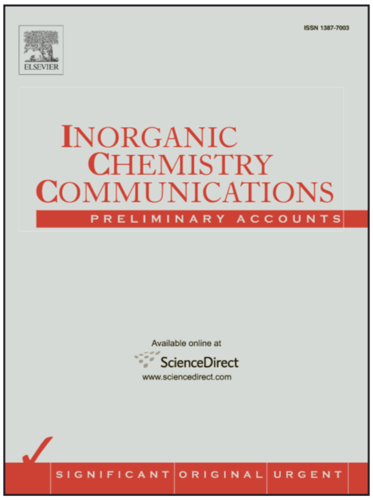

$CoFe_2O_4@SiO_2$-NH_2-Co^{II} NPs: an effective magnetically recoverable catalyst for Biginelli reaction

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$CoFe_2O_4@SiO_2-NH_2-Co^{II}$ NPs: an effective magnetically recoverable catalyst for Biginelli reaction.

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Abstract: Biginelli reaction entails acid-catalyzed one-pot synthesis of 3,4-dihydropyrimidin-2(1H)-ones (DHPMs) with simply-accessible initial substances, specifically, aldehyde, urea, and active methylene compound. DHPMs have stimulated a resurgence of attention in the previous two decades because of their broad-ranging pharmacological actions and the existence of varied all-natural products. Currently, green methods to asymmetric Biginelli reaction have been researched for anti-inflammatory DHPMs. In materials chemistry, DHPMs are increasingly decision applications in the creation of materials like polymers, adhesives, fabric dyes, etc. In light of the simplicity by which the Biginelli reaction is conducted, numerous interesting prospects expect its exploitation in variety fields. $CoFe_2O_4@SiO_2-NH_2-Co^{II}$ is herein turned out to be an effective catalyst at a three-component Biginelli reaction. The yield of the corresponding DHPMs was rather large (20 cases; average 92 percent). Finally, we herein suggest a procedure that shows lots of advantages and benefits such as the whole lack of solvents, mild reaction conditions, comparatively short reaction times. Also, $CoFe_2O_4@SiO_2-NH_2-Co^{II}$ NPs catalyst has been readily recovered from the reaction combination and reused, without the decrease of catalytic action.

Keywords: 3,4-dihydropyrimidin-2(1H)-ones, Biginelli reaction, $CoFe_2O_4@SiO_2-NH_2-Co^{II}$ NPs, urea, aldehyde, one-pot

1. Introduction

More than a century ago, the Biginelli reaction is a one-pot [1], three-component condensation of an aldehyde with β-keto esters and ureas or thioureas, commonly under acidic circumstances [2]. Dihydropyrimidine derivatives provide attractive pharmacological activities attributes inclusive antiviral, antimalarial, antihypertensive, and antibacterial properties, and different kinds of activities [2]. The main reactions are suffered from lower yields and limited substrate range, the developing pharmacological significance of dihydropyrimidines has led to the renewed investigation of the reaction conditions which has revealed a variety of suitable solvents (such as ionic liquids) and catalysts to improve the reaction [2-8]. Furthermore, the range of the Biginelli reaction has been broadened with alcohol instead of aldehydes as well as some alternative active hydrogen building blocks in place of β-keto esters [2-8]. Significantly, the effect of the stereogenic center considerably affects the biological activities of dihydropyrimidines. For instance, in Fig. 1, the R enantiomer of dihydropyrimidine, which is an antihypertensive agent, is shown to be more effective than its S enantiomer [9]. As a result, to enhance application range and potency in drugs getting enantioenriched materials is necessary. Over the years, some enantioselective synthetic protocols have been expanded. For the first time, the chiral ytterbium catalyst was used as an enantioselective catalyst for the Biginelli reaction, to afford the corresponding dihydropyrimidines in good efficiencies with excellent enantioselectivities [10].

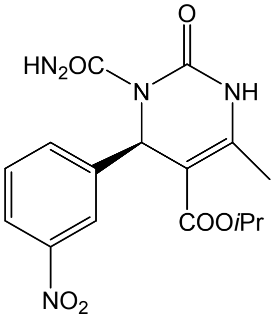


Fig. 1. Antihypertensive SQ 32926

In the presence of chiral amines (usually by achiral Brønsted acids as co-catalysts), pyrrolidinyl tetrazole, iodine, chiral Brønsted acids [2,11-13] proline derivatives, chiral ionic liquids, and in specific phosphoric acids [14-21] (and derivatives), asymmetric Biginelli reactions were then successfully done and provided aim chiral dihydropyrimidines has been obtained to excellent yields and enantioselectivities [17-21]. Multi-component reactions, especially the Biginelli reactions, are a reliable tool to form complex molecules with easiness and brevity. Truly, they allow the creation of corresponding products to be able to occur within a single operation through three or even more reactants, with bond-forming effectiveness, high atom-economy, adaptability with green solvents, and under mild circumstances. Therefore, they may be effectively classified as eco-compatible and sustainable procedures [22,23]. Though, some disadvantages exist, particularly the use of extremely toxic organic solvents, large values of catalyst, hard reaction conditions, and difficult and time-consuming target product separation. Consequently, the expansion of simple and environmentally friendly Biginelli procedures is in the requirement, and newly some fascinating green protocols have already been proposed [24].

While previously highlighted, valid and attractive techniques for the synthesis of dihydropyrimidines are generally recognized. Nevertheless, these reactions are generally done in organic solvents; catalysts are not reused and recovered.

Considering this and to additionally improve the catalytic efficiency of $CoFe_2O_4@SiO_2-NH_2-Co^{II}$ NPs (Fig. 2) which is an effective catalyst in Biginelli reaction, we thus report our investigations green Biginelli reactions between urea, aromatic aldehydes, and ethyl acetoacetate was done in the presence of the corresponding catalyst (Scheme 1).

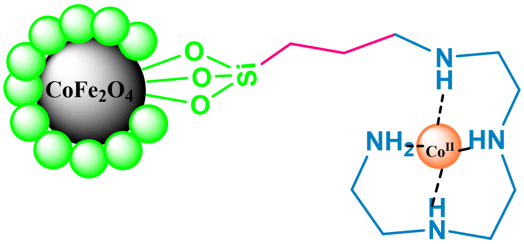
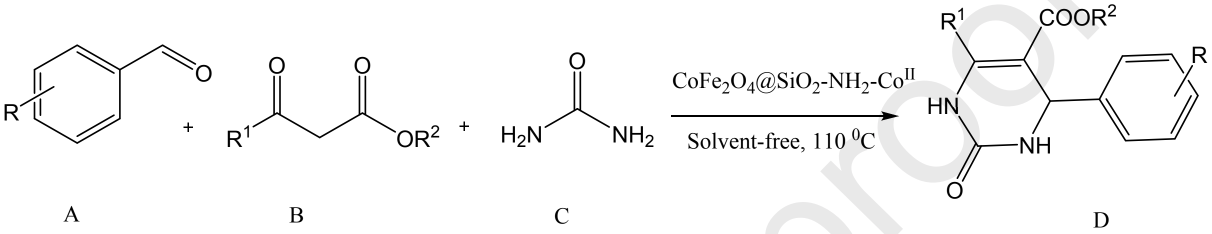


Fig. 2. CoFe$_2$O$_4$@SiO$_2$-NH$_2$-Co^{II} NPs



Scheme 1. Biginelli reaction catalyzed by CoFe$_2$O$_4$@SiO$_2$-NH$_2$-Co^{II} NPs

2. Experimental section

2.1. Chemicals

Reagents and solvents were produced in Merck or Fluka chemical companies. TLC on silica-gel polygram SILG/UV 254 plates were used to determine the purity of the products. An Electrothermal 9100 apparatus was used to measure melting points. A Perkin Elmer 781 spectrometer was used to take IR spectra in KBr pellets which were reported in cm^{-1}. A Bruker DPX-250 Avance instrument was used to measure ^{1}HNMR and ^{13}CNMR spectra at 250 MHz and 62.9 MHz in CDCl$_3$ or DMSO-d$_6$. The chemical shift was given in ppm relative to TMS as the internal standard. A Bruker D$_8$-advance X-ray diffractometer with Cu K$_\alpha$ (λ = 0.154 nm) radiation was used to carry out power X-ray diffraction (XRD). Using vibrating sample magnetometer (VSM) leak shore 7200, the magnetic properties were determined at 300 K Vsm leak shore. MIRA 3TESCAN-XMU spectrometer was used for scanning electron microscopy.

2.2. Catalyst preparation

2.2.1. Preparation of $CoFe_2O_4$ magnetic nanoparticles

At first, iron (III) nitrate nonahydrate and cobalt (II) nitrate hexahydrate in a molar proportion of 2:1 were dissolved and sonicated for 30 min within water (100 mL). At that point, NaOH (1M) was additional to the solution and vigorous stirring continuously for 2 h at 80°C. The respective black precipitate powder easily is separated by an external magnet and washed with DI water as long as the OH^- ion free and vacuum oven drying was carried out for 10 h at 80 ^oC [25].

2.2.2. Preparation of $CoFe_2O_4@SiO_2$ magnetic nanospheres

0.15 gr of $CoFe_2O_4$ were added to 50 mL EtOH (80 %) and dispersed under ultrasound conditions for 30 min. Afterward, the pH of the mix should be 11–12. $NH_3.H_2O$ solution should be added to increase the pH of the mixture to 11-12. In the next step, 2 mL of TEOS added drop by drop into the mixture with vigorous stirring at 25 ^oC for 20 h. Then, by an external magnet, the gray powder which was the synthesized $CoFe_2O_4@SiO_2$ was separated and washed with deionized water. Subsequently, at 80 ^oC, $CoFe_2O_4@SiO_2$ was dried for 10 h [25].

2.2.3 Preparation of NH_2-Pr

A mixture of triethylenetetramine (1 mmol) and triethanolamine (2 mmol) was dissolved in 30 mL EtOH (solution A) and 3-chloropropyltriethoxysilane (APTMS) were dissolved in 20 mL EtOH (solution B). Afterward, for 24 hours under reflux conditions, solution B was drop by drop added to this solution A. Eventually, remove the solvent by a rotary evaporator and precipitate the product to give a yellow powder.

2.2.4 Preparation of $CoFe_2O_4@SiO_2$ -NH_2

With 20 mL dry toluene, 0.7 mL NH_2-Pr was dissolved (solution A). In the next step, 0.2 g $CoFe_2O_4@SiO_2$ was dissolved in dry toluene (30 mL) (solution B). The solution A was added drop by drop into the solution B. Then, Under Ar atmosphere, the resulting mixture was stirred for 48 h at 105 ^{o}C. The precipitate was washed with toluene and ethanol and at 105 ^{o}C, $CoFe_2O_4@SiO_2$ $-NH_2$ was dried for 12 h [26].

2.2.5 Preparation of $CoFe_2O_4@SiO_2$ $-NH_2-Co^{II}$ NPs

To a suspension of $CoFe_2O_4@SiO_2$ $-NH_2$ (1 g) in 20 mL EtOH, Co $(NO_3)_2.6H_2O$ (4.2 mmol, 0.8 g in 20 ml EtOH) was added. The mixture is stirred under reflux for 25 h. By an external magnet, the resulting $CoFe_2O_4@SiO_2$ $-NH_2-Co^{II}$ NPs product was collected and washed repeatedly with EtOH. Then, dried beneath vacuum for 12 h at 80 ° C [27].

2.2.6 General procedure for the Biginelli reaction

A combination of aldehyde (1 mmol), urea or thiourea (1 mmol), β-keto esters (1 mmol), and $CoFe_2O_4@SiO_2$ $-NH_2-Co^{II}$ NPs (0.01 g) was stirred by refluxing for 15 min (Scheme 1). Afterward the end of the reaction, the combination was cooled down to ambient temperature and $CoFe_2O_4@SiO_2-NH_2-Co^{II}$ was collected via an external magnet. The reaction mix was crystallized using ethanol [28].

Selected spectral data

Ethyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (compound 1, Table 4): Solid, mp 202-204 °C, IR (KBr): 3416, 3232, 3107, 2935, 1701, 1648, 1598 cm^{-1}, ^{1}H NMR (DMSO-d_6): δ = 9.17 (s, 1 H), 7.72 (s, 1 H), 7.21–7.32 (m, 5 H), 5.14 (s, 1 H), 3.98 (q, J = 7.2 Hz, 2 H), 2.24 (s, 3 H), 1.08 (t, J = 7.2 Hz, 3 H), ^{13}C NMR (DMSO-d_6): δ = 165.4, 152.2, 148.4, 144.9, 128.4, 127.3, 126.3, 99.3, 59.2, 54.0, 17.8, 14.1

Methyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (compound 12, Table 4): Solid, mp 204-206 °C, IR (KBr): 3366, 3219, 3105, 2945, 1711, 1635, 1496 cm^{-1}, ^{1}H NMR (DMSO-d_6): δ = 9.21 (s, 1 H), 7.76 (s, 1 H), 7.31 (t, J = 8.4 Hz, 5 H), 5.44 (s, 1H), 5.16 (s, *J* = 2.8 Hz, 1 H), 4.01 (q, 2 H), 1.11 (t, 3 H), ^{13}C NMR (DMSO-d_6): δ = 165.81, 152.62, 148.83, 145.34, 128.86, 127.74, 126.72, 99.73, 59.66, 54.43, 18.25, 14.54.

3. Results and discussion

FT-IR analysis

Fourier transform infrared (FT-IR) spectroscopy indications the adjustment of $CoFe_2O_4$ NPs (a), $CoFe_2O_4@SiO_2$NPs (b), Pr-NH_2 (c), $CoFe_2O_4@SiO_2$-NH_2 NPs(d), $CoFe_2O_4@SiO_2$-NH_2-Co^{II} NPs (e). As appeared in Fig. 3a frequency 3398cm^{-1} O-H stretching by the hydroxyl groups attached to the surface of the cobalt oxide and showed that water molecules chemically adsorbed by the surface of the metal during the synthesis process. Furthermore, the frequency at 588cm^{-1} is the presence of an oxygen metal bond. The frequency at 1623 cm^{-1} is due to O-H in-plane and out of plane bending mode. The presence of water adsorption bonds, in and out of plane and oxygen metal bonds approves the existence of Co in the samples synthesized. Fig. 3b adsorption broadband at 1097 cm^{-1} is associated with Si-O. TETA grafted existence can be confirmed by the appearance of three different absorption bands at 2914, 1945, and 1456 cm^{-1} which can be attributed to the N-H bending vibrations (primary and secondary amines) (Fig. 3d). Besides, the vibration band for binding N-H stretching (3500-3000 cm^{-1}) cannot be defined with precision, due to overlap with the broad absorption band of OH…OH, bond. When Co^{II} coordination, the intensity of the bending vibration characteristic absorption band related to N-H was considerably decreased (Fig. 3e)

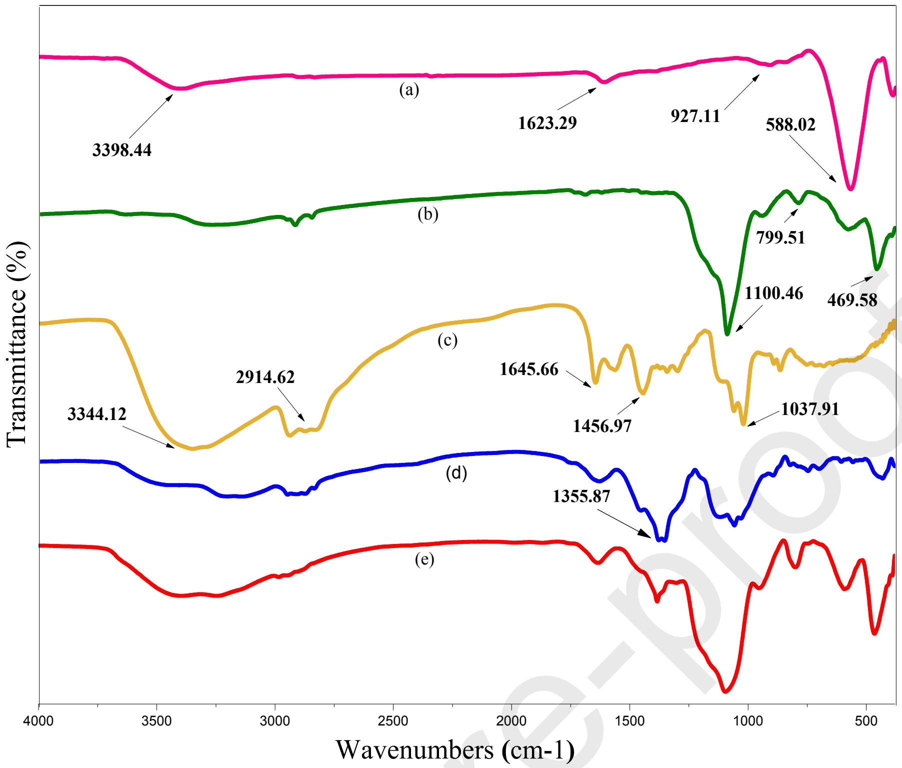


Fig. 3. FT-IR spectra of $CoFe_2O_4$ NPs (a), $CoFe_2O_4@SiO_2$NPs (b), Pr-NH_2 (c), $CoFe_2O_4@SiO_2$-NH_2 NPs(d), $CoFe_2O_4@SiO_2$-NH_2-Co^{II} NPs (e)

XRD analysis

Diffraction spectra X-ray uncoated particles and coated with the dispersion and the silica agents are shown in Fig. 4. From Fig. 4, it is clear that the synthesized nanoparticles $CoFe_2O_4$ using the decomposition method are characteristic of the cubic spinel phase corresponding to $CoFe_2O_4$ (JCPDS 22-1086). In Fig. (4) a wideband appears in each observation spectrum. This is usually typical of amorphous components and crystalline materials regarding ultrasmall wherein the diffraction peaks cannot be properly resolved.

It is reported that the amorphous SiO_2 affects the microstructure of composite materials significantly and gradually decreases with the increasing concentration of SiO_2. Overall, the growth of grain ferrites may be influenced in the presence of pores or inclusions in the grain boundaries. Diffraction patterns distinctive X-ray at $2\theta = 18.1°, 20.9°, 30.2°, 35.5°, 43.3°, 57.2°$, 62.8° and 74.6° of $CoFe_2O_4$ @ SiO_2-NH_2 Co^{II} NPs identified by an evaluation data literature and confirm the particles are polycrystalline structure.

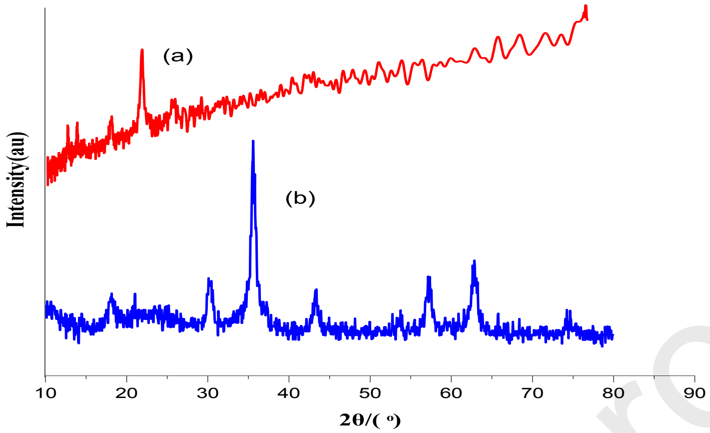


Fig. 4. XRD pattern of $CoFe_2O_4$ (a), and $CoFe_2O_4$ @ SiO_2-NH_2 Co^{II} (b)

TEM analysis

According to the TEM images, the average size $CoFe_2O_4$ @ SiO_2-NH_2 Co^{II} magnetic nanoparticles are approximately 20-90 nm (Fig. 5). Although the size of $CoFe_2O_4$ nanoparticles is about 2-6 nm. The TEM image shows the successful coating of the silica layer around the magnetic core.

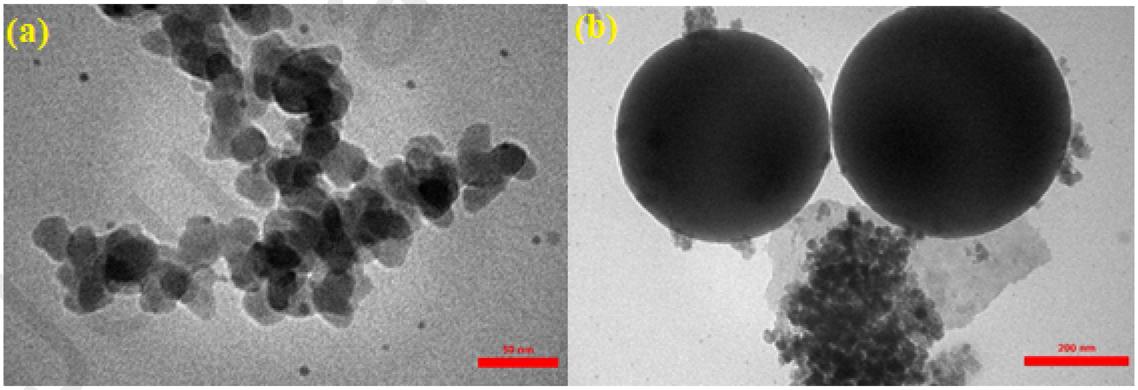
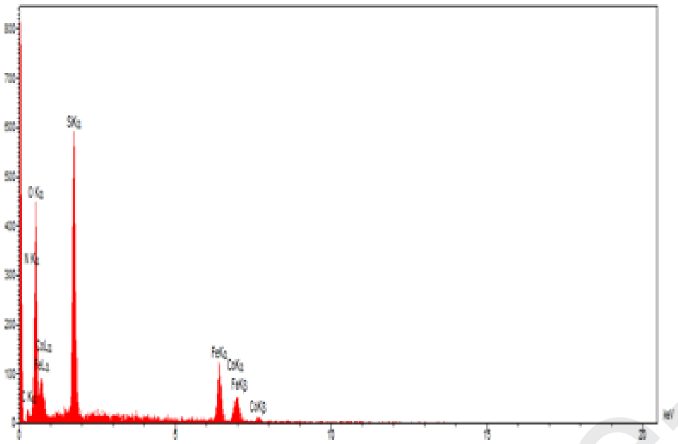


Fig. 5. TEM images of $CoFe_2O_4$ (a) $CoFe_2O_4$ @ SiO_2-NH_2 Co^{II} (b)

EDX analysis

EDX spectrum of $CoFe_2O_4$ @ SiO_2-NH_2 Co^{II}, which is shown in Fig. 6, clearly reveals the presence of all the major elements of the expected (Fe, Co, Si, N, C) consisting of a composite of these three components.



Elt	Line	W%	A%
C	Ka	8.66	14.90
N	Ka	4.28	6.32
O	Ka	44.34	57.27
Si	Ka	16.08	11.83
Fe	Ka	17.60	6.51
Co	Ka	9.04	3.17
		100.00	100.00

Fig. 6. EDX spectrum of $CoFe_2O_4$ @ SiO_2-NH_2 Co^{II}

VSM analysis

The magnetization curves of $CoFe_2O_4$ NPs and silica-coated $CoFe_2O_4$ nanocomposites, and $CoFe_2O_4$ @ SiO_2-NH_2 Co^{II} at 25 °C demonstrate in Fig. 7. According to Fig. 7(a), the saturation magnetization of $CoFe_2O_4$ NPs was 39.92 emu/g. Additionally, Fig. 7 (b,c) demonstrates the magnetization curves of silica-coated of $CoFe_2O_4$ nanocomposite and silica-coated of $CoFe_2O_4$ nanocomposite with diverse dispersing agents, for example, NH_2 and Co^{II} (in $CoFe_2O_4$ @ SiO_2-NH_2 Co^{II}). The saturation magnetization values for all these nanoparticles are 28.92, and 6.25 emu/g respectively. These results reveal a large decline in the saturation magnetization of this $CoFe_4O_2$@SiO_2 nanocomposite in comparison with the $CoFe_2O_4$ NPs. We can see in Fig. 4 variations in the magnetic attributes of the nanocomposites in effect the surface modification with the dispersing agents. It has been reported [29] that the magnetic behavior of the system due to the presence of the dispersing agent on the surface of the NPs, can change the surface anisotropy and the magnetic moment. The magnetic characteristics of nanoparticles are a mixture of several anisotropy mechanisms, such as surface anisotropy, magnetocrystalline anisotropy, and interparticle interactions, coating ferrite NPs by silica will probably influence interparticle interactions into the net anisotropy and the participation of the surface anisotropy [30].

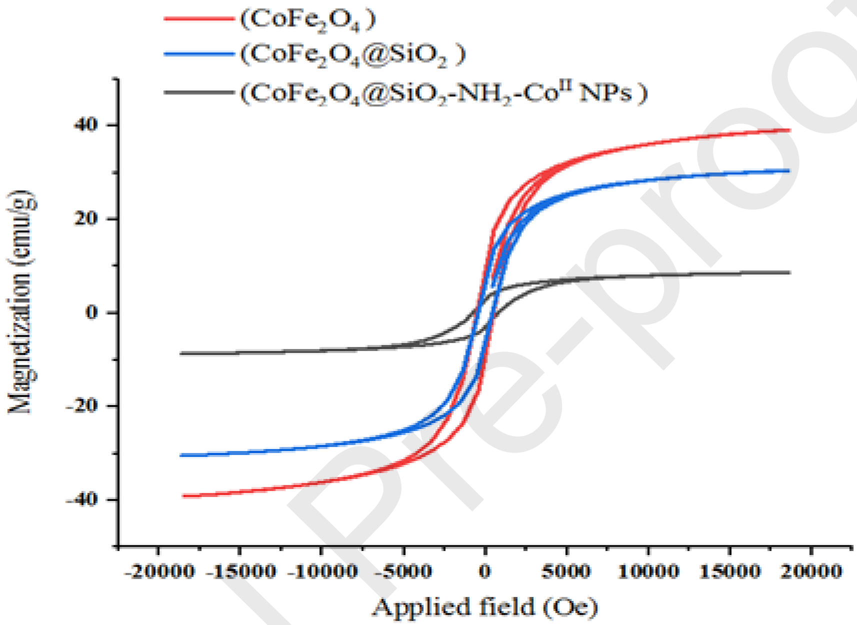


Fig. 7. VSM spectrum of $CoFe_2O_4$ NPs, $CoFe_2O_4@SiO_2$NPs, $CoFe_2O_4@SiO_2$-NH_2-Co^{II} NPs

3.5. Reaction optimization

In the presence of a catalytic amount of $CoFe_2O_4@SiO_2$ -NH_2-Co^{II} under varying circumstances, the model reaction among ethyl acetoacetate, urea, and benzaldehyde was initially investigated for the synthesis of dihydropyrimidines. As mentioned in Table 1, under neat conditions, under heating at 110°C and in the presence of 0.01 g of catalyst, the best result was obtained, which gave the corresponding product in excellent yield.

The amount of catalyst was also changed. Table 1 summarizes the results. The results presented that the reaction of the catalyst concentration affects performance crucial. Under the same conditions, reducing the catalyst concentration afforded lower yields result. The product decreased significantly with increasing catalyst concentration (more 0.01g). Consequently, because the reaction is completed within high performance, this condensation is better catalyzed by 0.01 g of $CoFe_2O_4$ @ SiO_2-NH_2 Co^{II} NPs. This product decreased significantly with increasing catalyst concentration (over 0.01 g). As a result, because the reaction is finished in high yield, it's the best condensation catalyzed by 0.01 g $CoFe_2O_4$ @ SiO_2 -NH_2-Co^{II} NP.

Table 1. Optimization of various amounts of $CoFe_2O_4@SiO_2$-NH_2-Co^{II} for the model reaction[a].

Entry	Catalyst (mg)	Temperature (℃)	Time (min)	Yield (%)
1	10	110	15	96
2	50	110	15	96
3	70	110	15	97
4	0	110	15	Trace
5	$CoFe_2O_4$	110	15	15
6	$CoFe_2O_4@SiO_2$	110	15	18
7	$CoFe_2O_4@SiO_2$-NH_2	110	15	20

Reaction conditions: benzaldehyde (1 mmol), urea (1 mmol), ethyl acetoacetate (1 mmol), 110 °C, solvent free.

The reaction was studied in diverse solvents (Table 2). The results showed that the reaction efficiency is influenced by different solvents. Low yield (10-68%) was obtained by acetonitrile, water, ethanol, and *n*-hexane while the results can be enhanced in the absence of solvent (solvent-free). As a result, 96% of the yield was obtained in the solvent-free.

Table 2. Optimization of various solvent condition for the model reaction^{a}.

Entry	Solvent	Temperature (℃)	Time (min)	Yield* (%)
1	Solvent-free	110	15	96
2	n-Hexane	Reflux	360	10
3	CH_3CN	Reflux	360	37
4	H_2O	Reflux	360	20
5	EtOH	Reflux	360	68
6	DCM	Reflux	360	15
7	EtOH/H_2O	Reflux	360	55

Reaction conditions: benzaldehyde (1 mmol), urea (1 mmol), ethyl acetoacetate (1 mmol), 110 ^{o}C, 0.01 g of $CoFe_2O_4@SiO_2$-NH_2-Co^{II}.

By carrying out the model reaction at different temperatures, the effect of the temperature of the reaction was studied. The best result was obtained within 110 ^{o}C (Table 3).

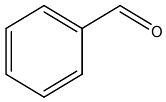
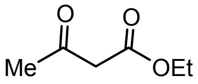
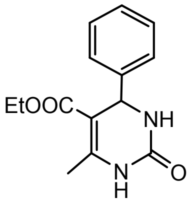
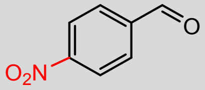
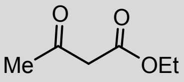
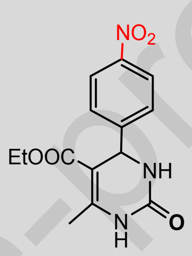
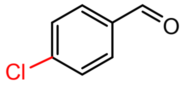
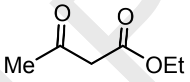
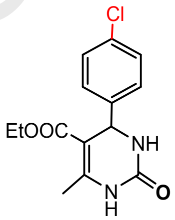
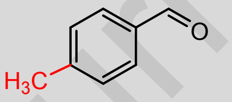
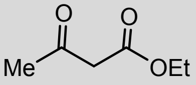
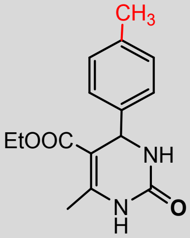
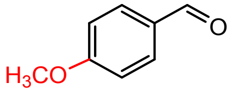
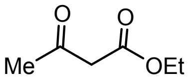
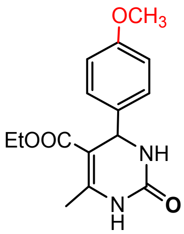
Table 3. Optimization of various temperature for the model reaction^{a}.

Entry	Temperature (oC)	Yield (%)
1	25	15
2	50	34
3	80	72
4	110	96

Reaction conditions: benzaldehyde (1 mmol), urea (1 mmol), ethyl acetoacetate (1 mmol), solvent free, 0.01 g of $CoFe_2O_4@SiO_2$-NH_2-Co^{II}.

To additional use the scope of this reaction was carried out the reactions of diversely substituted aldehydes, β-keto esters, carrying either electron-withdrawing or electron-donating groups with urea. Good results are obtained from the target products irrespective of electronic substituent effects (Table 4). Table 4 summarizes the results. In all cases, pay by dihydropyrimidines in good to excellent results (86-98%), the reaction takes place easily.

Table 4. Synthesis of novel functionalized biginelli reaction derivatives by $CoFe_2O_4@SiO_2\text{-}NH_2\text{-}Co^{II}$ catalyst[a].

Entry	A	B	Product (D)	Time(min)	Yield*(%)
1				15	96
2				15	98
3				15	95
4				15	94
5				18	95

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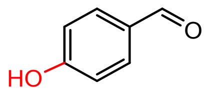
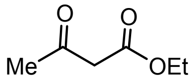
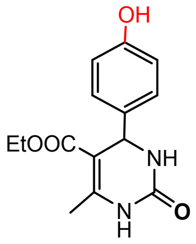
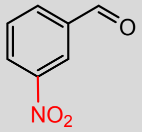
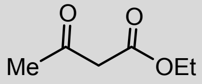
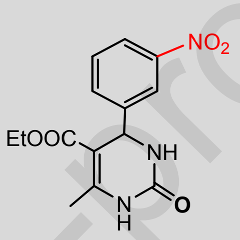
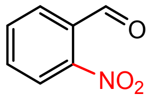
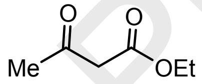
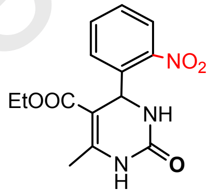
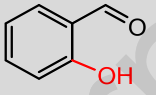
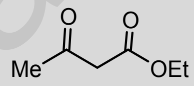
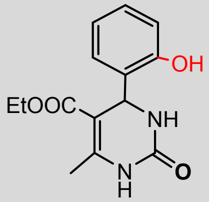
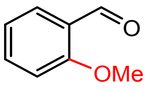
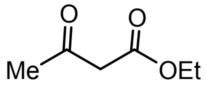
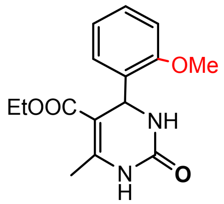
6				20	90
7				15	95
8				15	94
9				20	88
10				18	92

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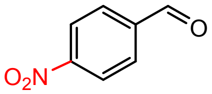
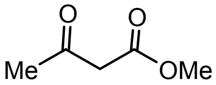
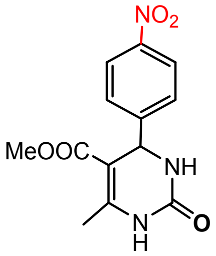
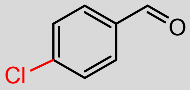
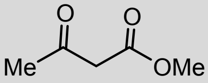
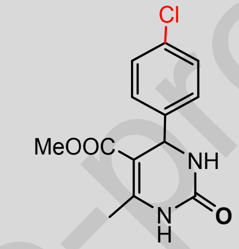
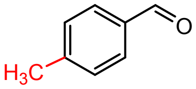
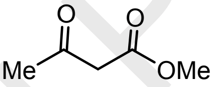
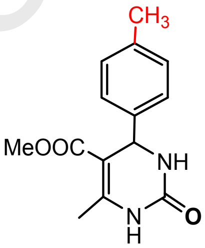
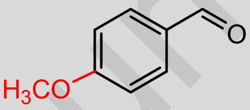
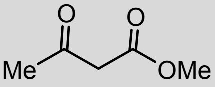
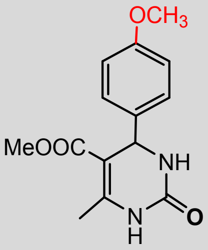
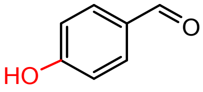
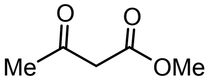
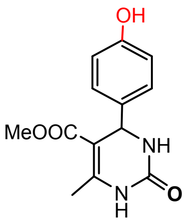
11				25	95
12				25	93
13				30	90
14				30	89
15				35	87

Countinued Table 4.

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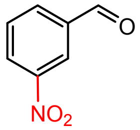
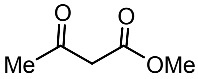
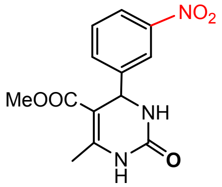
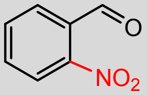
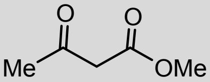
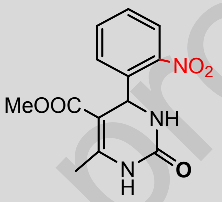
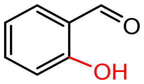
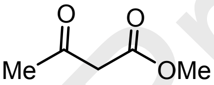
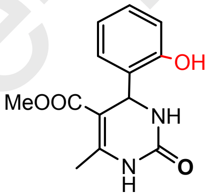
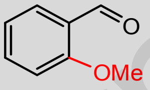
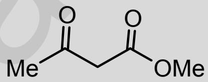
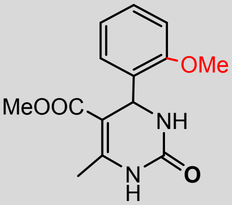
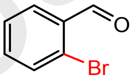
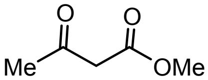
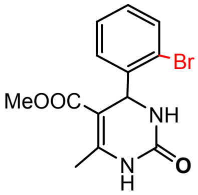
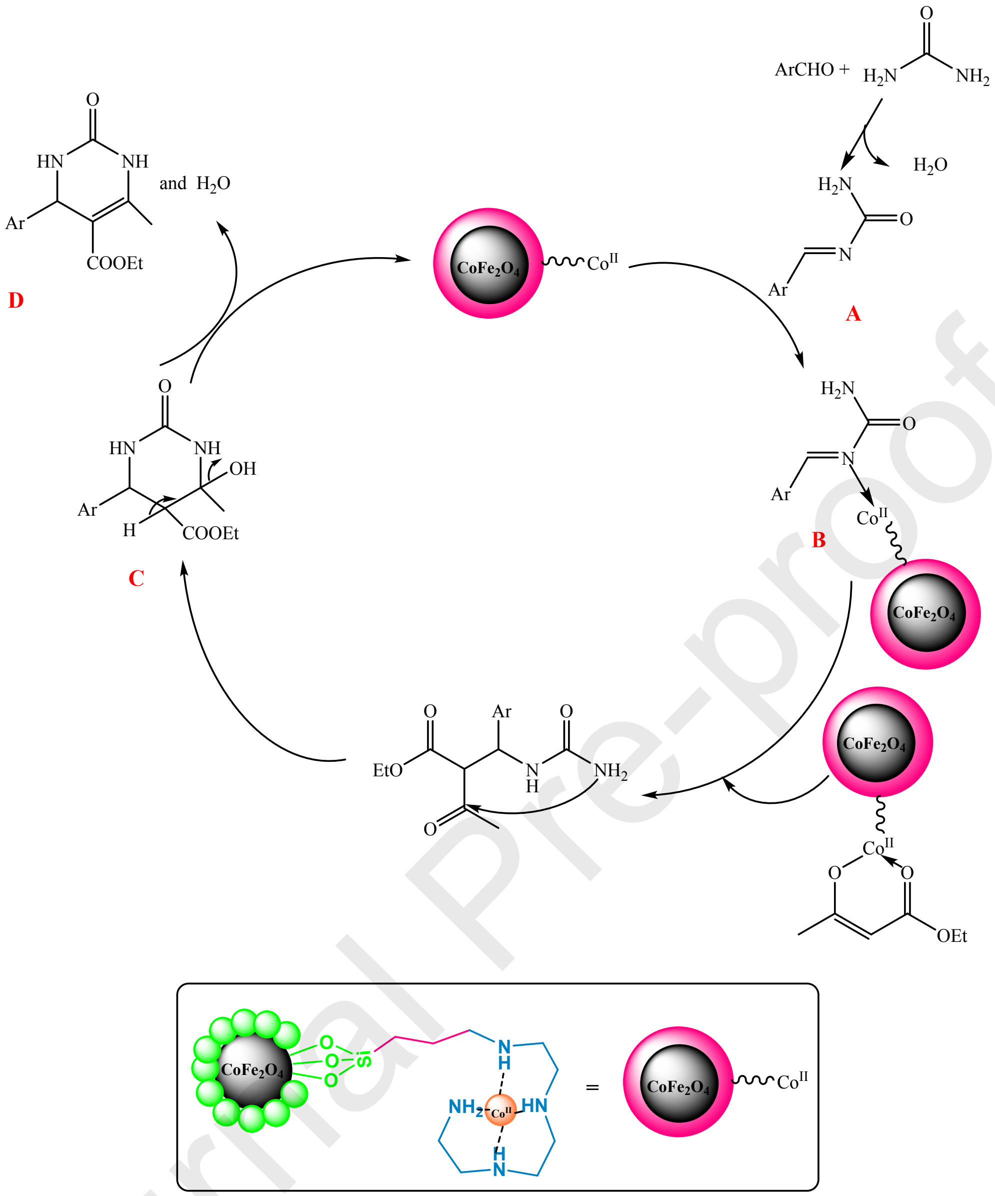
16				20	93
17				20	92
18				35	86
19				30	88
20				20	90

Compared with most of the work reported, this catalyst illustrations excellent catalytic activity and good results (96%) in a shorter time (see Table 5).

Table 5. Comparison of results utilizing $CoFe_2O_4@SiO_2-NH_2-Co^{II}$ with diverse catalysts

Entry	Catalyst	Solvent	Condition	Time (h)	Yield (%)^b	ref
1	$ZrCl_4$	C_2H_5OH	reflux	4	90	29
2	$Cu(NH_2SO_3)_2$	CH_3COOH	100	5	79	30
3	$Ag_3PW_{12}O_{40}$	EtOH	80	3	95	31
4	$H_3PMo_{12}O_{40}$	CH_3COOH	reflux	5	80	32
5	Fluoroboric acid	Neat	45	0.5	95	33
6	CaF_2	EtOH	45	2	98	34
7	Chloroferrate(III)Ionic Liquid	Neat	90	2	90	35
8	Triethyl ammonium tetrafluoroborate	Neat	145	1	80	36
9	$CoFe_2O_4@SiO_2-NH_2-Co^{II}$	Solvent-free	110	0.25	96	This work

In the suggested mechanism, the first step involves the imine formation (A). Co^{2+} in coordination with imine nitrogen atom to give an intermediate (B), which activates the C=N toward nucleophilic attack. Also, the complexation-ketoester with Co^{2+} enhances the nucleophilicity of α-carbon-enolate, which simplify the attack of carbon imine and amide group free of attack of carbonyl carbon outcomes in the formation of heterocyclic six-membered intermediate (C) which, as shown in scheme 2 by dehydration give desired DHPMs (D) [37].



Scheme 2. Biginelli reaction mechanism catalyzed by $CoFe_2O_4@SiO_2\text{-}NH_2\text{-}Co^{II}$

The catalyst may be recovered using an external magnet at the end of the reaction. Ethanol is utilized to wash the catalyst recycle which is then subjected to a next reaction process. The results of the performance of the product is only slightly reduced after six runs (Fig. 8).

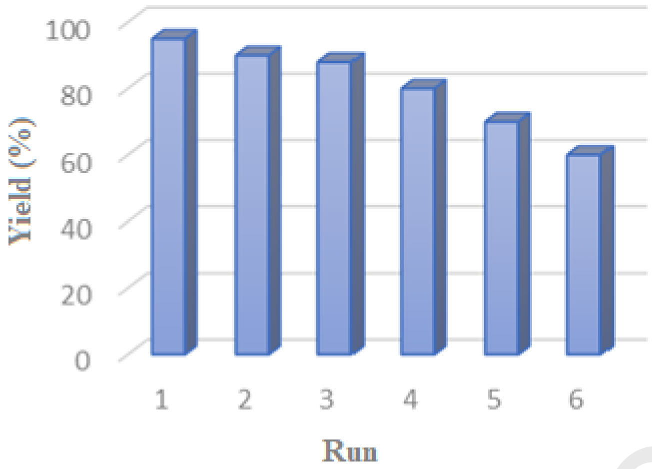


Fig. 8. Recyclability of $CoFe_2O_4@SiO_2$ -NH_2-Co^{II} NPs in the Biginelli reaction

Conclusions

In conclusion, using $CoFe_2O_4@SiO_2$ -NH_2-Co^{II}, a facile methodology was developed to prepare 3,4-dihydropyrimidin-2(1H)-ones derivatives nanoparticles as an efficient heterogeneous catalyst. At 110 ^{o}C, the catalyst represents an outstanding activity in solvent-free conditions. For a wide variety of substrates, a good to high yield of products was obtained within short reaction times. FT-IR, SEM, VSM, and XRD analyses were used to characterize the catalyst. With the negligible loss of efficiency, the catalyst was recycled for at least five consecutive runs. The advantages of the catalyst include the performance, preparation from cheap and accessible materials, environmentally benign nature, and cost-effectiveness. These advantages make it a suitable alternative for the preparation of 3,4-dihydropyrimidin-2(1H)-ones. Moreover, separation and recovery of the catalyst for another catalytic recycling are easy.

Acknowledgments

We gratefully acknowledge the support of this work by the University of Birjand.

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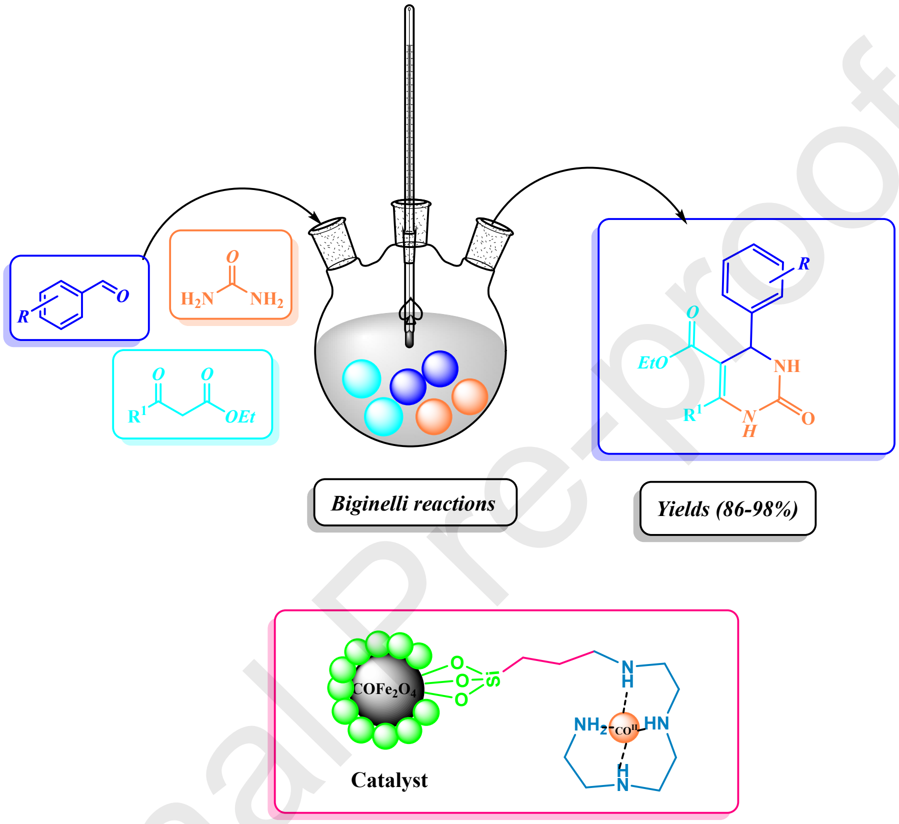
Graphical Abstract



Highlights

- The reused several times without significant loss of reactivity.

- $CoFe_2O_4$@SiO_2-NH_2-Co^{II} NPs: an effective magnetically recoverable catalyst for Biginelli reaction.presented excellent efficiency.

- Concise reaction time and excellent yields of products.

$CoFe_2O_4@SiO_2-NH_2-Co^{II}$ NPs: an effective magnetically recoverable catalyst for Biginelli reaction.

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Conflict of interest:

The authors declare that there is no conflict of interest.