (0.5 mmol%) changed the yield of the reaction in aqueous media considerably, whereas the reactions in toluene and $H_2O/{}^{t}BuOH$ were not successful (Entries 4–6). By increasing the amount of the catalyst from 0.5 mmol% to 1 mmol%, the reaction yield was increased from 45 to 96% in water (Entries 6 and 9). The same reaction, as in Entry 9, was repeated but in the absence of any base. As shown in Entry 11, it was realized that the presence of a base is necessary. Obviously,

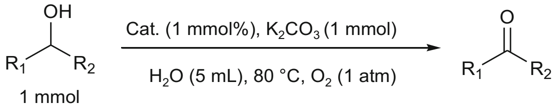
**Table 1.** Optimization of the conditions for the oxidation of benzyl alcohol[a].



| Entry | Base | Solvent | Catal. (mmol%) | Temp. (°C) | Time (h) | Yield[b](%) |
|---|---|---|---|---|---|---|
| **1** | $K_2CO_3$ | Toluene | – | 80 | 4 | Trace |
| **2** | $K_2CO_3$ | $H_2O/{}^{t}BuOH$ | – | 80 | 4 | Trace |
| **3** | $K_2CO_3$ | $H_2O$ | – | 80 | 4 | Trace |
| **4** | $K_2CO_3$ | Toluene | 0. 5 | 80 | 4 | Trace |
| **5** | $K_2CO_3$ | $H_2O/{}^{t}BuOH$ | 0. 5 | 80 | 4 | Trace |
| **6** | $K_2CO_3$ | $H_2O$ | 0. 5 | 80 | 4 | 45 |
| **7** | $K_2CO_3$ | Toluene | 1 | 80 | 4 | Trace |
| **8** | $K_2CO_3$ | $H_2O/{}^{t}BuOH$ | 1 | 80 | 4 | 18 |
| **9** | $K_2CO_3$ | $H_2O$ | 1 | 80 | 4 | 96 |
| **10** | $K_2CO_3$ | $H_2O$ | 0. 5 | 80 | 10 | 65 |
| **11** | – | $H_2O$ | 1 | 80 | 15 | Trace |
| **12** | $Na_2CO_3$ | $H_2O$ | 1 | 80 | 4 | 15 |
| **13** | $K_3PO_4$ | $H_2O$ | 1 | 80 | 4 | 15 |
| [c]**14** | $K_2CO_3$ | $H_2O$ | 1 | 80 | 24 | 60 |
| [d]**15** | $K_2CO_3$ | $H_2O$ | 1 | 80 | 24 | Trace |

[a] reaction conditions: 1 mmol alcohol and 1 mmol base in 5 mL solvent equipped with a balloon of $O_2$ at 80 °C.
[b] GC yields.
[c] in the presence of air as an oxidation source.
[d] in the absence of any oxygen source ($N_2$ bubbling).

**Table 2.** Oxidation of different alcohols using $Fe_3O_4@SiO_2@$triazole@Pd catalyst[a].



| No. | $R_1$ | $R_2$ | Time (h) | Yield (%)[b] | TON | TOF |
|---|---|---|---|---|---|---|
| **1** | $CH_3(CH_2)_6$ | H | 18 | 85 | 850 | 47.2 |
| **2** | $CH_3(CH_2)_4$ | Me | 18 | 83 | 830 | 46.1 |
| **3** | $C_6H_5$ | H | 4 | 96 | 960 | 240 |
| **4** | 4-$ClC_6H_4$ | H | 10 | 93 | 930 | 93 |
| **5** | 2-$ClC_6H_4$ | H | 12 | Trace | – | – |
| **6** | 4-$MeC_6H_4$ | H | 4 | 97 | 970 | 242.5 |
| **7** | 2-$MeC_6H_4$ | H | 10 | 41 | 410 | 41 |
| **8** | 4-$MeOC_6H_4$ | H | 4 | 97 | 970 | 242.5 |
| **9** | 2-$MeOC_6H_4$ | H | 10 | 39 | 390 | 39 |
| **10** | 4-$NO_2C_6H_4$ | H | 24 | 77 | 770 | 32 |
| **11** | 2-$NO_2C_6H_4$ | H | 24 | Trace | – | – |
| **12** | $C_6H_5$ | $C_6H_5$ | 16 | 90 | 900 | 56.25 |
| **13** | $C_6H_5$ | $C_6H_5CO$ | 16 | 85 | 850 | 53.13 |
| **14** | $C_6H_5$ | Me | 10 | 89 | 890 | 89 |
| **15** | $C_6H_5$ | Et | 10 | 85 | 850 | 85 |
| **16** | Cyclohexanol | | 12 | 93 | 930 | 77.5 |
| **17** | Cyclopentanol | | 12 | 90 | 900 | 75 |

[a] reaction conditions: 1 mmol alcohol and 1 mmol $K_2CO_3$ in 5 mL $H_2O$, the balloon of $O_2$.
[b] GC yields.

it seems that $K_2CO_3$ is the most suitable base among the others (compare Entry 9 with 12 and 13).

The reaction with optimum amounts of the ingredients was tested in the air, instead of the oxygen atmosphere. The yield was not desirable, and after 24 h, only 60% benzaldehyde was gained (Table 1, Entry 14). The reaction was also investigated in the nitrogen atmosphere (in the absence of any oxygen source). No product was obtained, which shows that palladium cannot act as the oxidant, solely (Table 1, Entry 15).

According to these data, the best result was obtained when 1 mmol% of $Fe_3O_4@SiO_2@$triazole@Pd catalyst along with 1 mmol of $K_2CO_3$ in water media and oxygen were used (Entry 9).

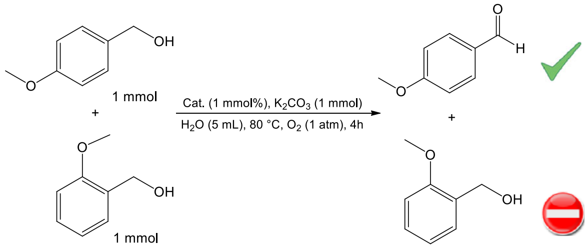
Encouraged by these results, the scope of the reaction was expanded for oxidation of various alcohols. The results have been summarized in Table 2. Different kinds of primary and secondary benzylic alcohols with both electron-withdrawing and electron-donating groups were selectively oxidized to their corresponding carbonyl compounds with excellent yields. The catalyst was also able to oxidize primary and secondary aliphatic alcohols 1-octanol and 2-heptanol to octanal and heptanone, respectively, with good to excellent yield (Table 2, Entries 1 and 2). It is noteworthy to mention that no over-oxidation of primary alcohols to carboxylic acids was observed.

In comparison to benzyl alcohol (as a primary alcohol), 1-phenyl ethanol (as a secondary one) needed more time and gave less yield, obviously due to the steric effects and less activity (Table 2, Entries 3 and 14).

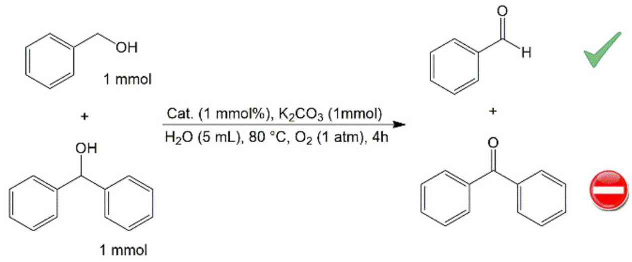
The reaction is substantially dependent on the electron nature of the substituents and their positions. Benzylic alcohols with electron donating groups at 4-position such as 4-methyl and 4-methoxy were oxidized with more yield in shorter reaction times (Table 2, Entries 6 and 8), while benzylic alcohols with electron-withdrawing groups such as 4-nitro need considerably more times (24 h) and afford less yield (77%) (Table 2, Entry 10).

The benzyl alcohols with a substituent at 2-position were substantially less active, because of steric hindrance. 2-Methyl- and 2-methoxybenzyl alcohols were converted to their corresponding aldehydes with only 41 and 39% yield after 10 h (Table 2, Entries 7 and 9). The less reactive 2-chloro and 2-nitrobenzyl alcohols were not oxidized to their corresponding aldehydes.

To show the merit of this restriction, we have investigated the oxidation of 1 mmol of 4-methoxybenzyl alcohol in the presence of 1 mmol of 2-methoxybenzyl alcohol and monitored the progress of the reaction after 2 and 4 h. The only product was 4-methoxybenzaldehyde with 52% and 97% yield, respectively, which shows the selectivity of the catalyst for oxidation of



**Scheme 3.** Selective oxidation of unhindered alcohol versus hindered one.



**Scheme 4.** Selective oxidation of primary alcohol versus secondary one.

unhindered alcohols versus hindered ones (Scheme 3). It is postulated that in the oxidation of alcohols by Pd-species, the reaction proceeds via the formation of a Pd(II)-alcoholate.[17f] As in the $Fe_3O_4$@$SiO_2$ @triazole@Pd catalyst, Pd (II) sites are chelated by several nitrogen/or oxygen atoms, it is understandable that less hindered alcohols react faster than the hindered ones.

In order to examine the chemoselectivity of the catalyst, a mixture of benzhydrol as a secondary alcohol and benzyl alcohol as a primary alcohol was examined according to optimized reaction conditions. No benzophenone was produced, while benzyl alcohol was quantitatively reacted to benzaldehyde. This approves the advantages of this catalyst for selective oxidation of unhindered primary alcohols in the presence of hindered secondary ones (Scheme 4).

### 3.3 *Leaching test*

In the middle of the model reaction, the catalyst was removed from reaction media by a magnet, and the yield of the product was determined by GC as 54%. The reaction was continued for the rest of the time. No change in the yield was observed, which is a confirmation to declare that during the reaction, the palladium species did not leach into the aqueous phase and hence, the catalyst acts as a really heterogeneous catalyst.

### 3.4 *Recovery test*

The separation of the catalyst from the reaction media was very easy. At the end of each reaction, the catalyst was easily removed just by applying an external magnetic field (Figure 5).

The catalyst was washed two times with methanol, dried at room temperature and reused for at least six more times, without any negligible reduction in reactivity (Figure 6).

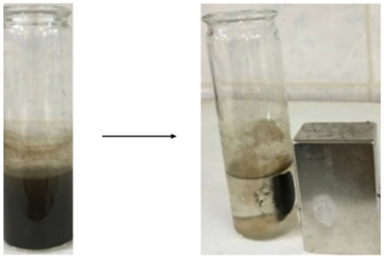


**Figure 5.** Removal of the catalyst with external magnetic field.

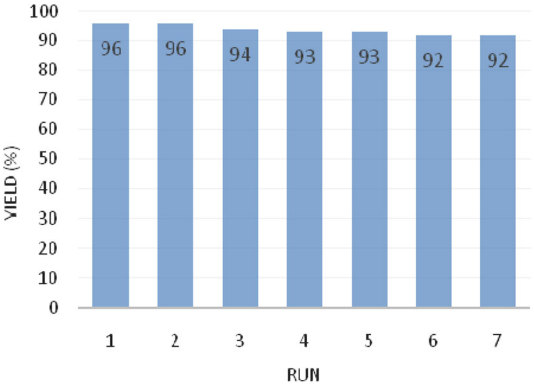


**Figure 6.** Reuse of catalyst in alcohol oxidation reaction.

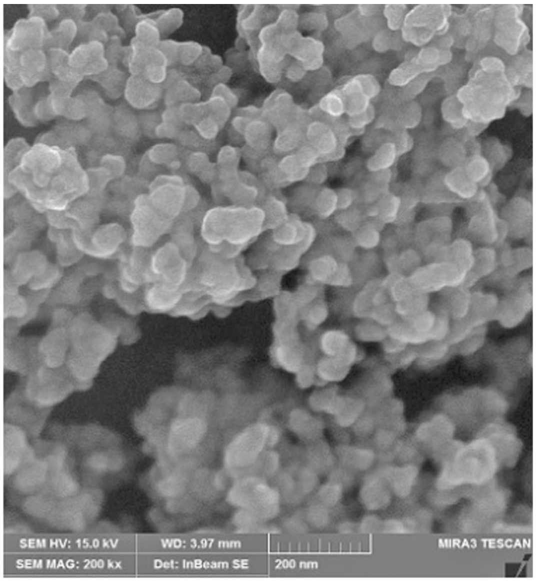


**Figure 7.** FESEM image of the catalyst after recovery.

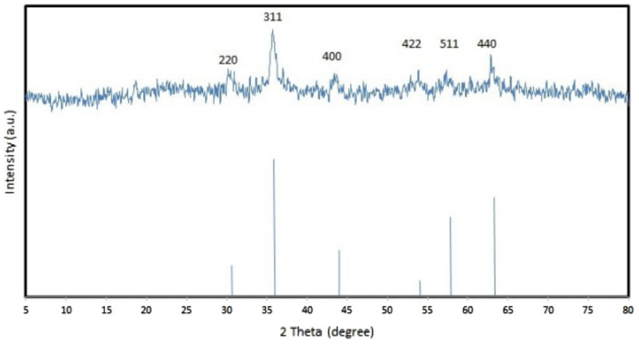


**Figure 8.** X-ray diffraction pattern of the catalyst after recovery.

The Pd content after the 7th run was measured by AAS which showed no significant loss of Pd (1.16 mmol.g$^{-1}$ vs. 1.24 mmol.g$^{-1}$ at the beginning).

The morphology of the recovered catalyst was analysed by FESEM (Figure 7). By comparing Figure 7 with Figure 1, it is clear that the size and the morphology of the particles remained unchanged.

Figure 8 is the powder X-ray diffraction pattern of the recovered catalyst, in the range of $2\theta$ from 5 to 80 degrees. The diffraction pattern corresponds quite well to the $Fe_3O_4/SiO_2$ sample previously reported, which means that the structure of the catalyst is unchanged.[30]

### 3.5 *Comparison of the effectiveness of the catalyst*

A comparison between the present catalyst and other catalysts for alcohols oxidation has been done and the results are shown in Table 3. It is obvious that our catalyst is comparatively good for selective oxidation of alcohols to their corresponding carbonyl compounds, in the presence of molecular oxygen as an oxidant, water as a green media, and in shorter reaction time.

The turnover frequency (TOF) and turnover number (TON) of the catalyst have been compared to some

**Table 3.** Comparison of different catalysts in the oxidation of benzyl alcohol.

| No. | Catal. | Solvent | Time (h) | Temp. (°C) | Yield (%) | Oxidant | Ref. |
|---|---|---|---|---|---|---|---|
| **1** | A | $H_2O$ | 4 | 80 | 96 | $O_2$ | This work |
| **2** | B | Toluene | 1 | rt | 99 | $O_2$ | 23 |
| **3** | C | Free | 1.5 | 50 | 85 | $O_2$ | 24 |
| **4** | D | $PhCF_3$ | 8 | rt | 100 | air | 12 |
| **5** | E | $H_2O$ | 0.33 | 50 | 91 | $H_2O_2$ | 25 |
| **6** | F | Toluene | 3.5 | 80 | 99 | $O_2$ | 26 |
| **7** | F | Toluene | 5.5 | 80 | 99 | air | 26 |
| **8** | G | Toluene | 12 | 80 | 80 | air | 25 |
| **9** | H | $H_2O$ | 4 | 50 | 100 | $O_2$ | 27 |

A: 1 mol% $Fe_3O_4$@ $SiO_2$@triazole@ Pd.
B: 0.4 mol% Au@periodic mesoporous organosilica.
C: 0.06 g $Fe_3O_4$/Cys-Pd.
D: 0.5 mmol $NaNO_2$, 0.5 mmol $FeCl_3{\cdot}6H_2O$, 0.2 mmol TEMPO.
E: 10 mol% $Fe_3O_4$.
F: 0.4 mol% Pd@SBA-15.
G: 10 mol% $Fe_3O_4$.
H: 0.2 mol% nanopartice-TEMPO.

**Table 4.** The Comparison of TON and TOF of different catalysts in the oxidation of benzyl alcohol.

| No. | Catal. | Time (h) | Temp. (°C) | oxidant | TON | TOF | Ref. |
|---|---|---|---|---|---|---|---|
| 1 | A | 5 | 80 | $O_2$ | 960 | 240 | This work |
| 2 | C | 1.5 | 50 | $O_2$ | 480 | 320 | 24 |
| 3 | I | 6 | 80 | $H_2O_2$ | 720 | 120 | 28 |
| 4 | J | 2.5 | 39 | NMMN | 445 | 178 | 29 |

A: 1 mol% $Fe_3O_4$@ $SiO_2$@triazole@ Pd.
C: 0.06 g $Fe_3O_4/$Cys-Pd.
I: 25 mmol% nano-$Fe_3O_4$_Pd.
J: 2 mmol% palladium triphenylphosphine complexes containing N-(2-pyridyl)–N-(salicylidene) hydrazine; NMMN: N-methyl morpholine N-oxide.

of the similar catalysts in literature. The data have been summarized in Table 4, which show an acceptable TON and TOF for benzyl alcohol oxidation by the $Fe_3O_4$@$SiO_2$@Triazole@Pd versus other mentioned catalysts.

## 4. Conclusions

In this work, we synthesized carbonyl compounds by selective oxidation of alcohols in the presence of recoverable $Fe_3O_4$@$SiO_2$@Triazole@Pd magnetic nanocatalyst in aqueous media as a green solvent. Molecular oxygen served as an oxidant. The absence of mediators like 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and eco-unfriendly oxidizing agents and toxic and hazardous organic solvents make this method more precious. The catalyst was removed from the reaction media by a magnetic field, washed with methanol, and reused for at least six more times without any considerable reduction in its reactivity. The notable features and major advantages are ease of catalyst preparation, recyclability and reusability for several times, operational simplicity, and easy work-up procedure. The chemoselectivity and regioselectivity of the catalyst can serve for selective oxidation of primary alcohols in the presence of secondary ones, and for the oxidation of unhindered alcohols in the presence of hindered ones.

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