



## Magnetic core–shell Nanoparticles Containing $I_3^-$ as a Novel Catalyst for the Facial Synthesis of Imidazole Derivatives in Solvent-free Conditions

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### ABSTRACT

A novel  $Fe_3O_4@SiO_2@(CH_2)_3N+Me_3I_3^-$  magnetite nanoparticle was prepared and utilized in the synthetic conversion of aldehydes to imidazole derivatives in solvent-free conditions. These functionalized magnetic core–shell nanoparticles (MNPs) were characterized by Standard technique such as TEM, SEM, EDX, FT-IR, XRD, and VSM. The work up of reaction was very simple containing only a magnetic decantation. This novel catalyst could be separated easily and recycled several times without any significant decreasing of catalytic activity.

**Key Words:**  $Fe_3O_4@SiO_2@(CH_2)_3N+Me_3I_3^-$ , Magnetic separation, Magnetic core-shell, Imidazoles, Solvent-free.

### INTRODUCTION

In the past quarter of the century, nanoparticle catalysts have attracted chemists attention because of their unique properties both in the reaction and workup. However, according their simple separation, in addition of their nano size advantages, their application have been developed more and more<sup>1</sup>. In the other hand, most catalysts such as nano particles have some drawbacks in usual separation methods, for instance, filtration or centrifugation. These general methods lead to loss

of catalysts and products over the reaction and process steps. The magnetic nano particles can omit or improve many of these drawbacks<sup>2</sup>. According the advantages of using magnetic nano particles, some of them have been introduced in organic chemistry and catalyst fields<sup>3-15</sup>.

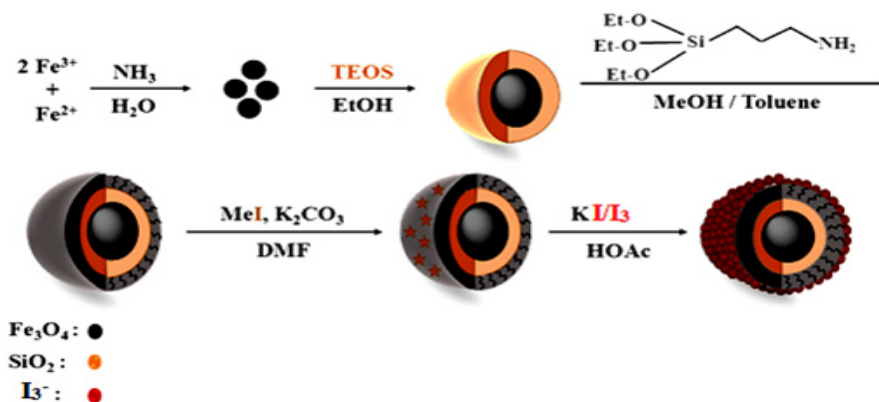
Imidazoles and their derivatives are a big class in organic chemistry. They have been introduced and utilized for many years because of their unique biological activity<sup>1</sup>. Imidazoles were usually produced by the reaction between a



carbonyl group and 1,2-diamine in the presence of a special reagent or forced reaction condition<sup>2</sup>. The using of numbers of reagents and catalysts indicating the importance of these compounds in organic synthesis. However, the majority of these reagents and catalysts suffer from some drawback such as low yields of the products, tedious work up, toxic reagents, high cost, long reaction time

and.... Therefore, introducing a new safe and green reagents are desirable.

In continue with our research about nano catalyst<sup>16</sup>, we report herein the synthesis of novel magnetically triiodide catalyst and its application to the synthesis of imidazole derivatives. The synthetic steps are summarized in scheme 1.



Scheme 1. Synthetic steps of  $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ (\text{CH}_2)_3\text{N}+\text{Me}_3\text{I}_3^-$  magnetic catalyst

The preparation of first magnetite particles as a magnetic core was performed by reaction between ferrous and ferric chloride with  $\text{NH}_4\text{OH}$ . An inert layer of  $\text{SiO}_2$  was coated around previous core. The outer surface modification was made through the grafting of amino propylsilane, conversion of amine group to fourth ammonium group and finally, adding the triiodide anion to nano particle surface. Moreover, this magnetic catalyst was characterized by known appropriate technique such as SEM, TEM, EDX, XRD, FT-IR and VSM. Finally, the produced catalyst was used as a novel catalyst for the synthesis of imidazole derivatives.

## EXPERIMENTAL

### Preparation of catalyst

Preparation of magnetic nanoparticles ( $\text{Fe}_3\text{O}_4$ ), silica-coated MNPs ( $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ ) and amino propyl modified silica-coated magnetic nanoparticles ( $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{APTES}$ )

### Preparation of triiodide modified nanoparticle ( $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ (\text{CH}_2)_3\text{N}+\text{Me}_3\text{I}_3^-$ )

The  $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{APTES}$  (100 mg)

was dispersed in DMF (50 mL) by the ultrasonic treatment for 30 min., MeI (2 mL) and  $\text{K}_2\text{CO}_3$  was added to the mixture under vigorous stirring for 6 hours. An external magnet was used to separation of  $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ (\text{CH}_2)_3\text{N}+\text{Me}_3\text{I}_3^-$  from the solution. Then the produced nano particles washed with water several times and dried in air. Afterward, this nano particle was dispersed in ethanol (20 ml) by ultrasonic treatment and a solution of  $\text{I}_2$  in ethanol was added to dispersed solution and was stirred for one day. The resulting dark violet nano catalyst was collected by an external magnet and washed with 5 mL ethanol.

### General procedure

A solution of substrate (1 mmol), aryl aldehyde (1 mmol), and  $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ (\text{CH}_2)_3\text{N}+\text{Me}_3\text{I}_3^-$  MNPs (0.007 gr) was heated at  $100^\circ\text{C}$  under magnetic stirring for the requested reaction time. The complication of reaction was demonstrate by TLC. The EtOH (10 mL) was added and the reined nano particles was collected by an external magnet. The mixture was poured into ice-water (30 mL) and the pure heterocyclic product was filtered, washed with ice-water, and dried.

## RESULTS AND DISCUSSION

### Characterization of magnetic nanoparticle TEM analysis

The size and morphology of the prepared novel catalyst were characterized by TEM (Fig. 1).

The TEM observation indicates all prepared nano particles have almost spherical core-shell structure (Fig. 1). The size of magnetic core is less than 20 nm and the diameter of all layers a shell are around 30 nm.

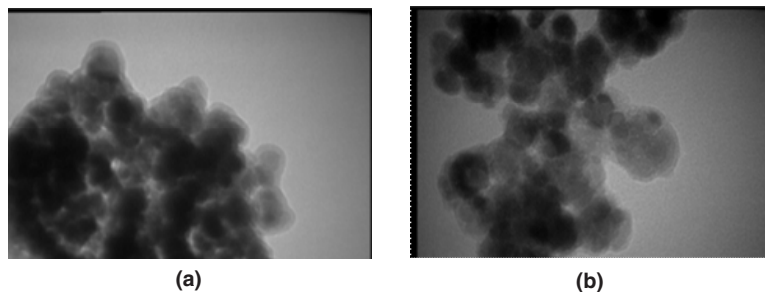


Fig. 1. TEM images of (a)  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  (b)  $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ (\text{CH}_2)_3\text{N}^+ \text{Me}_3\text{I}_3^-$ .

### SEM analysis

The Scanning Microscope Electronic (SE) images indicate size and morphology of prepared nano particles (Fig. 2). According this data, all nano particles have a spherical shape with a large surface area. These images show that  $\text{Fe}_3\text{O}_4$  is spherically with nano dimensions less than 15 nm,

but when TEOS coated The  $\text{Fe}_3\text{O}_4$  the average sizes increase to 20 nm (Fig. 2b). Furthermore, the SEM observation of  $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{APTES}$  determined a recognizable layers on  $\text{Fe}_3\text{O}_4$  magnetic core (Fig. 2c). Finally, Fig. 2d shows the structure of  $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ (\text{CH}_2)_3\text{N}^+ \text{Me}_3\text{I}_3^-$  as core shell structure with average size of particles less than 50 nm.

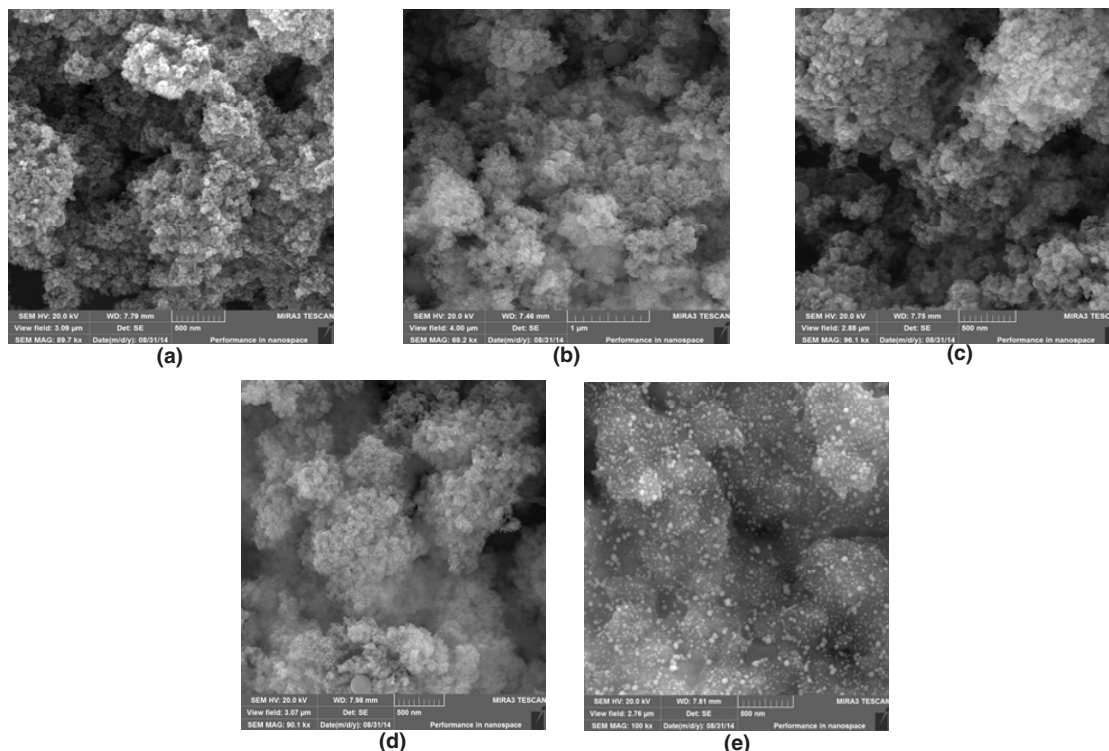


Fig. 2. SEM images of prepared nano particles: (a)  $\text{Fe}_3\text{O}_4$  (b)  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  (c)  $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{NH}_2$  (d)  $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{N}(\text{CH}_3)_2\text{I}^-$  (e)  $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{N}(\text{CH}_3)_2\text{I}_3^-$ .

### X-ray diffraction

XRD pattern of pure magnetic nano catalyst are showed in Fig 3. The most intense peak shows the average sizes of nano particles according Debye–Scherrer’s formula  $D = 0.9\lambda/\beta \cos\theta$ , ( $D$ = the average crystalline size;  $\lambda$ = X-ray wavelength

(1.542 Å);  $\beta$ = the angular line width of half-maximum intensity;  $\theta$ = Bragg’s angle in degree)<sup>19, 20</sup>. Based on this data averages sizes of synthesized nano particles are less than 50 nm that confirm the SEM and TEM data.

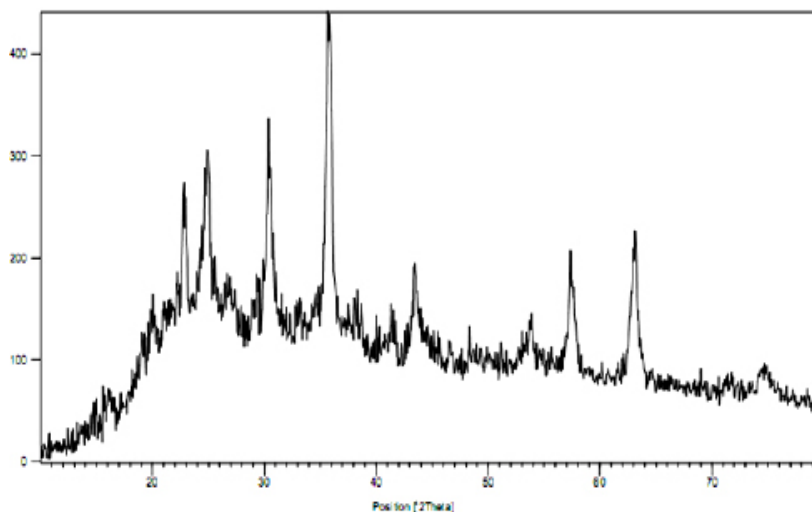


Fig. 3. XRD patterns of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{N}+\text{Me}_3\text{I}_3^-$

### EDS analysis

Duo to EDS patterns, clearly show the presence of N, C, O, Si, Fe and I (Fig. 4). The presence of Fe indicate iron oxide in nano articles. The higher intensity signals of Si and O, in addition, shows the grafting of  $\text{SiO}_2$  layer to magnetic core. The signal of C proves the presence of this element in the structure of nano particle. Likewise, the N and I signal demonstrate the alkylated ammonium group and triiodide anion respectively.

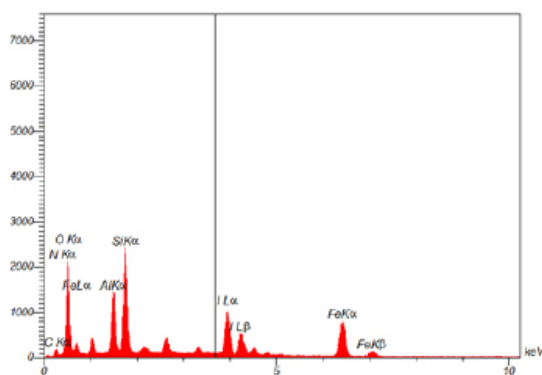


Fig. 4. EDX patterns  $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{N}+\text{Me}_3\text{I}_3^-$

### FTIR spectroscopy

In the Fig. 5a-c the FT-IR spectra of all prepared nano particles are showed. The Fe-O

bond showed a significant signal in  $585 \text{ cm}^{-1}$ <sup>21</sup>. It is noticeable that Si-OH and Si-O-Si groups were confirmed by bands at 804, 951 and  $1086 \text{ cm}^{-1}$ . The stretching vibration of -OH group was confirmed by a broad band at  $3300 - 3500 \text{ cm}^{-1}$  (Fig. 5b). The significant bands at 2965 and  $2850 \text{ cm}^{-1}$  belong to the stretching vibration of C-H bond of propyl amine group of APTES, which prove the successful grafting of this on silica layer. Furthermore, a band at  $1440 \text{ cm}^{-1}$  belong to the tertiary amine group. Overall, these results confirm that this novel nano particles successfully prepared.

### Magnetic properties

The magnetization curve of  $\text{Fe}_3\text{O}_4$ , silica coated  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{N}+\text{Me}_3\text{I}_3^-$  are presented in Fig. 6a-c. This kind of characterization would be called vibrating sample magnetometer (VSM). As can be seen from the diagrams, the magnetization of bare  $\text{Fe}_3\text{O}_4$  MNPs is about 60.0 emu/g at room temperature<sup>23</sup>. When the layers were added, the saturation magnetization would be decrease more and more. In fact, the saturation magnetization of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{N}+\text{Me}_3\text{I}_3^-$  would be around 40 emu/g, which is lower than the bare one. Decrease of the saturation magnetization result from the creation of a silica shell around the  $\text{Fe}_3\text{O}_4$  core.

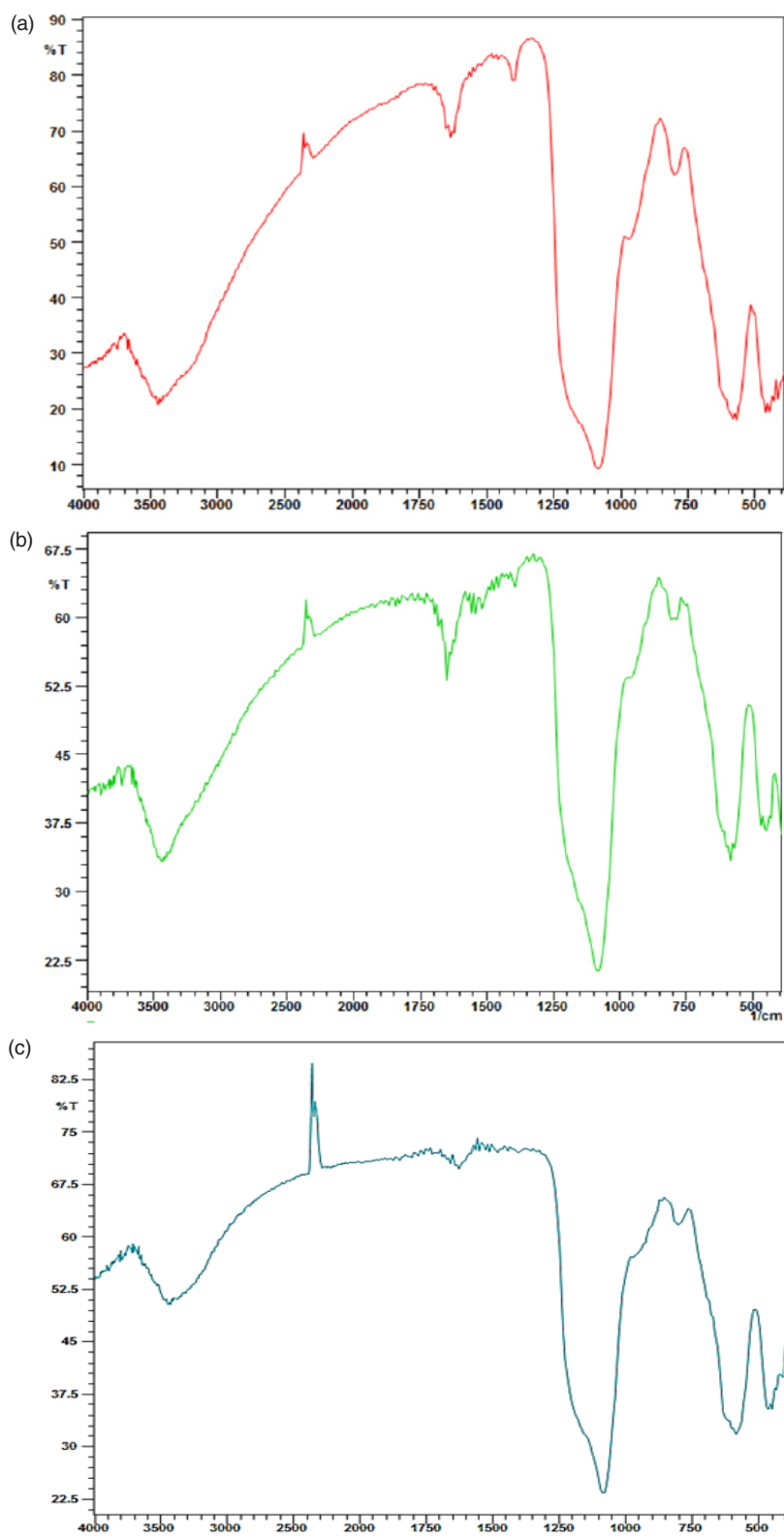


Fig. 5. FT-IR spectra: (a)  $\text{Fe}_3\text{O}_4 @ \text{SiO}_2$  MNPs; (b) APTES coated  $\text{Fe}_3\text{O}_4$  MNPs and (c)  $\text{Fe}_3\text{O}_4 @ \text{SiO}_2(\text{CH}_2)_3\text{N}^+\text{Me}_3\text{I}_3^-$ .

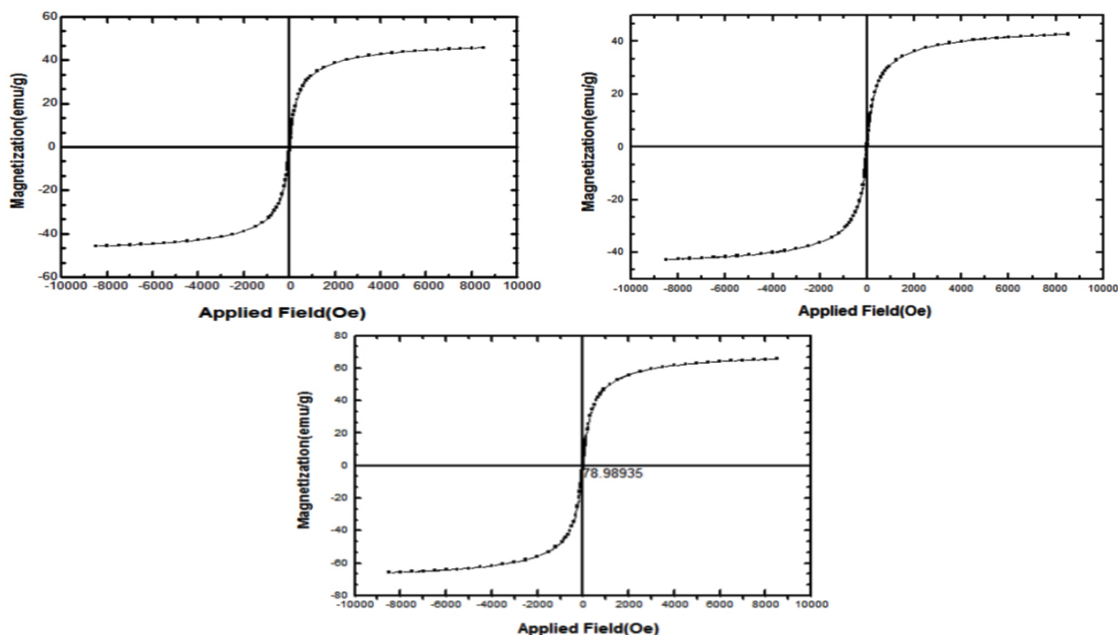


Fig. 6. VSM of prepared nano particles at room temperature of (a)  $\text{Fe}_3\text{O}_4$  MNPs; (b)  $\text{Fe}_3\text{O}_4@SiO_2$  MNPs; and (c)  $\text{Fe}_3\text{O}_4@SiO_2@(CH_2)_3N+Me_3I^-$ .

#### Optimization of nano catalyst for imidazole synthesis

The reaction process is simple and fast and proceeded in excellent yields of products. At the first step, the conversion reaction carried out in different protic and aprotic solvents and the product yields compared to solvent free condition (Table 1).

**Table 1: Effect of different solvent on product yield for the synthesis of 2-(4-chlorophenyl)-1H-benzimidazole**

Entry	Solvent a	Time(min.)/Yield(%)
1	$\text{CH}_3\text{CH}_2\text{OH}$	60/ trace
2	$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	60/ trace
3	$\text{CH}_2\text{Cl}_2$	60/ trace
4	THF	60/ trace
5	Toluene	60/ trace
6	$\text{CH}_3\text{CN}$	60/ trace
7	DMF	60/14
8	None <sup>b</sup>	60/36
9	None <sup>c</sup>	60/72
10	None <sup>d</sup>	15/94

The reactions were carried out with 4-chloro benzaldehyde (1mmol), orth-phenylene diamine (1mmol), and nano catalyst (0.07 g). a) reflux condition, b) in solvent- free condition at 50 °C, c) in solvent- free condition at 75 °C, d) in solvent- free condition at 100 °C

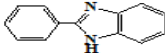
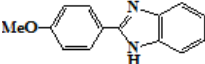
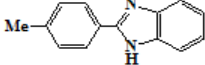
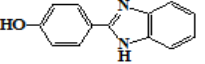
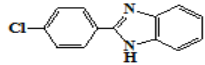
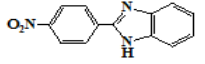
The imidazoles preparation reaction was performed in the both solvent and solvent free conditions. As regard the first, a variety of different solvents were utilized for this conversion, such as diethyl ether, ethanol, dichloromethane, THF, toluene, acetonitrile, and DMF. Although, very low yield of products were obtained in the presence of DMF as solvent, but no one performed a noticeable yields. As can be seen from the Table 1 only solvent free condition is the best case for this reaction. Likewise, the catalyst amount's effect was explored on reaction time and yields Table 2). Although, in the absence of this catalyst no products were found, but there are two basic trends in the presence of different amount of catalyst. The yield of products went up by increasing the catalyst amount from 0.025 to 0.07 g. But with higher amount of catalyst the yield of products were leveled off.

**Table 2: catalyst amounts effect on the preparation of 2-(4-chlorophenyl)-1H-benzimidazole**

Entry	Catalyst(g)	Time(min)/ Yield(%)
1	0.025	15/29
2	0.05	15/85
3	0.07	15/94
4	0.10	15/94
5	-	15/-

Reaction of 4-chloro benzaldehyde (1mmol), 1,2- diamino benzene (1mmol), and catalyst in solvent- free conditions at 100 °C.

**Table 3: Synthesis of some heterocyclic compounds using  $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{N}+\text{Me}_3\text{I}_3^-$** 

Entry	Ar	X	Product	Time (min.)/ Yield (%)	m.p.	
					Observed	Reported
1	$\text{C}_6\text{H}_4$	NH		17/92	290-292	290-293[27]
2	4-OMe $\text{C}_6\text{H}_4$	NH		13/90	220-222	223-226[28]
3	4-Me $\text{C}_6\text{H}_4$	NH		15/92	263-264	264-265[27]
4	4-OHC $\text{C}_6\text{H}_4$	NH		13/88	264-265	265-267[29]
5	4-Cl $\text{C}_6\text{H}_4$	NH		17/94	288-290	288-291[30]
6	4-NO $_2\text{C}_6\text{H}_4$	NH		20/90	321-323	322-323[27]

In general, all data show significantly that the best reaction condition is the solvent free at 100 °C in the presence of 0.07g of periodate magnetic nano catalyst.

The results of condition's optimization were used in the reaction of a variety of aldehyde derivatives with 1,2-diamino benzene to synthesis of some heterocyclic compounds (Table 3).

#### Synthesis of imidazole, thiazole and pirimidine derivatives using $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{N}+\text{Me}_3\text{I}_3^-$

As can be seen from the Table 3, there are 15 examples for catalytic conversion of aldehyde to the corresponding heterocyclic compounds using this novel catalyst containing  $\text{I}_3^-$ . The yields are excellent and the procedure is very simple. Likewise, the work up is easy too. The catalyst is readily separated by only using an external magnet.

#### Catalyst recovery and its stability

The reaction of 4-chlorobenzaldehyde and *o*-phenylene diamine in the presence of the catalytic amount of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{N}+\text{Me}_3\text{I}_3^-$  was performed for demonstrate recoverability of this catalyst. The catalyst was recycle and reused for five times without any losing of its activity. In fact, this unique nano catalyst could be recycled and reused times and times (Fig. 7). On the other hands, the catalyst shows very good shelf life too. This novel catalyst last for months. So, it can be stored for months without significant decline in its activity.

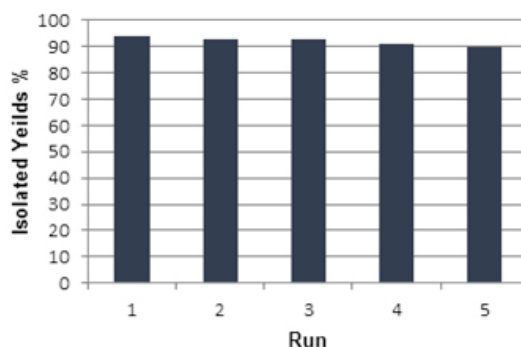


Fig. 7. Reusability of catalyst in

#### CONCLUSION

In this manuscript, we herein report a novel magnetic nano catalyst containing periodide ( $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{N}+\text{Me}_3\text{I}_3^-$ ) as a green, efficient and recoverable nano catalyst. The separation of this catalyst from reaction mixture is very simple too. It could be isolated using an external magnet vessel. The imidazole, thiazole, and pirimidine derivatives could be easily prepared using this novel nano catalyst in excellent yields.

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