ORIGINAL ARTICLE

Fe$_3$O$_4$ nanoparticle supported Ni(II) complexes: A magnetically recoverable catalyst for Biginelli reaction

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Abstract A novel magnetically recoverable functionalized magnetic(Fe$_3$O$_4$) nanoparticle supported-nickel(II) complex with a high surface area has been synthesized by chemical conjugation of magnetite nanoparticles with highly reactive silanols on the surface of magnetic Fe$_3$O$_4$ to improve the affinity of Fe$_3$O$_4$ nanoparticles for the target species. Functionalized Ni(II) complex containing surface of pyridine, methoxysilanyl and amino groups. Studies revealed that Fe$_3$O$_4$@[-Ni(bpy)$_2$(py-tmos)] is a new and highly efficient green catalyst for the synthesis of a diverse range of 3,4-dihydropyrimidin-2(1H)-ones under solvent free conditions, and in addition Fe$_3$O$_4$@[Ni(bpy)$_2$(-py-tmos)] could be easily recovered by a simple magnetic separation and recycled at least 5 times without deterioration in catalytic activity.

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1. Introduction

Of late, extensive research has been performed on functionalized magnetic catalyst (Prodius et al., 2009; Polshettiwar et al., 2008) which has led to substantial advances in nanomaterial synthesis because of its distinctive physicochemical characteristics and broad range of applications in catalysis, (Zeng et al., 2010) protein separations, adsorbents, (Ye et al., 2008) magnetic resonance imaging (MRI), (Gonzalez-Arellano et al., 2008), drug delivery, magnetic sensors and magnetic refrigeration (Borghard et al., 2009).

Although nanocatalysts are significantly effective in the organic reactions, their wider applications have been stalled due to two important barriers such as (i) complexity in recovery of the catalyst and (ii) prolongation of the particle dimension for repeated use. Usually, recovery of the nanocatalyst is

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Table 1 The effect of different catalysts (15 mg) on reaction of ethyl acetoacetate (0.01 mol) with urea (0.01 mol) and benzaldehyde (0.01 mol) under microwave (MW, 200 W, max. 130 °C) and thermal (Δ, 100 °C) conditions.

Entry	Catalysts	Time (min)		Yield[a] (%)	
		MW	Δ	MW	Δ
1	No catalyst	–	–	–	–
2	Fe_3O_4	12	65	80	78
3	[Ni(bpy)$_2$Cl$_2$]	10	60	85	80
4	Fe_3O_4-bpy-Ni(II)	6	45	92	90

[a] Isolated yield.

being made either by filtration or by centrifugation, wherein loss of a large amount of nanocatalyst is foreseeable (Sarkar et al., 2009). At this juncture, recovery of the catalyst from the product mixture using an external magnet has been budding of late as a novel and effective technique (Guin et al., 2007). As stated earlier, the second aspect that has to be borne in mind is the prevention of nanoparticle agglomeration either by depositing the nanoparticles on a suitable support or pursuing milder operating conditions.

Transition metal nanoparticles have received a great deal of attention due to a viable alternative to conventional materials in the field of catalyst, however most of them are precious and expensive, among these nickel catalysts are inexpensive and widely known for their application in organic transformation albeit the nickel-based catalysts have been widely used as catalyst, (Zăvoianu et al., 2005; Kappe, 1993) but efficient separation and recycling of these Ni catalysts are difficult. Herein we report the immobilization of nickel with functionalized magnetic nanoparticle as an efficient catalyst for multicomponent reaction. The objective is not only to easily separate the catalyst from the reactant by means of the simple application of an external magnetic field, but at the same time also, as MNPs have a high surface area, to immobilize Ni(II)complex on MNPs with high dispersion and higher activity.

The Biginelli reaction, renowned for a long time, has concerned much awareness with the innovation of dihydropyridine based calcium channel modulator drugs such as nifedipine. This important class of heterocyclic compounds has engrossed considerable interest over the past decade due to their ample array of pharmacological and therapeutic activities. (Kappe et al., 1997; Kappe, 2000; Atwal et al., 1991; Hu et al., 1998). The foremost negative aspect of this reaction involves the low product yields. In past few years several methods have been developed for organic transformation in particular using various catalysts, several procedures have been reported for Biginelli condensation, including the use of BF$_3$-OEt$_2$, (Maiti et al., 2003) lithium salts, (Lu and Ma, 2000) metal complexes, (Paraskar et al., 2003; Narsaiah et al., 2004) cadmium chloride (Ramalinga et al., 2001), bismuth (Ranu et al., 2000), indium chloride, (Bose et al., 2003) lanthanide compounds, (Sabitha et al., 2003) and polyphosphate ester (PPE) (Hankari et al., 2011). Considerable attention has also been focused on silane moieties as catalysts such as iodotrimethyl silane (Bose et al., 2004) and trimethylsilyl triflate (Kappe and Falsone, 1998). Recently, catalysts, like FeCl$_3$ embedded in Al-MCM-41 are used to catalyze these reactions efficiently. (Sapkal et al., 2010) Metal oxide nanoparticles are

known to be promising material for the rising heterogeneous catalysts in a synthesis of dihydropyrimidine derivatives. (Uhm et al., 2010; Martinez et al., 2003; Chun et al., 2011; Prakash Naik et al., 2009) In most of the cases recovery of the catalyst becomes difficult, since an easily recoverable and reuseable heterogenous catalyst is still in high demand. As part of our ongoing research we aimed at the development of reusable catalysts for various organic transformations (Ramesha et al., 2007; Vinay Kumar et al., 2011; Girija et al., 2011). Our approach is to develop a rapid and efficient scientifically based framework for greener preparation of these dihydropyrimidinones using supported magnetic nanoparticle.

2. Experimental details

2.1. Materials

All chemicals (AR grade) were commercially available and used without further purification. FeCl$_2$·4H$_2$O, FeCl$_3$·6H$_2$O, ammonium hydroxide (35% NH$_3$ solution) nitric acid (68%), tetraethylorthosilicate (TEOS), 3-chloropropyl-trimethoxysilane (CPTS), amino pyridine and solvents were purchased from Merck.
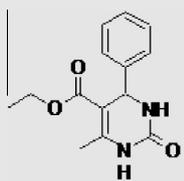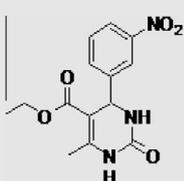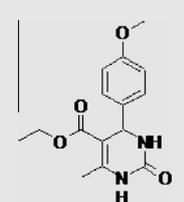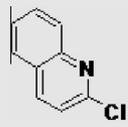
2.2. Instrumentation

The melting points of the products were determined by open capillaries and are uncorrected. Thin-layer chromatography was performed usi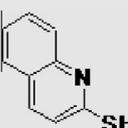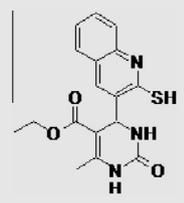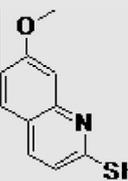ng commercially prepared 60-mesh silica gel plates and visualization was effected with short wavelength UV light (254 nm). IR spectra were recorded on a Shimadzu model impact 400D FT-IR Spectrophotometer using KBr pellets. ^{1}H NMR was recorded on a Buckner AC-300F 300 MHz spectrometer in CDCl$_3$ using TMS as an internal standard with ^{1}H resonant frequency of 300 MHz. The microwave oven (2.45 GHz, maximum power 300 W) used for sample preparation was a focused single mode microwave synthesis system (Discover, CEM, USA). Temperature was controlled by automatic adjusting of microwave power. X-ray powder diffraction (XRD) patterns were recorded using a Rigaku D/max 2550 V X-ray diffractometer with high-intensity Cu Kα radiation ($k = 1.54178$ Å) and a graphite monochromator. A JEOL JEM 6700F field emission scanning electron microscope was used for the determination of the morphology of the particles. Atomic absorption spectroscopic (AAS) studies were carried

Table 2 Comparative synthesis of compound **4a** using solution versus the solvent-free conditions under microwave (MW, 200 W, max. 130 °C).

Entry	Solvents	Time (min) MW	Yield[a] (%) MW
1	No solvent	6	92
2	DMF	20	15
3	Acetonitrile	18	20
4	Dioxane	14	16
5	Methanol	10	72
6	Ethanol	8	84

[a] Isolated yield.

Table 3 Nano-Fe$_3$O$_4$-bpy-Ni(II) catalyzed synthesis of 3,4-dihydropyrimidine derivatives in solvent free condition under microwave (MW 200 W, 130 °C).

Entry	R	Y	Product	Time (min) MW	Yield[a] (%) MW	Observed M.P. (°C)	Literature M.P. (°C)
1	C$_6$H$_5$	Et		6	90	203	203–204[15]
2	C$_6$H$_5$NO$_2$	Et		6	86	122–124	121–123[15]
3	C$_6$H$_5$OCH$_3$	Et		6	82	209–211	208–210[15]
4		Et		7	78	234–239	239[31]
5		Et		5	87	213–214	215[31]
6		Me		5	88	250–252	251[31]
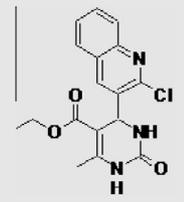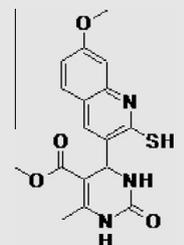
Table 3 (continued.)

Entry	R	Y	Product	Time (min) MW	Yield[a] (%) MW	Observed M.P. (°C)	Literature M.P. (°C)
7		Me		6	89	232–233	233[31]
8		Me		8	86	226–227	225[31]
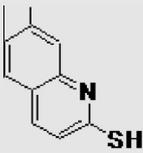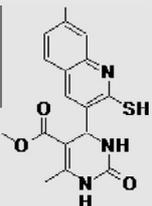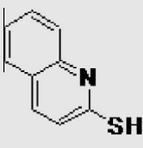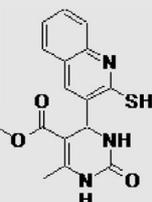
[a] Isolated yield.
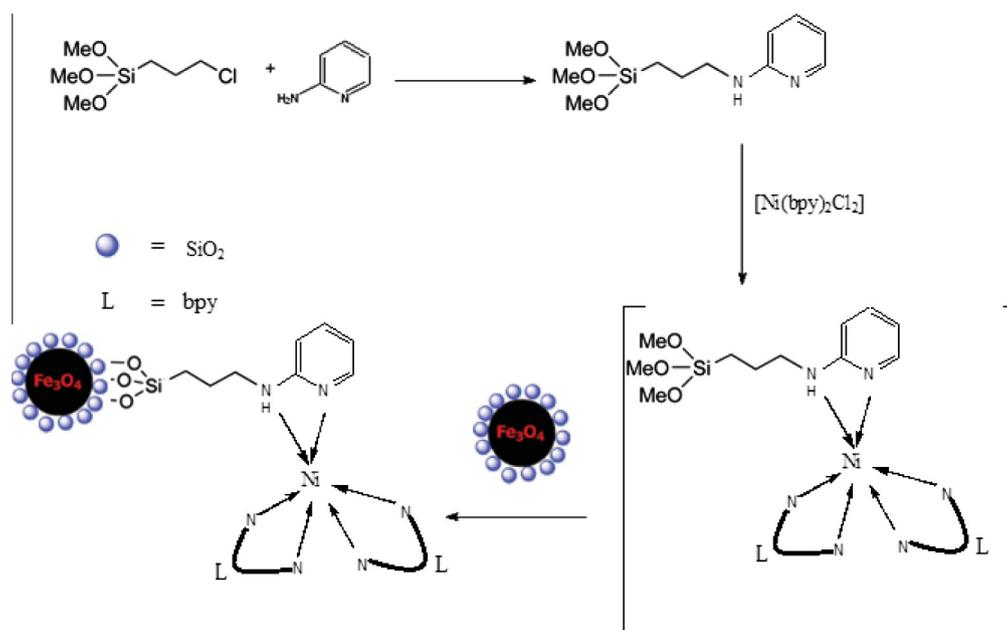
Scheme 1   Synthesis of functionalized iron oxide nanoparticle-nickel (II) polypyridine complex (Fe$_3$O$_4$-bpy-Ni(II)).

out using MODEL 210 VCP atomic absorption spectrophotometer.

2.3. Preparation of functionalized iron oxide nanoparticle supported-nickel(II) complex

A mixture of FeCl$_3$.6H$_2$O (2.35 g, 8.7 mmol) and FeCl$_2$·4H$_2$O (0.86 g, 4.3 mmol) was dissolved in 40 mL deionized water. The resultant solution was left to be stirred for 30 min at 80 °C. Then 5 mL of NH$_4$OH solution was added with vigorous stirring to produce a black solid and the reaction

was continued for another 30 min according to the reported procedure (Liem et al., 2007). The black magnetite nanoparticles were isolated by magnetic decantation, washed several times with deionized water and then dried at 80 °C for 10 h. To introduce reactive silanol on the surface of magnetic nanoparticle (MNP) 0.5 g of dried Fe$_3$O$_4$ nanoparticles was suspended in a mixture of 50 mL ethanol and 5 mL of NH$_3$.H$_2$O (25%). Then, 0.2 mL of tetraethoxysilane (TEOS) was added to solution and the mixture was ultrasonicated for 2 h. Afterward silica coated MNPs (MNP@SiO$_2$) were magnetically separated, washed three times with ethanol and dried at
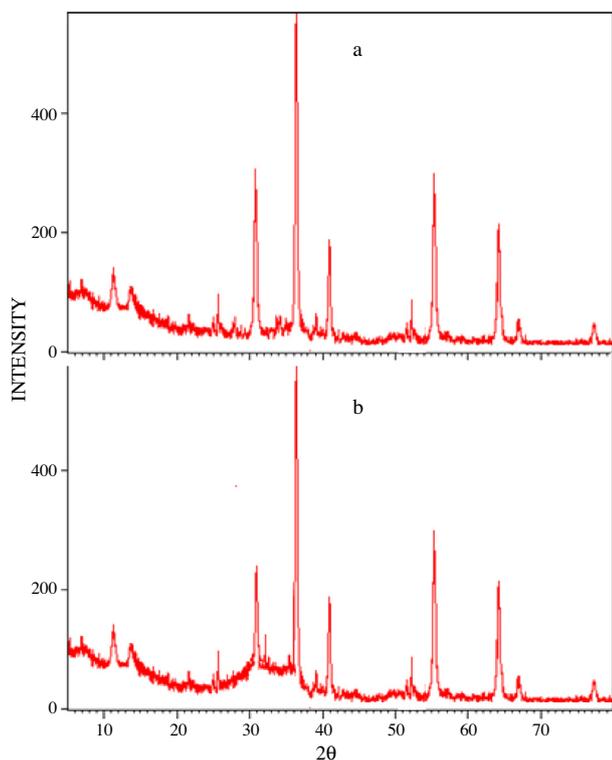
Figure 1 XRD pattern of the Fe$_3$O$_4$-bpy-Ni(II) Catalyst: (a) before reaction and (b) after reaction.

80 °C for 10 h. MNP@SiO$_2$ (100 mg) was dispersed in 15 mL of dry toluene by ultrasonication under nitrogen atmosphere.

The ligand pyridine-2-yl-(3-trimethoxysilanyl-propyl)-amine (py-tmos) **3** was prepared by dissolving 1 mmol of amino pyridine **1** in 15 mL of dry ethanol and 3-chloropropyl-trimethoxysilane **2** (0.8 mmol), the reaction mixture was allowed to stir under nitrogen atmosphere overnight under reflux conditions (Alizadeh et al., 2012; Zeng et al., 2011). The synthesized ligand Pyridine-2-yl-(3-trimethoxysilanyl-propyl)-amine (py-tmop) **3** and [Ni(bpy)$_2$Cl$_2$] (Harris and McKenzie, 1967) were suspended in 20 mL DMF, refluxed under nitrogen atmosphere with stirring for about 10 h for

the formation of [Ni(bpy)$_2$(py-tmos)]Cl$_2$ **4** complex. Magnetic silica nanoparticles (MSN) were dispersed in ethanol (10 mL), to this solution, solution of Ni complex in ethanol (10 mL) was added with stirring, and the mixture was heated to reflux overnight. After the reaction, the functionalized (Fe$_3$O$_4$-bpy-Ni(II)) **5** was separated by centrifugation and washed several times with ethanol to remove the traces of [Ni(bpy)$_2$(py-tmos)]Cl$_2$ complex before being dried at 60 °C for 12 h.

2.4. General procedure for the preparation of 3,4-dihydropyrimidine derivatives

A 2–5 ml microwave reactor vial was charged with ethyl aceto-acetate (0.01 mol), urea (0.01 mol), and aromatic aldehyde (0.01 mol) and 15 mg of nano catalyst was added. The vial was sealed with an aluminum cap fitted with a pressure and temperature-calibrated Teflon seal. The vial was inserted into the cavity of the microwave reactor, and the reaction mixture was irradiated with monomode irradiation at 130 °C and 9.6 bar for the time indicated in Table 1. The reaction progress was monitored by TLC. After completion of reaction, the reaction mixture was cooled to room temperature and solidified within an hour. The residue was extracted with ethyl acetate (2 × 10 mL) followed by drying with anhydrous Na$_2$SO$_4$. After evaporation of the solvent, the residue was purified by recrystallization to afford the desired product. The catalyst was magnetically separated with a 5350 G neodymium iron boron permanent magnet. The same procedure was carried out for the synthesis of 3,4-dihydropyrimidine derivatives. All the synthesized 3,4-dihydropyrimidine derivatives were characterized using analytical techniques such as IR and ^{1}H NMR. Also the identity of these compounds was established by comparison of their melting point with those of reported samples (Maiti et al., 2003; Ramesha et al., 2007) (Table 3).

3. Results and discussion

In the present study, the catalyst Fe$_3$O$_4$-bpy-Ni complex was prepared by a concise route depicted in Scheme 1. Tetraethoxysilane (TEOS) was employed to introduce highly reactive silanols on the surface of magnetic Fe$_3$O$_4$ to improve the
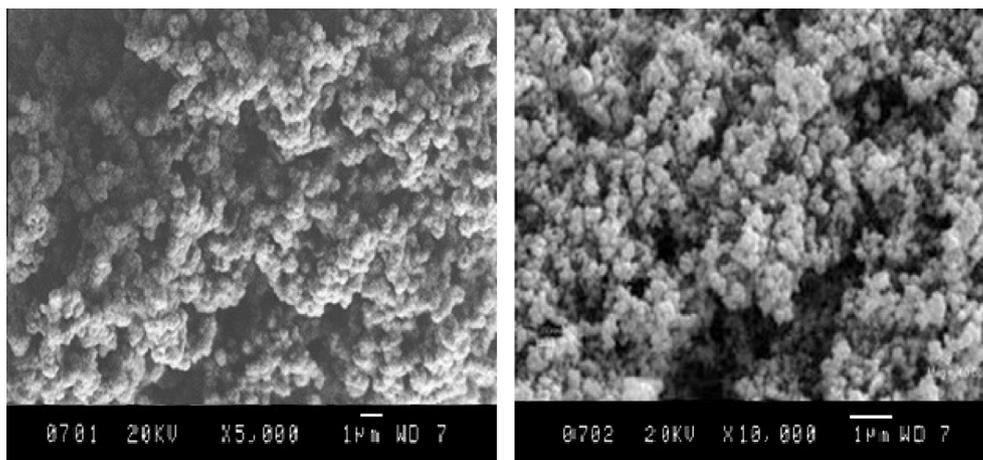

Figure 2 Scanning electron microscopy (SEM) image of synthesized Fe$_3$O$_4$-bpy-Ni(II).
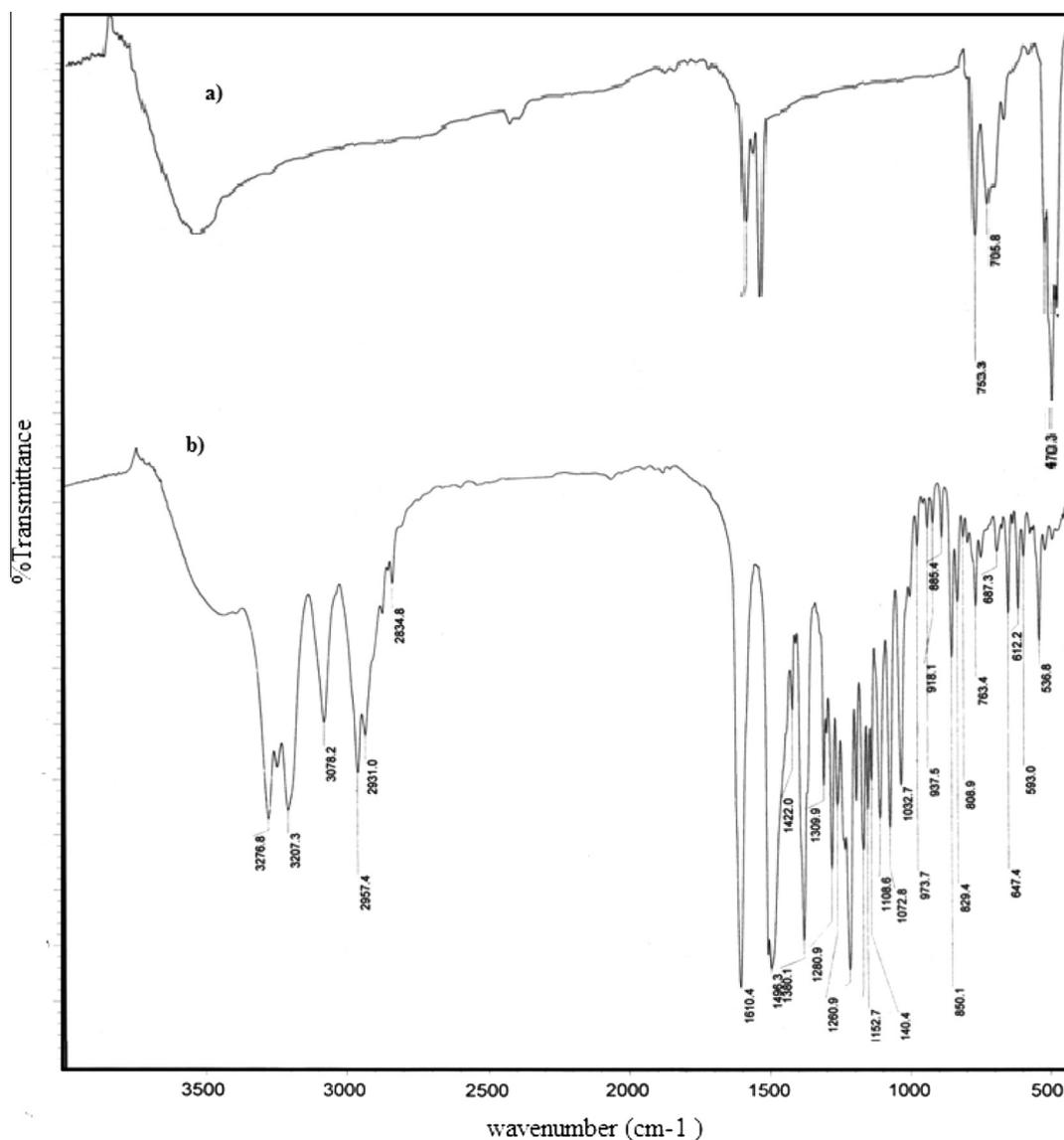
Figure 3   (a) FT-IR spectra of bare silica coated Fe_3O_4 and (b) Fe_3O_4-bpy-Ni(II) complex.

affinity of Fe_3O_4 nanoparticles for the target species. Initially Pyridine-2-yl-(3-trimethoxysilanyl-propyl)-amine (py-tmos) was synthesized and forms complex with [Ni(bpy)$_2$Cl$_2$]. This silane based Ni complex was coated over the surface of synthesized magnetic nanoparticle.

3.1. Catalyst characterization

The XRD pattern of nano sized catalyst Fe_3O_4-bpy-Ni(II) is shown in Fig. 1. The diffraction patterns and relative intensities of all the peaks matched well with those of magnetite (JCPDS card No. 19–0629). Indicative of a cubic spinel structure of the magnetite were observed that conforms well to the reported value (Yang et al., 2005; Giri et al., 2005). The crystallite size, calculated from the Scherrer formula, was found to be about 30 nm; XRD peaks at $2\theta = 35.46$ and 15.3 indicate the formation of nickel complex (Fig. 1a). No substantial variation was observed in the XRD patterns of fresh and used catalysts, revealing the retention of the original structure of Fe_3O_4 in the

used catalyst (Fig. 1b). The presence of a broad peak at 25–29 is in a good agreement with the amorphous structure of silica layer. The elemental analysis of the nano catalyst Fe_3O_4-bpy-Ni(II) before the reaction by AAS which indicated the content of the Ni about 7.25%. Atomic absorption analysis was carried out by direct method to estimate the total metal content. A number of reference standard solutions of each metal were prepared in various concentration ranges. Absorbances of these solutions were measured at the specific wavelength of each metal using the background correction technique. Calibration graphs were plotted for metal solutions. The concentrations of unknown solutions were calculated from their respective absorbances by using the standard values (see Fig. 2).

The morphology of the sample was investigated with scanning electron microscopy (SEM) Fig. 2 which shows Fe_3O_4-bpy-Ni(II) catalyst to be in nanostructure. This may be the result of the presence of silane moiety, which acts as an immobilizing agent. These nanoparticles are generally random and not uniform.
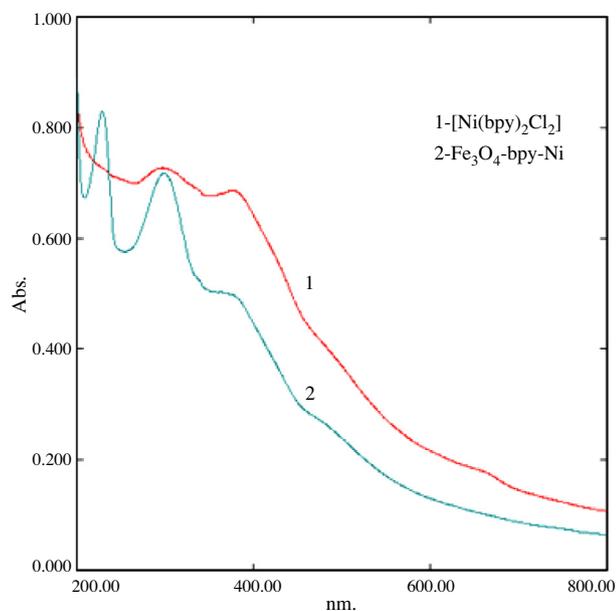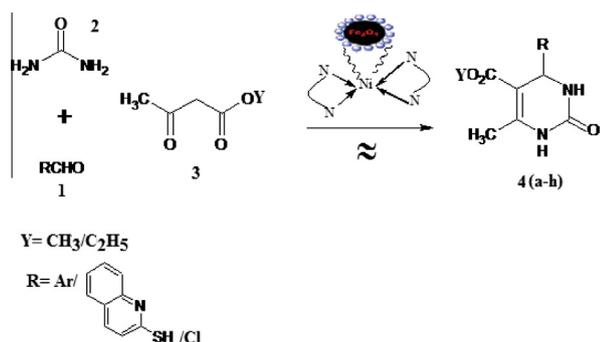
Figure 4 UV–Visible spectra of nano Fe$_3$O$_4$-bpy-Ni(II) catalyst.

Scheme 2

Figure 5 Recyclability of Fe$_3$O$_4$-bpy-Ni(II) catalyst.

respectively, confirming the successful immobilization of the nickel(II) complexes to the magnetic nanocomposites (McWhinnie and Miller, 1969).

To study the surface group on magnetic nanoparticle, very dilute samples were examined by ^{1}H NMR (Willis et al., 2005), ^{1}H NMR resolved spectra of ligands bound to a paramagnetic nanocrystal are difficult to perform due to large broadening effects caused by paramagnetic features.

3.2. Catalytic reactivity

To demonstrate the coordination chemistry found at the surface of these particles, we decided to evaluate the catalytic reactivity through Biginelli condensation under MW conditions.

We have focused on the development of method for Biginelli reaction that would avoid the use of added acids, easy to perform and is economical for large scale preparations. Experiments were performed to achieve 3,4-dihydropyrimidine derivative by Biginelli reaction using Fe$_3$O$_4$-bpy-Ni(II) catalyst under microwave irradiation conditions. (Scheme 2).

To obtain the optimal reaction conditions, the synthesis of 5-Ethoxycarbonyl-4-phenyl-6-methyl-3,4-dihydropyridin-2(1H)-one (**4a**) was used as a model reaction. For this particular reaction, the effect of [Ni(bpy)$_2$Cl$_2$], [Ni(bpy)$_2$(py-tmos)]Cl$_{2,}$ (Fe$_3$O$_4$-bpy-Ni(II)) catalysts was examined under microwave and thermal conditions to evaluate their capabilities. The results are summarized in Table 1. A control experiment was conducted in the absence of Fe$_3$O$_4$-bpy-Ni(II) catalyst. Product (**4a**) was not obtained and the substrate remained unchanged, while good results were obtained in the presence of nano catalyst (Table 1, entries **4**), higher yield in shorter reaction time was obtained in both conditions when nano catalyst was used, while Ni complex also showed reasonable yield. Due to ease of separation of the catalyst, Fe$_3$O$_4$-bpy-Ni(II) nano catalyst was chosen as catalyst for all reactions.

A mixture of 0.01 mol of ethyl acetoacetate, 0.01 mol of urea, 0.01 mol of benzaldehyde and 15 mg of nano catalyst was irradiated under microwave in different solvents (10 mL). In order to select the appropriate microwave power, the model reaction was examined at microwave power (100–300 W) with controlled temperature (max. 130 °C) in the presence of nano particles. The best results were obtained at 200 W. Higher yield and shorter reaction time were attained at 200 W.

The FTIR spectrum for the silica coated magnetite nanoparticles (Fig. 3a) shows a stretching vibrational 3434 cm^{-1} which incorporates modes of the O–H bonds which are attached to the surface. The presence of an adsorbed water layer is confirmed by a stretch for the vibrational mode of water found at 1629 cm^{-1}. The absorption band at 705.8 cm^{-1} is attributed to the Fe–O bonds and 593 cm^{-1} for Fe$_3$O$_4$ (Inskeep, 1962). In the spectrum for the Fe$_3$O$_4$-bpy-Ni(II) catalyst (Fig. 3b) additional stretches are attributed to the presence of Aryl C–H stretches found at 2957 and 2834 cm^{-1}. The amine C–N stretch is found at 1292 cm^{-1} which was covered by a stronger absorption of Si–O at 1380 cm^{-1}. The band at 850 cm^{-1} is due to the presence of Fe–O–Si bonds in the sample. Spectrum shows bands at 1610, 1496, and 763 cm^{-1} for the bipyridine group, and 462 cm^{-1} is for Ni–N bond (Inskeep, 1962; Nakamoto, 1986).

The UV–vis absorption spectra of a suspension of silica-coated magnetic NPs and nickel(II) complex in ethanol are shown in Fig. 4. Compared to the spectra of [Ni(bpy)$_2$Cl$_2$] in ethanol the UV–vis absorption bands of the functionalized nickel(II) complex at 310 nm and 400–450 nm are assigned as the intraligand (IL) and the metal-to-ligand charge transfer (MLCT) transitions of the nickel(II) polypyridine complex,
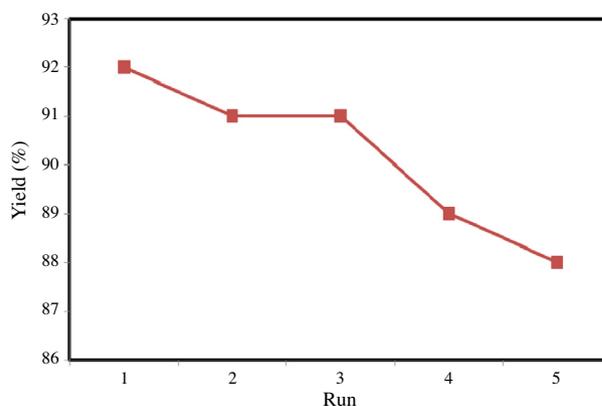
To compare the efficiency of the solvent-free versus solution conditions, the reaction was examined in several solvents under microwave. Thus, a model reaction was performed in different solvents (10 mL). The results are depicted in Table 2, lower yields and longer reaction times were observed in solution conditions. Therefore, the solvent-free method is more efficient.

The efficacy of the catalyst was further evaluated with a variety of substituted benzaldehydes possessing a wide range of electron-donating and electron-withdrawing functional groups, and the results are summarized in Table 2. The nature and the position of substitution in the aromatic ring did not have much effect on the reaction. This system was successfully applied to our previous research work (Ramesha et al., 2007) with 3-formyl-2-mercaptoquinoline. These afforded the corresponding products in excellent yields. Even though sterically hindered formyl quinoline (Table 3, entry **4–8**) underwent the condensation reaction in presence of the catalyst without any difficulty. As indicated in Table 2, Fe_3O_4-bpy-Ni(II) catalyst is highly efficient in catalyzing this three-component coupling reaction at elevated temperature and for different aldehydes it takes only 5–10 min for the completion of reactions.

To examine the reusability, the Fe_3O_4-bpy-Ni(II) catalyst was magnetically recovered from the reaction mixture and was reused as such for subsequent experiments (up to five cycles) under similar reaction conditions. The observed fact that yields of the product remained comparable in these experiments (Fig. 5), established the recyclability and reusability of the catalyst without significant loss of activity.

4. Conclusion

In conclusion we have developed the synthesis of functionalized iron oxide nanoparticle supported-nickel(II) complex and examined its catalytic activity for the synthesis of 3,4-dihydropyrimidine derivatives. The catalyst shows environmentally friendly character, and its magnetic recyclability helps in the development of a greener strategy. Moreover, the procedure offers several advantages including high yields, operational simplicity, clean reaction conditions and aspects of avoiding toxic catalyst.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.arabjc.2014.08.008.

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