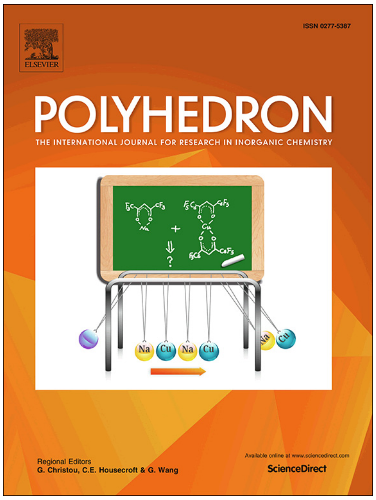

Synthesis of Fe_3O_4@Sio_2/Isoniazid/Cu(II) magnetic nanocatalyst as a recyclable catalyst for a highly efficient preparation of quinolines in moderate conditions

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Highlighted Revised Manuscript

Synthesis of Fe_3O_4@Sio_2/Isoniazid/Cu(II) magnetic nanocatalyst as a recyclable catalyst for a highly efficient preparation of quinolines in moderate conditions

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Abstract

This paper reports the investigation on an efficient procedure to prepare Fe_3O_4@SiO_2/Isoniazid/Cu(II) as a recoverable magnetic nanocatalyst. The prepared nanocatalyst, Fe_3O_4@SiO_2/Isoniazid/Cu(II), was identified via vibrating sample magnetometer (VSM), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), thermogravimetric analysis (TGA), x-ray powder diffraction (XRD) and Fourier transform infrared (FT-IR). The nanocatalyst was applied on Friedländer synthesis for highly efficient preparation of quinoline derivatives from α-methylene ketones and 2-aminoaryl ketones under moderate conditions. This method has the advantages of short reaction times, good yields as well as simple catalyst separation by external magnet and solution decanting to recover the catalyst for next cycles, with ability to be used for 4 times without significant loss in catalytic activity.

Key words: Heterogeneous nanocatalysts; Isoniazid/Cu(II); Friedländer synthesis; Quinolines

1. Introduction

Over the past few years, the application of heterogeneous catalysts in various organic transformations has proved strategically essential and eco-friendly. Owing to the solubility in reaction media, homogeneous catalysts display better catalytic activities in chemical reactions than their heterogeneous peers, increasing the availability of catalytic active sites for the substrate and consequently easing the reaction [1]. Nonetheless, the serious issues related to separating the homogeneous catalysts have limited their use in industry. Therefore, it is necessary to develop efficient, easy, and appropriate methods for the preparation of a wide range of organic compounds under heterogeneous catalytic conditions.

Among various types of heterogeneous catalysts, Fe_3O_4 magnetic nanoparticles have been greatly favored owing to the fact that they are simply synthesized and surface modified and can be recovered from the reaction mixture using a magnet. Therefore, various catalysts such as metals and polymers can be supported on Fe_3O_4 nanoparticles because they can be easily separated out after being employed in the reaction several consecutive times [2-6]. However, the use of magnetic particles alone causes aggregation, changing the surface and catalytic activity, hence the necessity of a suitable covering to elude such restrictions [7]. Lately, core-shell magnetic nanomaterials, as efficient magnetic nanocatalysts, have gained much research attention; these nanomaterials incorporate features of magnetic cores and diverse functional shells for various uses and have the following advantages: useful and efficient applications in medicine [8, 9], high stability [10], comfortable surface modification [11, 12], optical properties [13], and environmental friendly [14]. The Fe_3O_4 magnetic core–shell structure is reported in the literature as a heterogeneous nanocatalyst for the synthesis of organic compounds [15, 16].

Today, silica is among the materials which is widely used for the shell and increases its stability. Additionally, the surface hydroxyl functional groups (-OH) of silica provide an active surface, simplifying the linkage of other organic functional groups for chemically modifying the surface. This method has been successfully used to immobilize a broad variety of catalysts such as organocatalysts, transition metal catalysts, and biocatalysts [17-20].

Heterocyclic compounds are the biggest and most diverse organic compounds in nature, widely applied in pharmaceutical chemistry owing to their unique chemical properties [21]. Among the significant heterocyclic aromatic compounds, quinoline derivatives are reported in different studies due to their unique medicinal properties and potential biological activities [22]. A reported reaction is Friedländer which involves the reaction between ketones or 2-aminoaryl aldehydes with carbonyl compounds, capable of enolization in the presence of an acidic catalyst [23, 24]. Nowadays, there exist several methods for the synthesis of heterocyclic compounds such as chitosan-SO_3H [25], PEG-OSO_3H [26], $HClO_4$-SiO_2 [26], CF_3COOH [27], SBA-15/propyl-SO_3H [28], $NaHSO_4$/silica-gel [29] and HO_3SO-SiO_2 [30, 31]. Although most of these procedures are of significance, many have one or more of the following disadvantages: difficulty in separating the nanocatalyst, time-consuming reaction workup, and costly reaction conditions.

Accordingly, it is important to provide an efficient synthesis method that can cover the drawbacks of previous methods.

In this research, efforts were made to synthesize and characterize a new heterogeneous Cu nanocatalyst (Fe_3O_4@SiO_2/ISN/Cu(II)) to prepare quinoline derivatives. The Fe_3O_4@SiO_2/ISN/Cu(II) catalyst was synthesized via decorating Cu(II) ions onto Fe_3O_4@SiO_2 nanoparticles. The catalyst was easily separated by an external magnet with no significant decrease in catalytic activity, and was reused 4 times without a considerable reduction in the yield of quinolines produced.

2. Experimental

2.1 Materials and Methods

Isoniazid, as a pharmaceutical grade material, was purchased from the DarouPakhsh Pharmaceutical Company Tehran, Iran. $FeCl_3\cdot6H_2O$, $FeCl_2\cdot4H_2O$, $Cu(OAc)_2$, TEOS (tetraethyl orthosilicate), CPTES (3-Chloropropyltriethoxysilane), and aryl halides were obtained from Merck. Other reagents and solvents used in this investigation were obtained from Sigma Aldrich, Fluka or Merck Chemicals. All chemicals and solvents were used as received, without prior purification.

Melting points were determined by a Stuart SMP_3 melting point instrument. The Fourier transform infrared (FT-IR) spectra were recorded with a Shimadzu, IR Prestige 21 spectrometer in the range of 400-4000 cm^{-1}. Nanocatalysts were characterized using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) (Holland Philips XL300), transmission electron microscopy (TEM) (Holland Phillips CM10), x-ray powder diffraction (XRD) (Holland Philips PW-1840), and vibrating sample magnetometer (VSM) (Meghnatis Daghigh Kavir Co., Iran).

2.2 Preparation of Fe_3O_4 and Fe_3O_4@SiO_2 magnetic nanostructures

Fe_3O_4 and Fe_3O_4@SiO_2 nanostructures were synthesized according to the reported methods [32]. For this purpose, 3g of $FeCl_3.6H_2O$ and 1g of $FeCl_2.4H_2O$ salts were poured into the round-bottom flask; then, 120 mL water was added and stirring was applied vigorously for a complete dissolution. The concentrated NH_3 (28%) solution was then added to reach a solution pH of 11. The solution under N_2 atmosphere at 60 °C was stirred vigorously for one hour. The black precipitate was decanted by a magnet, washed with distilled water several times, and dried at 50 °C in an oven for 24 hours. In order to prepare Fe_3O_4@SiO_2 nanostructures, 1 gr of Fe_3O_4 nanoparticles was dispersed by ultrasound in isopropyl alcohol/water solvent; next, 1.0 mL tetraethyl orthosilicate (TEOS) and 4.80 mL NH_3 (28%) were added to the solution at ambient temperature under vigorous stirring. The final product was separated by a magnet and washed several times with distilled H_2O/EtOH to remove impurities. The product was dried at 50 °C and stored for the next step.

2.3 Synthesis of the Fe_3O_4@SiO_2/Isoniazid/Cu(II)

0.5 g of Fe_3O_4@SiO_2 nanostructure was dispersed by ultrasonic bath in toluene solvent; after that, 0.6 mL of 3-Chloropropyltriethoxysilane (CPTES) was added to the mixture and stirred vigorously at 100 ºC for 48 hours. The precipitate (Fe_3O_4@SiO_2-pr-Cl) was separated by a magnet that was washed several times with EtOH and dried at 60 °C in an oven for 48 hours. Next, 0.5 g of Fe_3O_4@SiO_2-pr-Cl nanoparticle was dispersed by ultrasonic bath in toluene solvent, and 2 mmol of isoniazid ligand was added. This mixture was stirred vigorously under nitrogen atmosphere at 80 °C for 24 hours. The precipitate was collected by a magnet, and washed several times with ethanol/water, dried at 40°C for 48 hours. To preparation of Fe_3O_4@SiO_2/isoniazid, 0.5g of it was dispersed by ultrasonic bath in acetonitrile. Then, 50 mg of $Cu(OAc)_2$ salt was added to the reaction mixture and stirring was applied vigorously at 50 °C for 10 hours. The product (Fe_3O_4@SiO_2/Isoniazid/Cu(II)) was separated by a magnet that was washed several times with distilled H_2O and EtOH to remove impurities; the product was dried at 50°C for 24 hours. Scheme 1, represents the synthetic trend of Fe_3O_4@SiO_2/Isoniazid/Cu(II).

2.4 Preparation of quinolines

1.2 mmol α-CH-acid, 1.0 mmol 2-aminoaryl ketone, and 0.07 g nanocatalyst were poured in a bottom round flask containing ethanol solvent, and were heated and vigorously stirred until the end of the reaction. Once the reaction was completed, understood via TLC technique, the nanocatalyst was decanted from the reaction mixture by a magnet, which was then washed with EtOH (about 5 mL). The final product was recrystallized by ethanol and stored for characterization. All products were known compounds characterized by their M.p. which was compared with literature reports.

3. Results and discussion

3.1 Characterization of $Fe_3O_4@SiO_2$/ISN/Cu(II) nanocatalyst

3.1.1 FT-IR

FT-IR technique was applied to confirm the immobilization and coating of silica and other functionalized molecules. Fig. 1 shows the FT-IR spectra of Fe_3O_4 magnetic nanoparticles (MNPs), $Fe_3O_4@SiO_2$/ISN core-shell MNPs and $Fe_3O_4@SiO_2$/ISN/Cu(II) MNPs. In Fig. 1a (FT-IR of Fe_3O_4), the bond at 562 cm^{-1} is attributed to the vibration of Fe-O band, while the band at 3410 cm^{-1} is related to the symmetrical and asymmetrical stretching vibration of hydroxyl groups (─OHs) [33], indicating the presence of some amount of ferric hydroxide in Fe_3O_4. The band at 1620 cm^{-1} is ascribed to the bending vibration of the adsorbed water. Fig. 1b displays the FT-IR spectrum of $Fe_3O_4@SiO_2$/ISN core-shell MNPs and shows some new absorption peaks in comparison with Fig.1a. The sharp peak at 1079 cm^{-1} is attributed to the stretching vibration bands of Si–O–Si, while the band at 959 cm^{-1} is assigned to the bending vibration of the silanol group (Si–OH) [34]. The characteristic peaks of C-H bonds are seen at 2941 and 2861 cm^{-1} which can be attributed to symmetric and antisymmetric stretch of CH_2 groups. The primer of isoniazid groups to the surface of $Fe_3O_4@SiO_2$ MNPs is verified through the bands at 1619, 3016 and 1399 cm^{-1} assigned respectively to the C=C, aryl C-H stretches and C-N stretching of amine. The observations indicated which isoniazid molecules as acceptor ligand were successfully attached to the silica shell. Meanwhile, after coordination of nanocomposites with Cu(II) intensity of 1619 and 1399 cm^{-1} peaks decreases that can be ascribed to the bonding interactions between the functional groups of the nanocomposites and the Cu(II). Every band reveals that the exterior of Fe_3O_4 nanoparticles have successfully been modified with isoniazide groups for the metal-ligand coordination.

3.1.2 XRD

The XRD pattern of $Fe_3O_4@SiO_2$/ISN/Cu(II) is illustrated in Fig. 2. A strong characteristic diffraction was detected in the sample at 2θ of 30.12°, 35.69°, 43.39°, 54.14°, 58.02° and 63.94° corresponding to the diffraction of (220), (311), (400), (422), (511), and (440) of the Fe_3O_4, implying that the modified nanoparticles were synthesized successfully without damaging the crystal structure of Fe_3O_4 core. The silica coating and functionalization with CPTES and

Isoniazid (Fe_3O_4@SiO_2/ISN/Cu(II)) showed the peak at 2Ө = 16–26°, which can be due to the presence of non-crystalline SiO_2. The presence of a broad peak is in agreement with the amorphous structure of silica layer [35].

3.1.3 VSM

The magnetic properties of Fe_3O_4@SiO_2/ISN/Cu(II) prepared nanocatalyst was measured by VSM at ambient temperature (Fig. 3). Saturation magnetization of bare Fe_3O_4 nanoparticles was reported [34] as 61.8 emu g^{-1}, and the saturation magnetization of the prepared catalyst in the present study was 48.2 emu g^{-1} (Fig. 3). These results indicate that the magnetization properties of bare Fe_3O_4 decrease when modified using Cu^{+2} and the silica groups. This result demonstrated that the prepared catalyst has good magnetic properties. Thus, the aforementioned evidence suggested a simple and effective method of dispersing and recycling the procured catalyst form the solution by an external magnetic force.

3.1.4 TGA

The thermogravimetric analysis (TGA) of Fe_3O_4@SiO_2/ISN/Cu(II) prepared nanocatalyst is shown in Fig. 4. The weight loss at about 150 °C is due to the solvent adsorbed on the surface and inside of structures. The decomposition temperature of the organic compounds (ligand and propyl) in the sample started at about 180°C and continued up to 600 °C. The organic molecules were full decomposed at temperatures higher than 600 °C and the residual weight of Fe_3O_4@SiO_2/ISN/Cu(II) was 90%. In other words, it can be concluded that 5% of organic molecules was immobilized on the surface of Fe_3O_4@SiO_2/ISN/Cu(II). These results showed which isoniazid and chloro propyl successfully immobilized Fe_3O_4@SiO_2, indicating that the prepared catalyst has a good thermal stability which can be used in the reactions at high temperatures.

3.1.5 TEM, SEM and EDX

TEM and FESEM images were taken to determine the size and morphology of the prepared hybrid organic-inorganic nanocatalyst (Fe_3O_4@SiO_2/ISN/Cu(II)). TEM was used to observe the morphology of Fe_3O_4@SiO_2/ISN/Cu(II) catalyst. Fig. 5a shows that NPs have a core‒shell structure with a distinct contrast between silica shells and Fe_3O_4 cores, implying that silica shells (Fe_3O_4@SiO_2) successfully coated the hydrophilic Fe_3O_4 NPs, seen as a bright gray area around the Fe_3O_4 dark core. This revealed that the true core-shell morphology was grafted on isoniazid functionalized Fe_3O_4@SiO_2 NPs. The TEM image of the Fe_3O_4@SiO_2/ISN/Cu(II) nanocatalyst revealed that Cu(II), with a nearly spherical morphology, was formed on the surface of the modified Fe_3O_4 nanoparticles with amino groups as organic shell. In the TEM images, the average size of the Fe_3O_4 nanoparticles was approximately 10 to 20 nm, and that of Fe_3O_4@SiO_2 was 20 to 30 nm. In addition, the FESEM image of the nanocatalyst showed that they are spherical and mono-disperse. However, some particle aggregations were observed in the catalyst due to the magnetic attraction between the particles (Fig. 5b). Furthermore, the energy-dispersive x-ray spectroscopy (EDX) analysis of the nanocatalyst demonstrated the expected elements, namely Cu, C, N, Si, Fe, and O; the spectrum and data are indicated in Fig. 6 and Table 1.

3.2. Evaluation of Fe_3O_4@SiO_2/ISN/Cu(II) in the preparation of quinolines

The reaction of 2-amino-5-chlorobenzophenone and acetylacetone was selected to optimize reaction conditions such as nanocatalyst dosage, solvent and temperature. First, different amounts of the nanocatalyst (0.02, 0.05, 0.07 and 0.1 g) were optimized for a predefined reaction time of 2 hours at 60°C (Table 2, entries 1-4). The obtained results displayed the most optimal yield (95%) obtained with a nanocatalyst amount of 0.07 g. In the next step, the model reaction at various temperatures (r.t, 60 and 80°C) were optimized (Table 2, entries 5 and 6). With the increase in temperature, the reaction rate was increased. A good yield of 95% was observed at 60°C for 2 hours of reaction time; furthermore, the best results were obtained when ethanol was used as reaction solvent. Further work indicated that the best results were obtained when the reaction was carried out at 60°C, for 2 h in ethanol. Further observed was that Fe_3O_4@SiO_2/ISN/Cu(II) showed higher catalytic activity compared with the corresponding homogenous Fe_3O_4. In the optimized condition, different derivatives of quinolines were prepared using different types of cyclic and noncyclic α-methylene ketones. The results are summarized in Table 3. Good yields were observed in all derivatives, corroborating the strength of the preparation method. As shown in Table 3, chloro and without substituents on the amino aryl ketones did not show evident effects in terms of yields. However, the use of cyclohexanone reduced the yield (Table 3, entry 10). As demonstrated in Fig. 7, the nanocatalyst was successfully and efficiently recycled 4 times with 24% activity loss.

4. Conclusions

In this research, the synthesis of new nanocatalyst (Fe_3O_4@SiO_2/ISN/Cu(II)) via functionalization of silica-coated magnetic nanoparticles with $Cu(OAc)_2$ was reported. To investigate the structure and bonding of the synthesized nanocatalyst, TEM, FESEM, VSM, TGA, XRD, EDS, and FT-IR techniques were applied. The core-shell nanoparticles were stable, reusable, non-toxic and inexpensive heterogeneous nanocatalyst with great potential applications in organic syntheses. The new nanocatalyst was used for the synthesis of quinoline derivatives via Friedländer synthesis from α-methylene ketones and 2-aminoaryl ketones with excellent yields and short times. Furthermore, the advantages of the introduced nanocatalyst are good catalytic activity, easy separation by an external magnet, and good reusability for quinolines preparation via Friedländer synthesis. The proposed nanocatalyst was also successfully applied for the synthesis of quinoline derivatives via Friedländer synthesis with a reusability of 4 times with a relatively low reduction in catalytic activity of 24%.

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Figure and scheme captions:

Scheme 1. Schematic diagram of Fe_3O_4@SiO_2/ISN/Cu(II) nanocatalyst preparation.

Fig. 1. FT-IR spectra of (a) Fe_3O_4, (b)Fe_3O_4@SiO_2/ISN and (c) Fe_3O_4@SiO_2/ISN/Cu(II).

Fig. 2. XRD patterns of Fe_3O_4@SiO_2/ISN/Cu(II) prepared nanocatalyst.

Fig. 3. VSM of $Fe_3O_4@SiO_2$/ISN/Cu(II) prepared nanocatalyst.

Fig. 4. TGA of $Fe_3O_4@SiO_2$/ISN/Cu(II) prepared nanocatalyst.

Fig. 5. TEM (a) and SEM (b) images of $Fe_3O_4@SiO_2$/ISN/Cu(II).

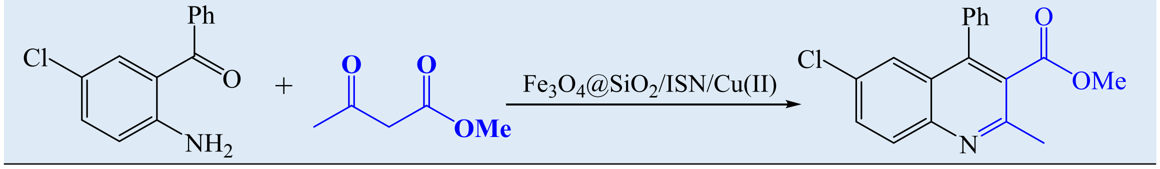
Fig. 6. EDX spectrum of $Fe_3O_4@SiO_2$/ISN/Cu(II) MNPs.

Fig. 7. Reusability of the catalyst for the synthesis of quinolines.

Table 1. EDX data of $Fe_3O_4@SiO_2$/ISN/Cu(II) MNPs (Wt %)

Sample	C (%)	O (%)	Si (%)	N (%)	Fe (%)	Cu (%)	Total (%)
$Fe_3O_4@SiO_2$/ISN/Cu(II)	27.03	46.18	17.75	3.69	5.09	0.26	100

Table 2. Optimization of amount of catalyst and temperature of reaction [a]

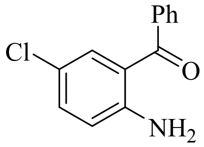
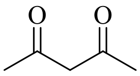
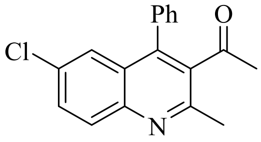


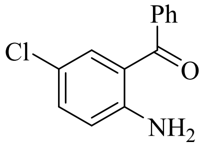
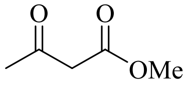
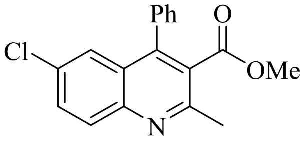
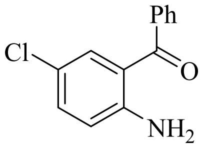
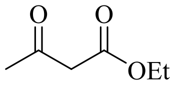
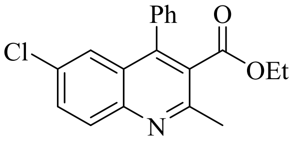
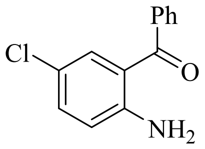
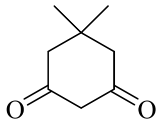
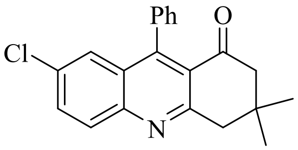
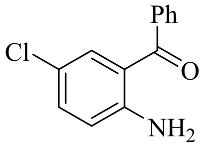
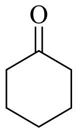
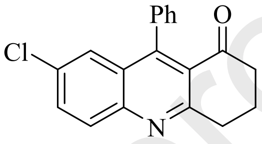
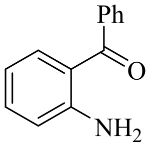
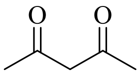
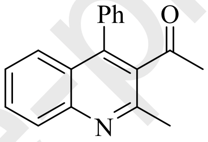
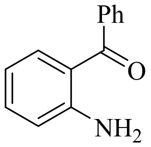
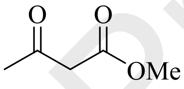
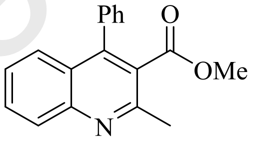
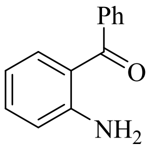
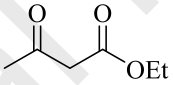
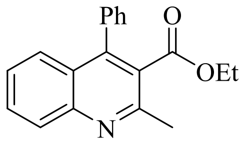
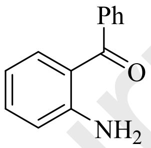
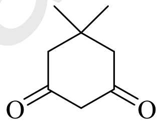
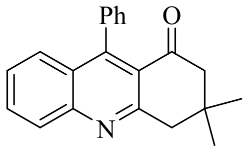
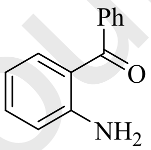
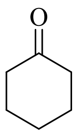
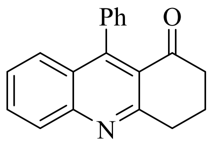
Entry	Catalyst (mg)	Temperature (°C)	Time (h)	Yield (%) [b]
1	0.02	60	2	46
2	0.05	60	2	69
3	**0.07**	**60**	**2**	**95**
4	0.1	60	2	95
5	0.07	r.t	2	70
6	0.07	80	2	76

[a] Reaction conditions: acetylaceton (1.2 mmol), 2-aminoaryl ketone (1 mmol), and the nanocatalyst.

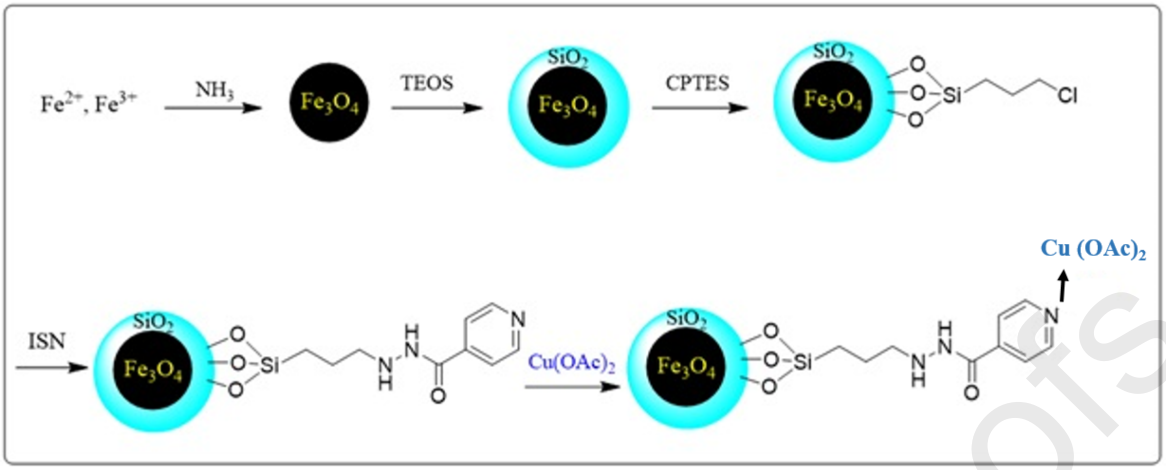
[b] Isolated yields.

Table 3. Synthesis of quinoline derivatives through Friedländer synthesis by Fe_3O_4@SiO_2/ISN/Cu(II) catalyst**.**

Entry	Amino aryl ketone	Ketone	Product	Yield[b]	Mp°C
1				96	152

2				90	134
3				92	107
4				95	210
5				95	161
6				94	113
7				87	105
8				91	100
9				93	192
10				68	139

[a] Conditions: acetylaceton deravatives (1.2 mmol) aminoaryl deravatives (1 mmol), and the nanocatalyst.
[b] Yields isolated product.



Scheme 1.

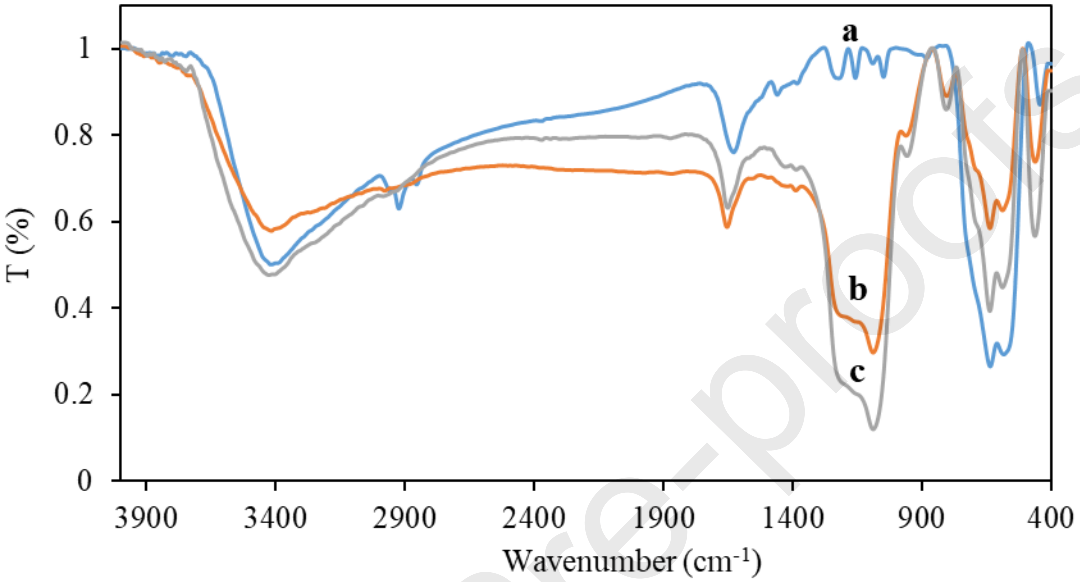

a
b
c
T (%)
1
0.8
0.6
0.4
0.2
0
3900
3400
2900
2400
1900
1400
900
400
Wavenumber (cm-1)

Fig. 1.

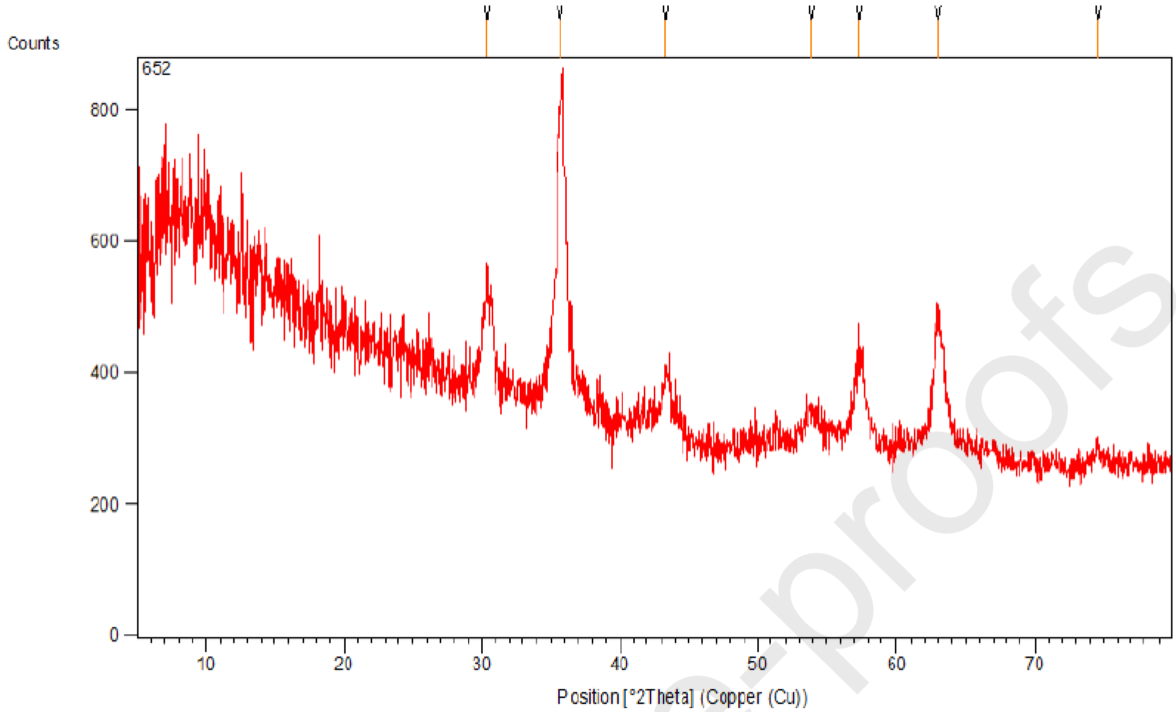

Counts
652
800
600
400
200
0
10
20
30
40
50
60
70
Position [°2Theta] (Copper (Cu))

Fig. 2.

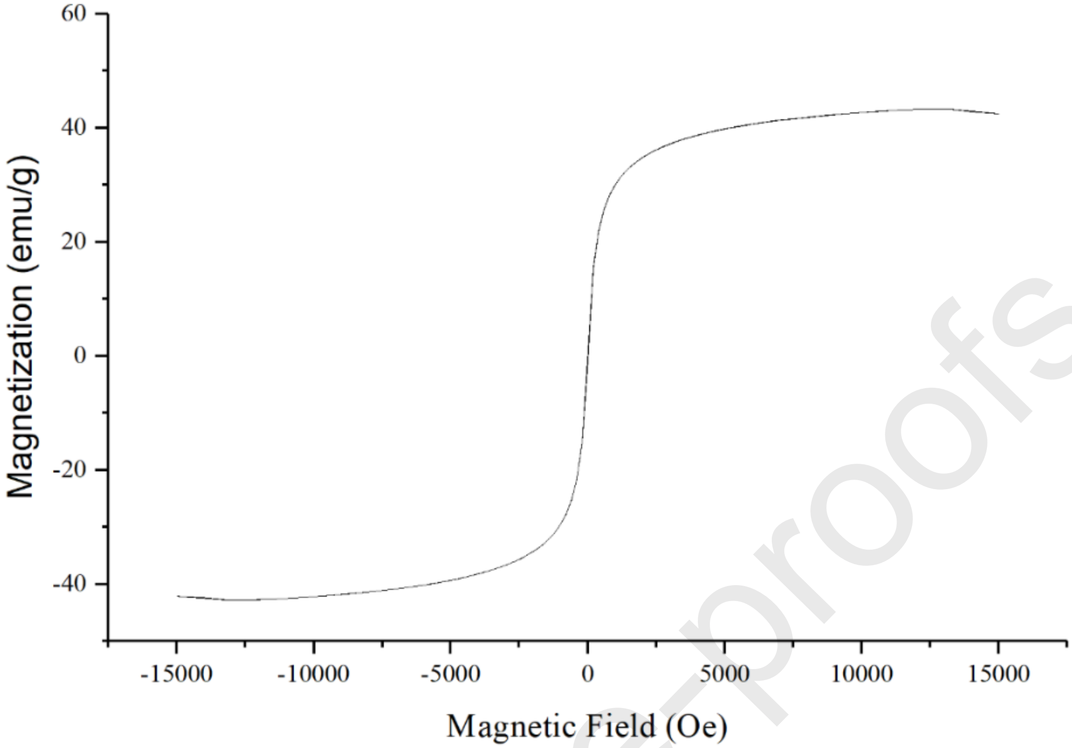

Magnetization (emu/g)
60
40
20
0
-20
-40
-15000
-10000
-5000
0
5000
10000
15000
Magnetic Field (Oe)

Fig. 3.

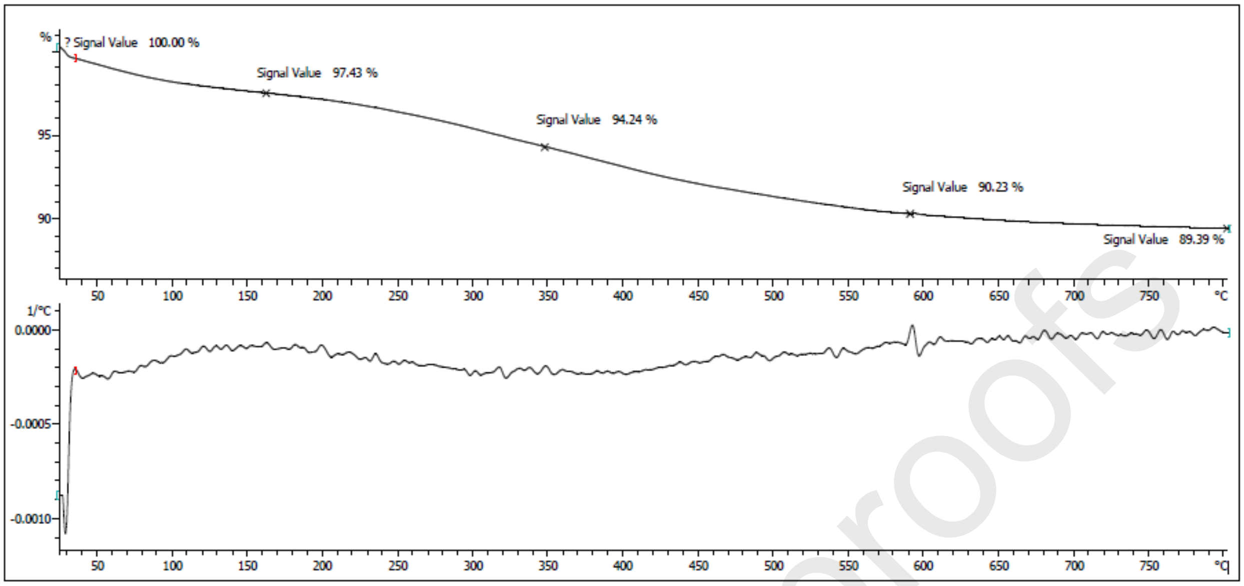

%
? Signal Value 100.00 %
Signal Value 97.43 %
Signal Value 94.24 %
Signal Value 90.23 %
Signal Value 89.39 %
95
90
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
°C
1/°C
0.0000
-0.0005
-0.0010

Fig. 4.

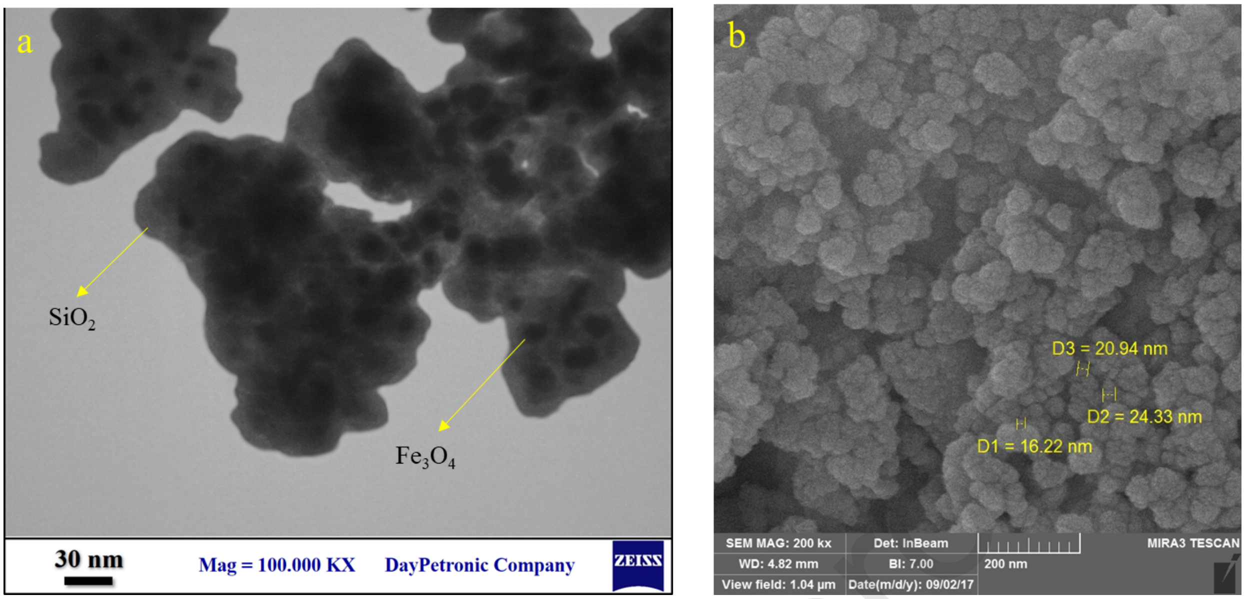

a
SiO2
Fe3O4
30 nm
Mag = 100.000 KX
DayPetronic Company
b
D3 = 20.94 nm
D2 = 24.33 nm
D1 = 16.22 nm
SEM MAG: 200 kx
Det: InBeam
WD: 4.82 mm
BI: 7.00
View field: 1.04 μm
Date(m/d/y): 09/02/17
200 nm
MIRA3 TESCAN

Fig. 5.

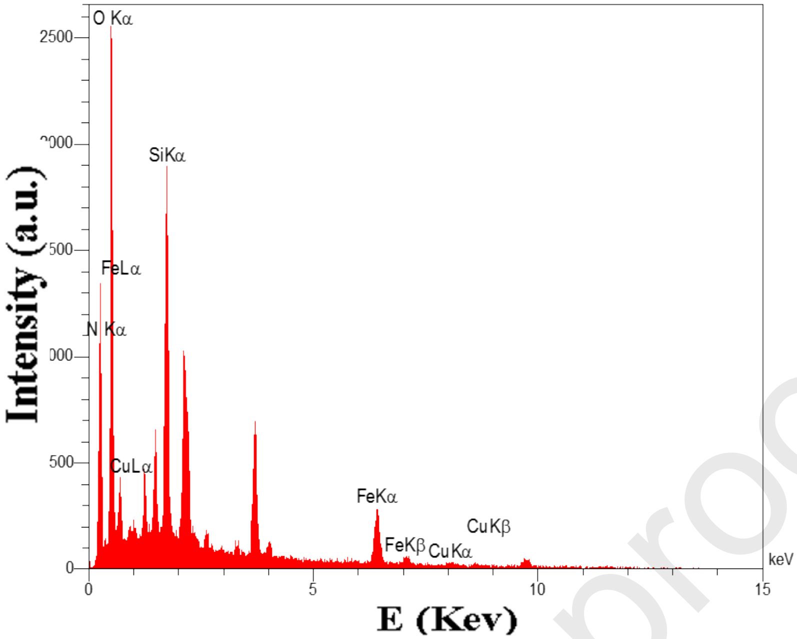

O Kα
SiKα
FeLα
N Kα
CuLα
FeKα
FeKβ
CuKα
CuKβ
2500
2000
1500
1000
500
0
0
5
10
15
keV
Intensity (a.u.)
E (Kev)

Fig. 6.

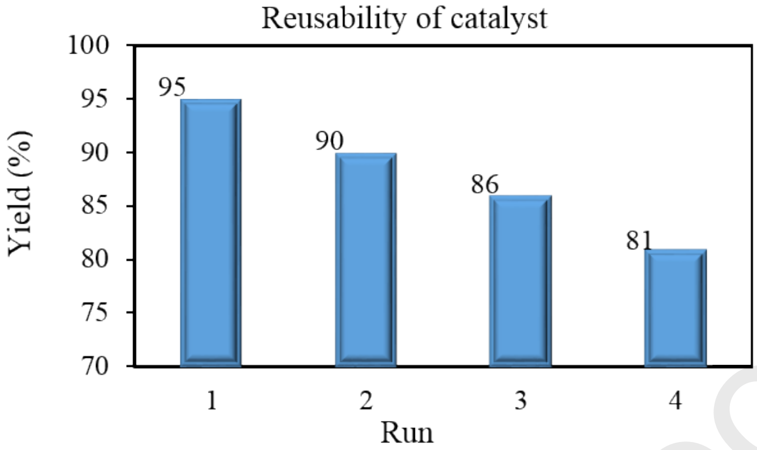
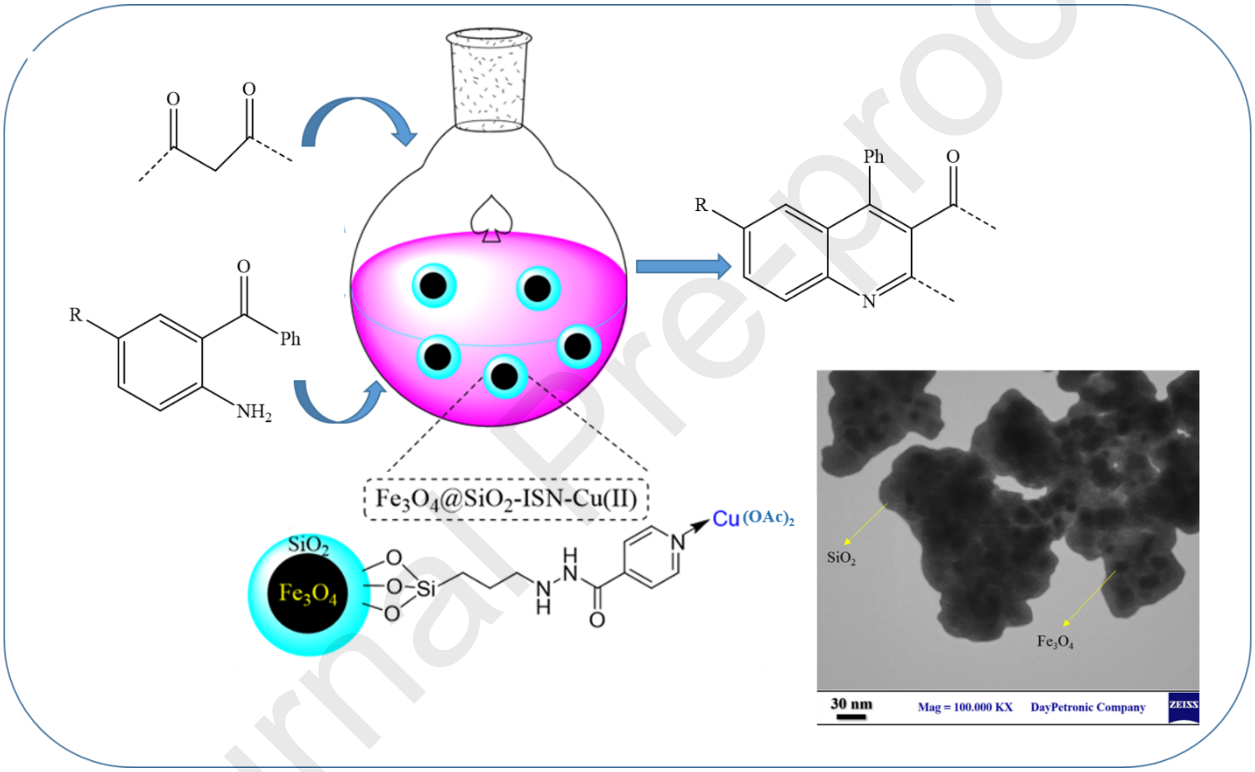

Reusability of catalyst
Yield (%)
100
95
90
85
80
75
70
95
90
86
81
1
2
3
4
Run

Fig. 7.

Graphical Abstract

Synthesis of Fe_3O_4@SiO_2/isoniazid/Cu(II) magnetic nanocatalyst as recyclable catalyst for highly efficient preparation of quinolines in moderate condition

Shahram Lotfi, Ahmad Nikseresht and Nasrin Rahimi



This paper reports the study on an efficient procedure for preparation of Fe3O4@SiO2/Isoniazid/Cu(II) as a recoverable magnetic nanocatalyst. The structure of the synthesized nanocatalyst was investigated via different techniques namely VSM, TEM, SEM, EDS, TGA, XRD and FT-IR. Then the nanocatalyst was applied on Friedländer reactions for a highly efficient preparation of quinoline derivatives.