

Synthesis, characterization and using $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeCl}_3$ as a new nanocatalyst for aza-Michael reaction between amines and ethyl crotonate

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ABSTRACT

In this article, recyclable $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeCl}_3$ was synthesized and entirely characterized by various techniques including XRD, FT-IR, SEM, EDX and VSM analysis. The catalytic ability of produced $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeCl}_3$ was studied in the aza-Michael reaction of diethyl amine and ethyl crotonate which lead to high yield of product. Also, this procedure was used to synthesize other derivatives resulted from different amines. Synthesized $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeCl}_3$ nanocatalyst has some great advantages such as easy preparation method, simple recovery and high efficiency.

Keywords: Aza-Michael reaction, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeCl}_3$ nanocatalyst, α,β -Unsaturated carbonyl compounds.

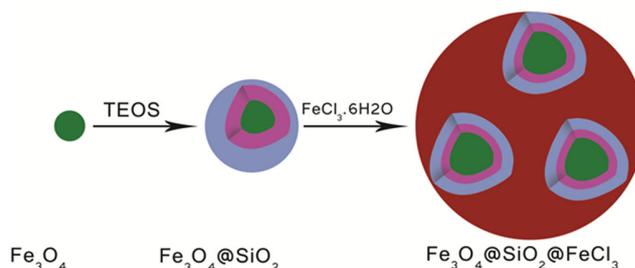
1. Introduction

Using recyclable nanocatalysts to precede organic reactions has gained major attentions in recent decades [1]. Huge range of biologically-active compounds such as antibiotics, auxiliaries, natural products and N-containing heterocycles can be formed by reusable catalysts through bond-formation reactions [2]. Among these reactions, Aza-Michael addition is an important transformation in organic chemistry. The Aza-Michael reaction is a method for the preparation of β -amino ketone by linking electron poor olefins with a range of amines. This reaction was performed for first time by Arthur Michael in 1887 [3, 4]. From then, several catalysts were used to perform Aza-Michael addition such as organocatalysts [5], β -cyclodextrin [6], PEG [7], ionic liquids [8] and iodine [9]. But all these methods suffered from recycling issue and recovery of catalyst. Consequently, these issues should be modified to improve the ability of catalyst.

Ferrite with a cubic inverse spinel structure, which is known as magnetite (Fe_3O_4), has wide range of applications such as biological assays [8], targeted drug delivery [3], magneto optical solid devices [4],

separation and purification [10], cell separation [11], and magnetic resonance imaging enhancement [12]. According to the importance of ferrite, synthesis of various core/shell materials based on Fe_3O_4 has been reported until now [13].

Herein, to improve the catalytic activity of Fe_3O_4 and using it as a recyclable magnetic nanocatalyst, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeCl}_3$ was synthesized via a hydrothermal method (Scheme 1) and characterized by various techniques including XRD, FT-IR, SEM, EDX and VSM analysis. The catalytic potential of synthesized $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeCl}_3$ was studied in the Aza-Michael reaction between amines and ethyl crotonate. Gained results showed that synthesized nanocatalyst have great ability to precede Aza-Michael reaction with good to high yield in reasonable reaction times. Also this procedure was used to synthesize other derivatives of this reaction.



Scheme 1. Preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeCl}_3$.

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2. Experimental

2.1. Materials

All chemicals and solvents were purchased from Merck and Aldrich. The FT-IR spectroscopy were recorded by Shimadzu IR-470 spectrometer, scanning electron microscopy (SEM) images were recorded by Sigma Zeiss, energy dispersive X-ray (EDX) spectra were taken on a Numerix DXP-X10P, NMR spectra were recorded by Bruker DRX-300 Avance spectrometer, and X-ray diffraction (XRD) measurements were taken on a JEOL JDX-8030.

2.2. Synthesis of $Fe_3O_4@SiO_2$ nanoparticles

The magnetite (Fe_3O_4) nanoparticle was synthesized by a chemical co-precipitation technique of ferric and ferrous ions in alkali solution [14]. Fe_3O_4 nanoparticles were synthesized based on a reported method with minor modifications. Under vigorous stirring, 1.99 g of $FeCl_2 \cdot 4H_2O$ was combined with 3.25 g of anhydrous $FeCl_3$ in 20 mL of water. A NH_4OH solution (0.6 M, 200 mL) was then added to the stirring mixture at room temperature, immediately followed by the addition of a concentrated NH_4OH solution (25%, w/w, 30 mL) to maintain the reaction pH between 11 and 12. For 1 hour, the resulting mixture was stirred at room temperature condition. After this period of time, above mixture was refluxed for about 1 h. The resulted magnetic nanoparticles were then centrifuged. Coating of a layer of silica on the surface of the Fe_3O_4 nanoparticles was achieved by premixing (Ultrasonic) a dispersion of the purified nanoparticles (8.5%, w/w, 20 mL) obtained previously with methanol (80 mL) for 1 h at 40 °C. After the addition of concentrated ammonia solution, the resulting mixture was stirred (40 °C, 30 min). Afterward, 1.0 mL of tetraethyl orthosilicate (TEOS) was added to above mixture and the mixture was stirred (40 °C, 24 h). The resulted silica-coated nanoparticles were separated by a magnet, washed and dried (100 °C in vacuum, 24 h).

2.3. Synthesis of $Fe_3O_4@SiO_2@FeCl_3$ nanoparticles:

40mg $Fe_3O_4@SiO_2$ was dispersed in 50 ml EtOH and sonicated for 20 min. Then, 10 mmol $FeCl_3 \cdot 6H_2O$ was added to solution and stirred for 120 min at room temperature, the magnetic solution separated by external magnet and washed with deionized water. This solution was moved into autoclave (40 ml Teflon lined stainless steel) and maintained still (120 °C, 18h) to give the final product. The obtained products were washed several times with deionized water and dried (80 °C, 4 h).

2.4. General procedure for the aza-Micheal reaction of amines with ethyl crotonate using $Fe_3O_4@SiO_2@FeCl_3$

To a mixture of ethyl crotonate (1 mmol) and amine (1.2 mmol), 30 mg of $Fe_3O_4@SiO_2@FeCl_3$ was added and the mixture stirred at room temperature for 7h. The reaction was continuing until the final product gained, which was monitored by TLC. After completion of the reaction, $Fe_3O_4@SiO_2@FeCl_3$ was separated by external magnet, and the resulted product was recrystallized and washed with acetone and dried on oven. The isolated product was analyzed by melting point and NMR spectroscopy.

3. Results and Discussion

$Fe_3O_4@SiO_2@FeCl_3$ nanoparticles were characterized by X-ray diffraction (XRD), FT-IR, Field-emission scanning electron microscopy (FESEM) images, Energy-dispersive X-ray spectroscopy (EDX) and vibrating sample magnetometer (VSM).

The crystalline structure of catalyst was characterized by XRD. As shown in Fig. 1, the interplanar spacing, lattice parameter and values for the prepared $Fe_3O_4@SiO_2@FeCl_3$ catalyst are closed to reported values and gained patterns can be readily referred to magnetite and $FeCl_3$.

The XRD pattern of the synthesized Fe_3O_4 and $Fe_3O_4@SiO_2@FeCl_3$ nanoparticle was displayed in Fig. 1. The diffraction peaks at $2\theta = 30.54^\circ$, 35.78° , 43.30° , 53.73° , 57.43° , and 63.06° shows the presence of the magnetite phase with cubic spinals [15]. The average crystallite size was calculated by Debye-Scherrer method about 11.78 nm.

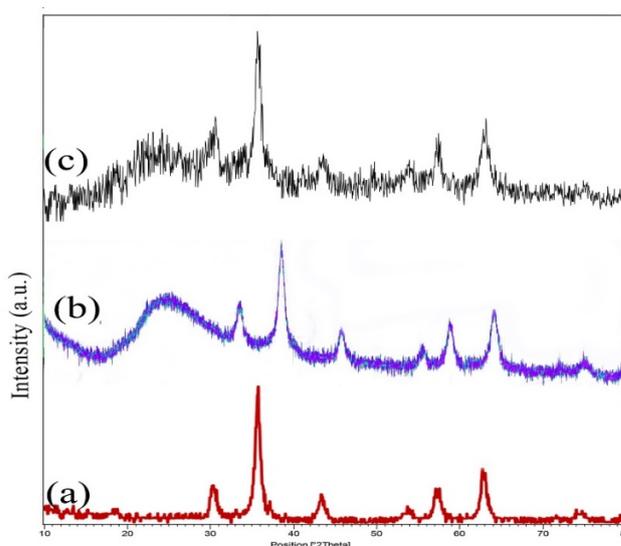


Fig. 1. XRD pattern of (a) Fe_3O_4 (b) $Fe_3O_4@SiO_2$ (c) $Fe_3O_4@SiO_2@FeCl_3$ nanoparticle.

The SEM images of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeCl}_3$ nanoparticles are shown in Fig. 2. As can be seen, in compare to Fe_3O_4 , functionalization of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ with FeCl_3 affected the surface morphology and its properties. Also the size distributions of nanoparticles were between about 15-30 nm.

The EDX spectrum of $\text{Fe}_3\text{O}_4@\text{SiO}_2@ \text{FeCl}_3$ (Fig. 3) confirms presence of Fe (25.17%), Si (23.73%), O (45.93%) and Cl (5.17%) elements in the catalyst.

Superparamagnetic properties of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeCl}_3$ nanoparticles were confirmed by VSM analyses. From this analyses, $M_s = 6.5 \text{ emu/g}$. Magnetization curve of the catalyst is depicted in Fig. 4 [16].

The FT-IR spectra of Fe_3O_4 , $\text{SiO}_2/\text{Fe}_3\text{O}_4$ and the prepared magnetic adsorbent ($\text{FeCl}_3 / \text{SiO}_2/\text{Fe}_3\text{O}_4$) are shown in Fig.5. The Si-O-Si symmetric stretching vibration band at 802 cm^{-1} also to 783 cm^{-1} and gradually decreases in intensity. The band at about 1100 cm^{-1} is ascribed to the stretch of (Si-O) band. The bound Si-OH groups are characterized by the very broad IR absorption band in the $2800\text{-}3700 \text{ cm}^{-1}$ region the stretching band at 1635 cm^{-1} indicates the presence of

residual physisorbed water molecules. Two basic characteristic peaks of three adsorbents at about 3300cm^{-1} (O-H stretching) and 550 cm^{-1} (Fe-O vibration), were attributed to the presence of Fe-OH in Fe_3O_4 .

After characterization of catalyst, its catalytic activity was tested in the synthesis of β -amino ketone derivatives. As a model reaction, ethyl crotonate was reacted with amine in the presence of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeCl}_3$ as catalyst.

To optimize the reaction condition, various conditions including amount of catalyst, solvent and temperature were studied. From optimization studies, it could be understood that the best result could be gained in the absence of solvent. Also, by increasing the amount of catalyst to 40 mg, the yield of the reaction stayed unchanged. On the other hand, by using 20 mg of catalyst, lower yield of product was gained. So, 30 mg of catalyst is the optimized condition. In addition, by studying the temperature, it was found that the optimized temperature is room temperature.

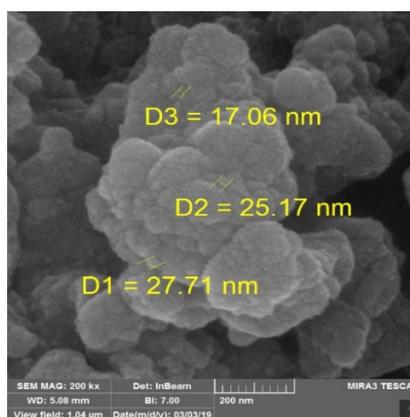
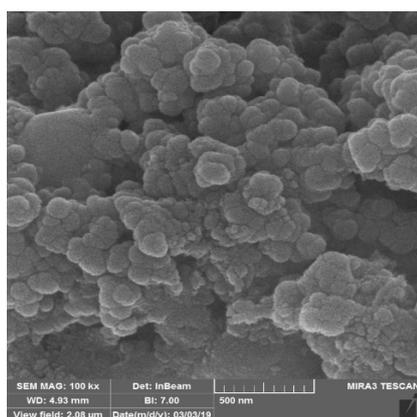


Fig. 2. SEM micrograph of $\text{Fe}_3\text{O}_4@\text{SiO}_2@ \text{FeCl}_3$ nanocatalyst.

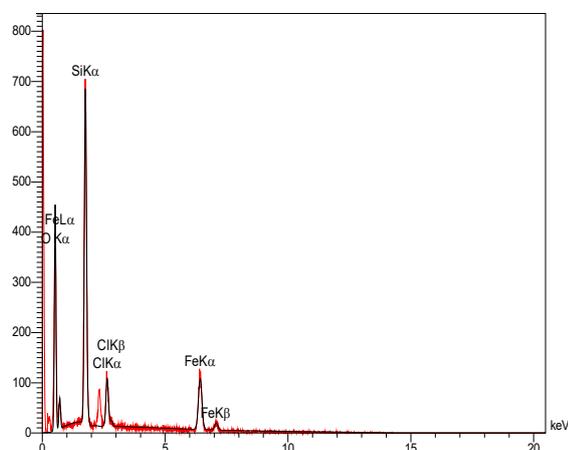


Fig. 3. EDX spectra of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeCl}_3$ nanocatalyst.

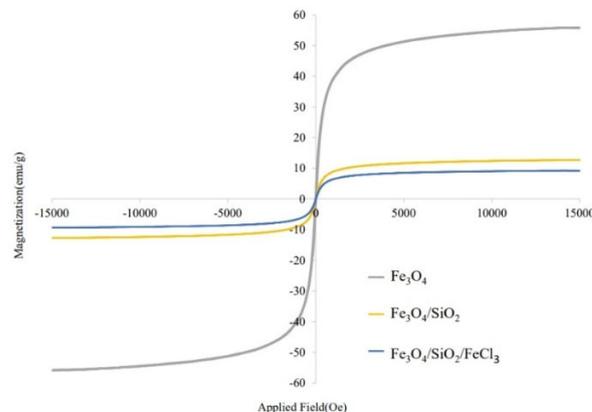
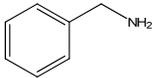
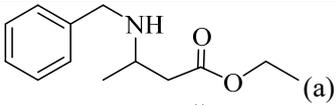
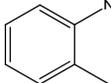
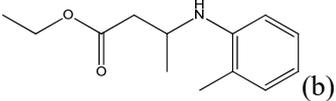
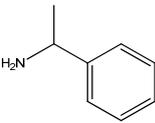
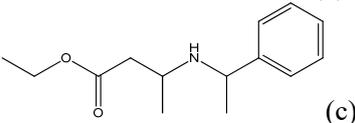
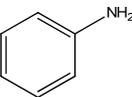
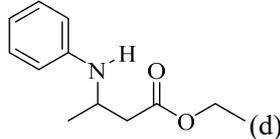
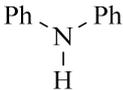
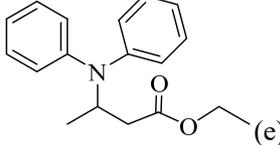
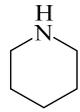
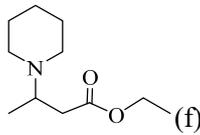
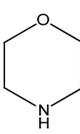
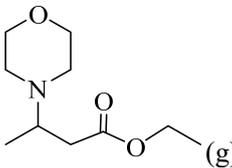
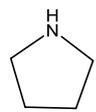
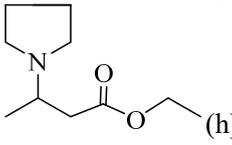
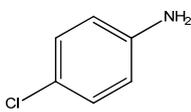
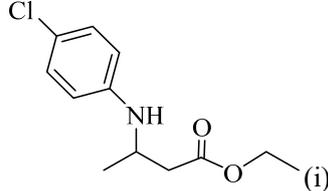
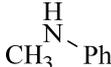
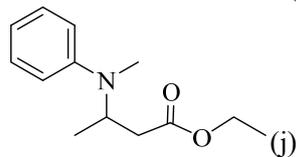
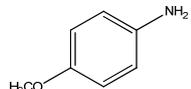
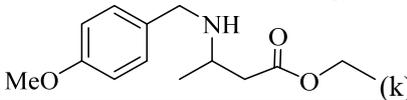


Fig. 4. VSM analysis for determination of superparamagnetism properties: Fe_3O_4 (black), $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (yellow) $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeCl}_3$ (blue) nanoparticles.

Table 2. Conjugate addition of amines to ethyl crotonate catalyzed by $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeCl}_3$ ^a

Entry	Amine	Product	Yield ^b
1			75
2			85
3			85
4			70
5			65
6			75
7			90
8			90
9			60
10			75
11			70

^aEthyl crotonate (1 mmol), amine (1.2 mmol) $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeCl}_3$ (30 mg), 7 h reaction time.^bIsolated yield (oil products).

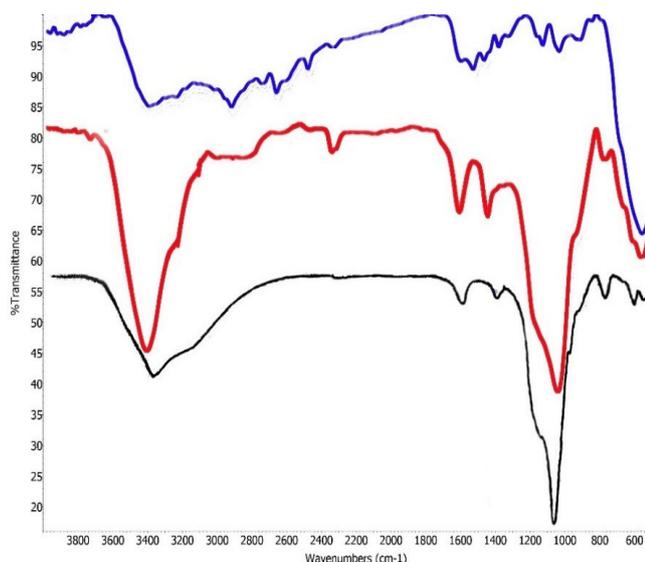


Fig. 5. FT-IR spectra of the Fe_3O_4 (blue), $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (red), $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeCl}_3$ (black).

To determine the scope of this procedure for the synthesis of triazoles and tetrazoles, different amines were reacted with ethyl crotonate according to optimized conditions and corresponding β -amino esters was prepared with good to high yields (Table 2).

To study the stability of synthesized nanocatalyst, its recyclability was examined. By using ethyl crotonate and diethyl amine in 6 h, the corresponding β -amino ketones were gained after five consecutive runs in following yield: 95%, 95%, 92%, 90% and 90% in five consecutive runs (Fig. 5).

To compare our method with reported literatures, the results of some catalytic systems were studied. As can be seen in Table 3, final yield of products is much better using $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeCl}_3$ than other catalytic systems in the reaction of diethyl amine and ethyl crotonate.

4. Conclusions

In this research, an efficient magnetic nanocatalyst was synthesized and its catalytic activity was studied in Aza-Michael reaction. By a simple hydrothermal method, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeCl}_3$ nanocatalyst was synthesized and completely characterized by various techniques including XRD, FT-IR, SEM, EDX and VSM analysis. By using synthesized nanocatalyst to precede Aza-Michael reaction, various derivatives were gained and characterized. Synthesized $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeCl}_3$ nanocatalyst showed excessive advantages such as easy preparation method, simple recovery and high efficiency.

Table 3. Conjugate addition of diethyl amine (1.2 mmol) to ethyl crotonate (1 mmol) under different catalyst.

Entry	Catalyst	Time (h)	Yield (%)	Ref.
1	Cr_2WO_6	7	25	This work
2	PCl_5	7	30	This work
3	$\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Na}_2\text{WO}_4$	7	30	This work
4	$\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeWO}_4$	7	38	This work
5	$\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Na}_2\text{WO}_4.\text{Sn}.\text{Bu}_3$	7	35	This work
6	AlCl_3	7	30	[17]
7	CuCl	7	33	[18]
8	Graphene Oxid	5	92	[19]
9	FeCl_3	42	96	[20]
10	$\text{FeCl}_3/\text{K10}$	5	50	[21]
11	$\text{FeCl}_3.6\text{H}_2\text{O}$	7	40	[22]
12	I_2	12	70	[16]
13	SBA-15-Ph- PrSO_3H	7	40	[23]
14	$\text{ZrOCl}_2.8\text{H}_2\text{O}/\text{K10}$	0.5	57	[24]
15	$\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeCl}_3$	7	90	This work

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