



Synthesis and characterization of $\text{Fe}_3\text{O}_4@\text{Sal}@\text{Cu}$ as a novel, efficient and heterogeneous catalyst and its application in the synthesis of 2-amino-4H-chromenes

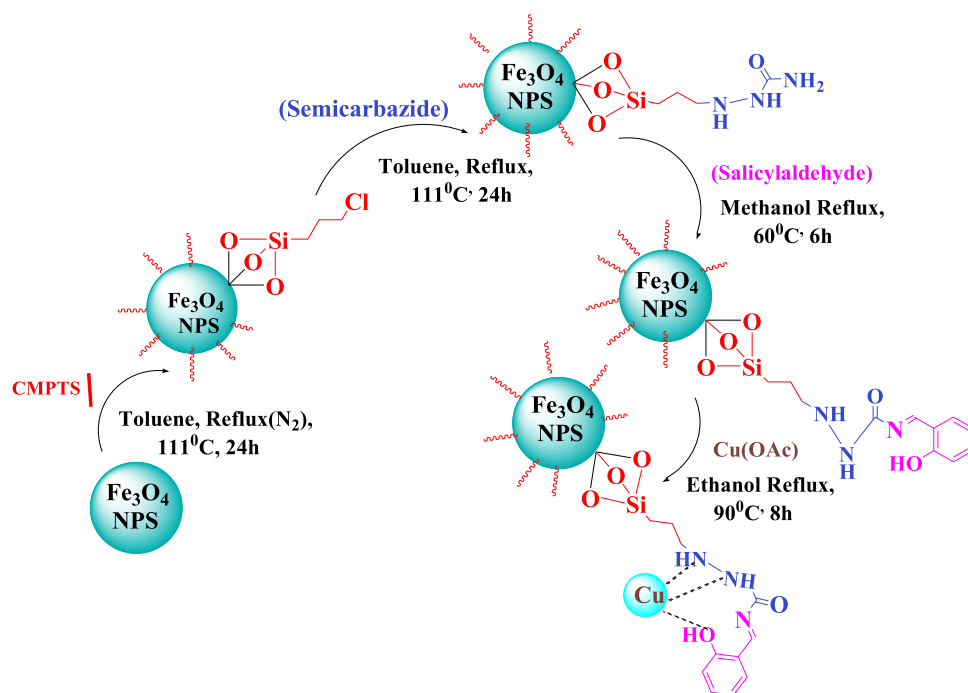
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Abstract

This research paper presents the synthesis and characterization of the magnetic nanoparticle, $\text{Fe}_3\text{O}_4@\text{Sal}@\text{Cu}$, [$\text{Fe}_3\text{O}_4@\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{NH}-\text{CO}-\text{N}=\text{CH}-(2-\text{HO}-\text{C}_6\text{H}_4-)\text{Cu}$] as a green and retrievable catalyst. This catalyst was characterized by FTIR, XRD, EDX and TGA analyses. In addition, the catalytic activity of this new catalyst was investigated for the synthesis of 2-amino-4H-chromenes by producing good-to-excellent yields under mild reaction conditions. The other advantages of the developed nanocatalyst are its ecofriendliness, being easy to handle, high reusability and being magnetically separable. The synthesis of some new derivatives of 2-amino-4H-chromenes in the presence of this nanocatalyst is also reported.

Graphical abstract



Keywords $\text{Fe}_3\text{O}_4@\text{Sal}@\text{Cu}$ · Nanoparticle · 2-amino-4H-chromenes · Salicylaldehyde

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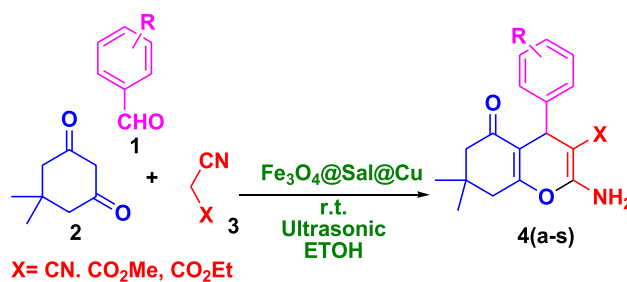
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Introduction

The use of magnetic nanocatalysts is an interesting area for the development of sustainable and green procedures due to external magnetic separation and no need for catalyst filtration or centrifugation and providing simple and practical method for the recovering of these catalysts [1]. In addition, multi-component reactions (MCRs) are very powerful weapons in the organic and medicinal chemistry for the preparation of the bulky products in a one-pot and almost one-step from small starting materials [2–7]. The MCRs for the synthesis of 2-amino-4H-chromenes derivatives have also gained considerable attention in organic synthesis such as synthesis of 2-amino-4H-chromenes derivatives using nano-ZnO catalyst [8], under solvent-free condition using MOF-5 [9], choline chloride/urea [10], nanocrystalline MgO [11], by $\text{Fe}(\text{ClO}_4)_3/\text{SiO}_2$ [12], on water $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ -catalyzed synthesis of 2-amino-4H-chromenes [13], the synthesis of 2-amino-4H-pyran derivatives using DABCO-CuCl complex [14], preparation of 3-amino-1H-chromenes using ZnO nanoparticles thin-film [15], synthesis of 4, 5-dihydropyrano [c] chromene derivatives over TiO_2 nanoparticles [16] and synthesis of aminobenzochromenes using $\text{Ag}_2\text{Cr}_2\text{O}_7$ nanoparticles [17].

Also, copper-catalyzed synthesis of chromenes has been already extensively reported in the literature, especially which supported copper catalyst on magnetic nanoparticles [18] such as one-pot synthesis of 2-amino-4H-chromene derivatives by MNPs@Cu [19, 20], sonochemically promoted preparation of silica-anchored cyclodextrin derivatives for efficient copper catalysis [21] and synthesis of benzimidazole derivatives using Cu-Schiff base complexes embedded over MCM-41 [22].

The combination of magnetic nanocatalysts and multi-component reactions will become a worthy protocol for the introducing of green procedure in green synthesis [23–32]. In addition, due to useful biological activities in the field of medicinal chemistry [33] and to have anti-cancer and anti-coagulant activities of 2-amino-4H-chromenes [34] and to evaluate catalytic activity of prepared catalyst, $\text{Fe}_3\text{O}_4@\text{Sal}@\text{Cu}$ was utilized in the one-pot preparation of 2-amino-4H-chromenes using aryl aldehydes, dimedone and malononitrile, ethyl and methyl 2-cyanoacetate in good-to-high yield in ethanol at room temperature (Scheme 1).



Scheme 1 Synthesis of 2-amino-4H-chromenes using $\text{Fe}_3\text{O}_4@\text{Sal}@\text{Cu}$

Results and discussion

Characterization of the nanocatalyst

The FTIR spectra of the catalyst are shown in Fig. 1. The broad band at 3436 cm^{-1} confirms the presence of NH and OH group of amide, amine and phenolic OH, loaded on the surface of $\text{Fe}_3\text{O}_4@\text{Sal}@\text{Cu}$. The band 1615 cm^{-1} is related to C=O. The band in 573 cm^{-1} is related to Fe–O.

In addition, the XRD pattern of the catalyst is shown in Fig. 2. The reflection planes at 14, 30, 36, 44, 55, 59 and 64 which are attributed to the diffraction scattering of Fe_3O_4 were readily recognized from the XRD pattern. These characteristic peaks adopted with those of standard Fe_3O_4 (JCPDS file No 04-0755). The observed diffraction peaks were indicated that Fe_3O_4 mostly exists in a face-centered cubic structure.

The loading of organic compounds on Fe_3O_4 was determined by EDX analysis, and the content of C, N, O, S, Fe and Cu in $\text{Fe}_3\text{O}_4@\text{Sal}@\text{Cu}$ was proved (Fig. 3).

The SEM images of the synthesized magnetic nanocatalyst are shown in Fig. 4. As can be seen from SEM images, the geometric shape of the nanoparticles is spherical and the nanoparticles have sizes between 15 and 36 nm.

Typical thermal TGA curves are given in Fig. 5. The range of 0–140 °C (region a) is related to release of adsorbed water; the second from 140 to 600 °C (region b) is related to the decomposition of organic matter on the Fe_3O_4 and region c is represented to Fe_3O_4 . The TGA curve of the synthesized catalyst demonstrates thermal stability, with decomposition starting at around 140 °C under a nitrogen atmosphere.

Catalytic activity evaluation

Firstly, the model reaction was simply carried out by mixing 3-nitro benzaldehyde (1 mmol), malononitrile (1 mmol), dimedone (1 mmol) in ethanol, methanol,

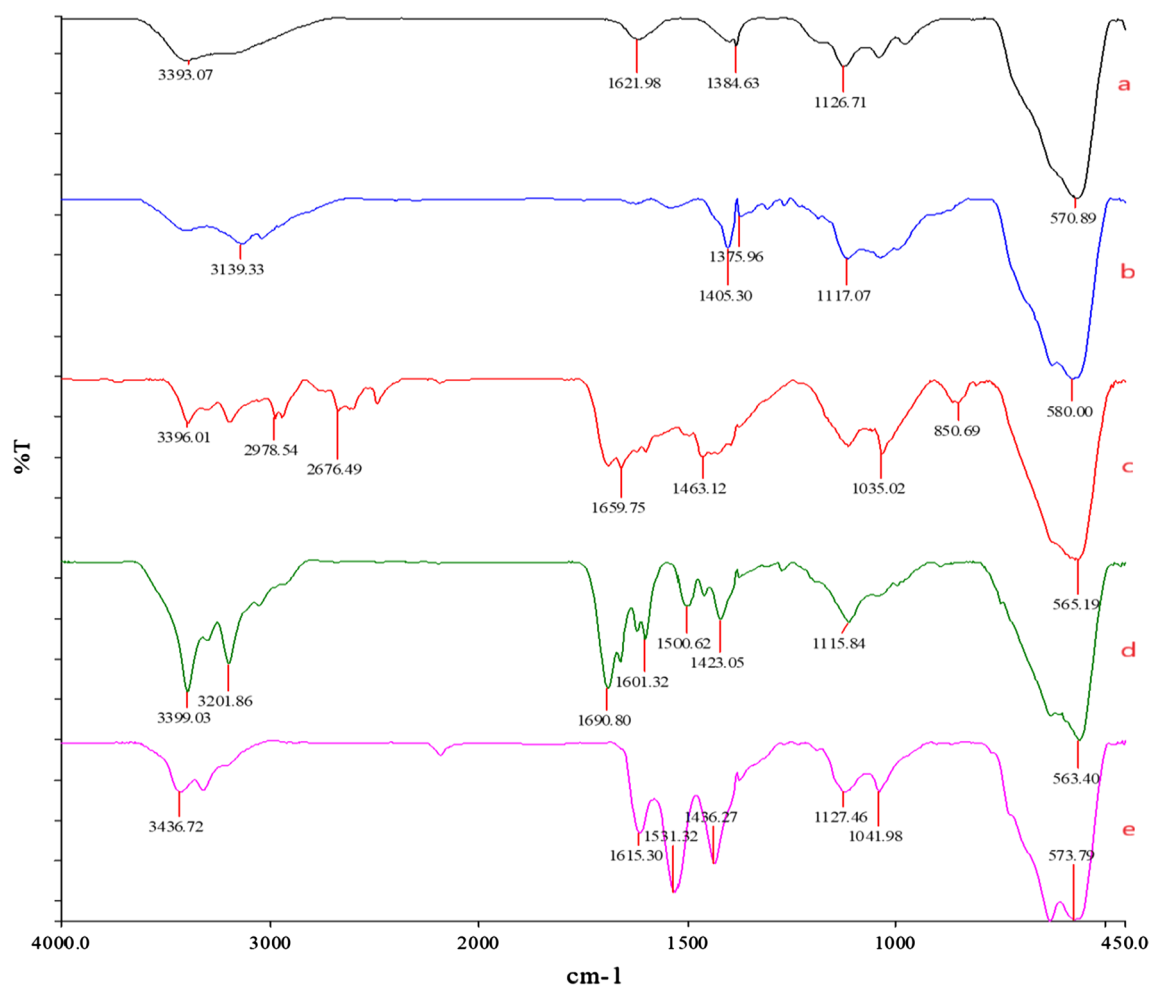


Fig. 1 FTIR spectra of **a** Fe₃O₄, **b** Fe₃O₄@3-Cl-propyl, **c** Fe₃O₄@propyl-semicarbazide, **d** Fe₃O₄@propyl-semicarbazide-salicylaldehyde, **e** Fe₃O₄@propyl-semicarbazide-salicylaldehyde-Cu

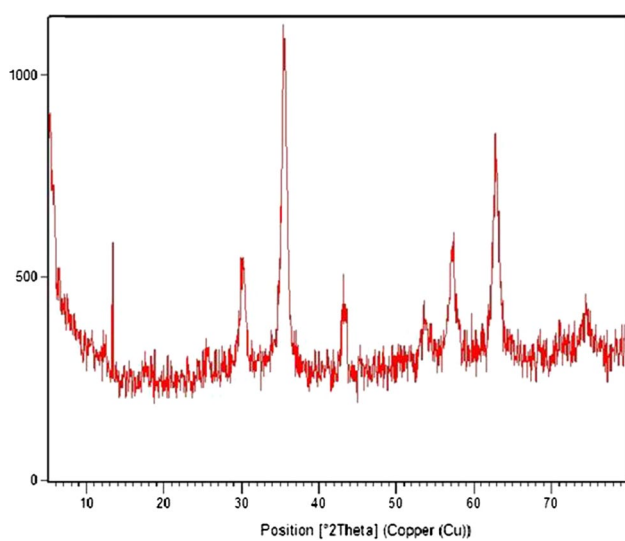


Fig. 2 XRD analysis of Fe₃O₄@Sal@Cu

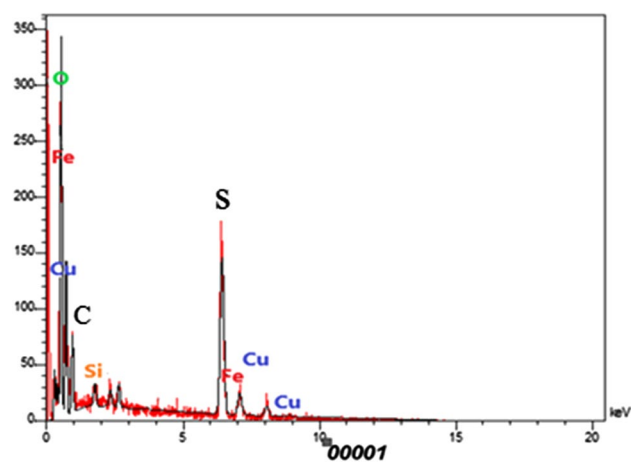


Fig. 3 EDX analysis of Fe₃O₄@Sal@Cu

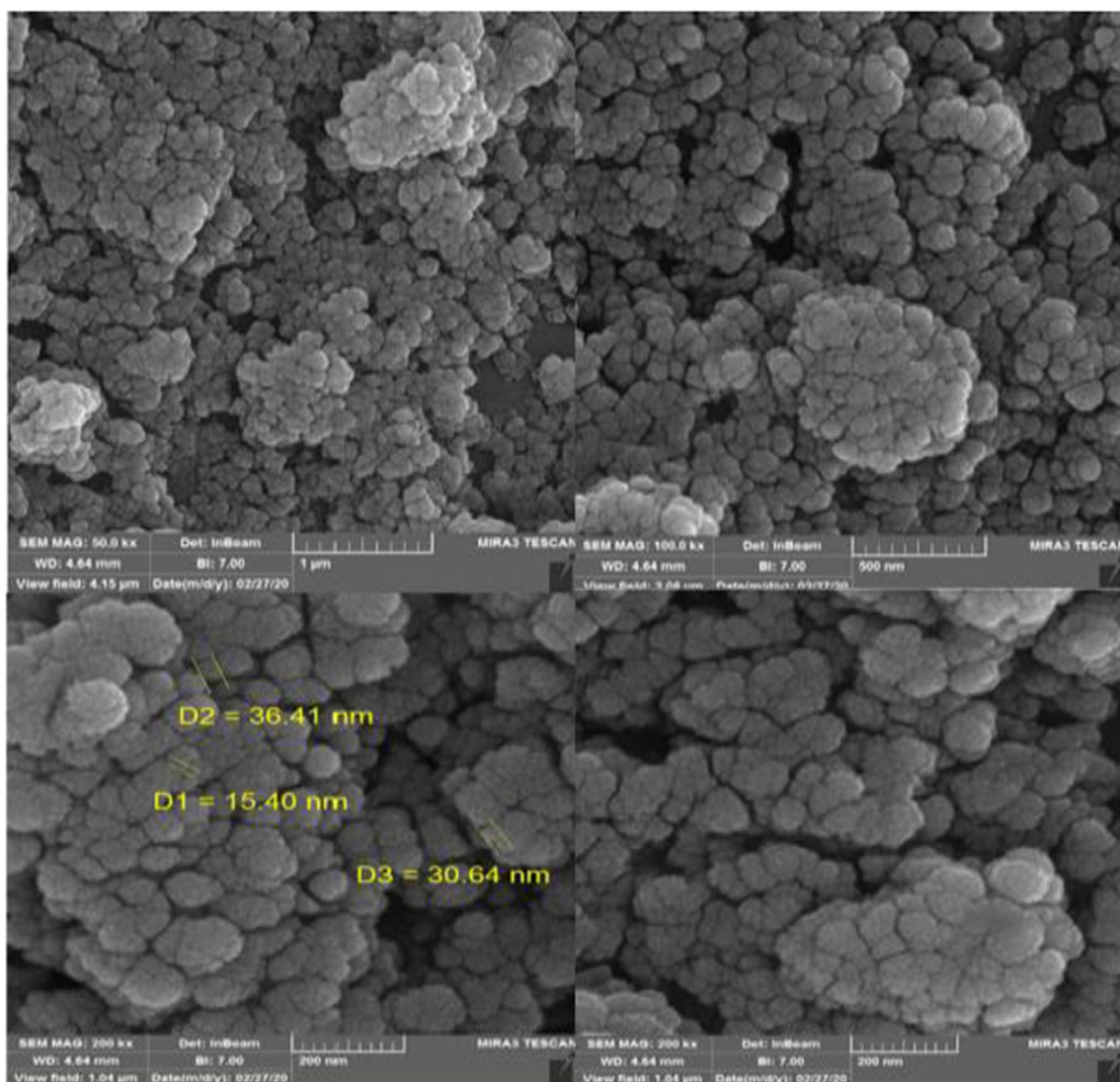


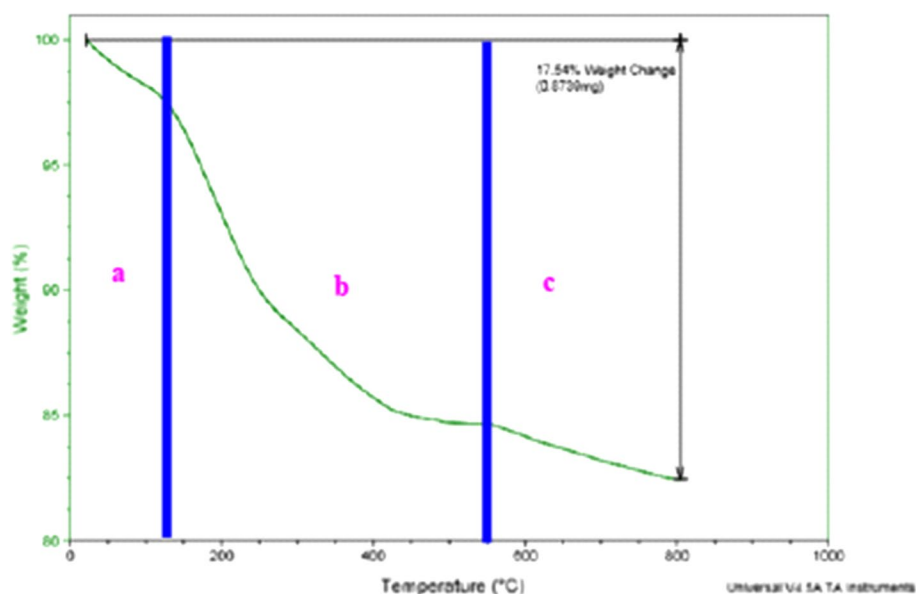
Fig. 4 SEM analysis of $\text{Fe}_3\text{O}_4@\text{Sal}@\text{Cu}$

n-hexane, chloroform and water as solvent at room temperature in the presence of different amounts of the catalyst (2, 4 and 8 mg). The product was obtained as shown in Table 1. As indicated in Table 1, the best condition reaction is 8 mg of the catalyst in ethanol as solvent at ambient temperature.

However, the scope and generality of this three-component one-pot synthesis of 2-amino-4*H*-chromenes have been illustrated with different aldehydes and the results are summarized in Table 2. This method has the ability to tolerate a variety of other functional groups such as hydroxyl, methyl, nitro and chloro under the reaction conditions. This protocol is suitable for both electron-rich and electron-deficient aldehydes leading to high yields of products **4a–s**.

Also, in a series of reactions, ethyl and methyl cyanoacetate was employed instead of malononitrile under

reaction condition to give the corresponding ethyl or methyl 2-amino-4*H*-chromene carboxylate. In these cases, the reactions were evaluated using a variety of structurally diverse aldehydes (entries 13–17, Table 2), respectively. The yields obtained were good-to-excellent. Therefore, the reaction profile is clean and this one-pot three-component procedure presents some improvements and advantages over existing methods. One of the major advantages of this protocol is the isolation and purification of the products, which have been achieved by simple separation (the use of external magnet) and crystallization of the crude products, and there are no by-products were formed in using catalyst. All the products were identified by comparison of analytical data with those of authentic samples. Also, some new compounds were synthesized by this protocol (entries 13–15, Table 2).

Fig. 5 TGA analysis of Fe₃O₄@Sal@Cu**Table 1** Optimizing of the reaction conditions in the synthesis of **4b**

Entry	Catalyst	Catalyst amount (mg)	Solvent	Temp (°C)	Time (min)	Yield (%)	References
1	–	–	–	R.t	15	Trace	[35]
2	–	–	–	100	15	Trace	[35]
3	–	–	H ₂ O	R.t	15	20	[35]
4	–	–	H ₂ O	Reflux	15	35	[35]
5	Fe ₃ O ₄ @Sal@Cu	–	n-hexane	Reflux	60	Trace	This work
6	Fe ₃ O ₄ @Sal@Cu	–	CHCl ₃	Reflux	60	Trace	This work
7	Fe ₃ O ₄ @Sal@Cu	2	EtOH	R.t	5	88	This work
8	Fe ₃ O ₄ @Sal@Cu	4	EtOH	R.t	5	91	This work
7	Fe ₃ O ₄ @Sal@Cu	8	EtOH	R.t	5	96	This work
8	Fe ₃ O ₄ @Sal@Cu	8	MeOH	R.t	20	75	This work
9	Fe ₃ O ₄ @Sal@Cu	8	H ₂ O	R.t	15	85	This work

A reasonable pathway for the formation of 2-amino-4H-chromenes in the presence of magnetic nanocatalyst is disclosed in Scheme 2.

Also, we study the efficiency of our presented protocol in a comparative with some previously reported methods for the synthesis of 2-amino-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **4b**. Reviewing the collected results as inserted in Table 3 represents higher catalytic performance for our presented catalyst.

Experimental

Chemicals were purchased from Merck Chemical Company. NMR spectra were recorded in CDCl₃ and DMSO-d₆ on a Bruker Advance DPX-300 instrument using TMS as an

internal standard. SEM analysis was determined by using FE-TESCAN, model Mira3-XMU at accelerating voltage of 15 kV. XRD analysis was performed on a Bruker D8-advance X-ray diffractometer or on an X'Pert Pro MPD diffractometer with Cu K α ($\lambda = 0.154$ nm) radiation. TGA analysis was recorded using a Shimadzu Thermogravimetric analyzer (TG-50). FTIR spectra were recorded on a JASCO FT-IR 460 plus spectrophotometer.

Preparation of Fe₃O₄ NPs

Fifty milliliters of FeCl₃·6H₂O (0.3 M) was added to 0.5 mL HCl (0.2 M), and the reaction flask was located in the ultrasonic probe and irradiation under 85 kHz at room temperature for 5 min. Then, 20 mL Na₂SO₃ (0.3 M) was added into

Table 2 Synthesis of chromenes using Fe₃O₄@Sal@Cu

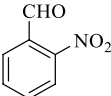
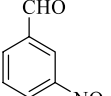
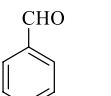
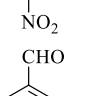
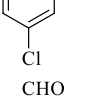
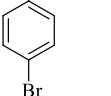
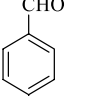
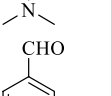
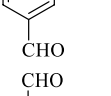
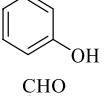
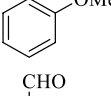
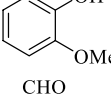
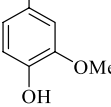
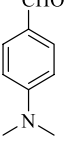
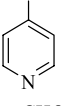
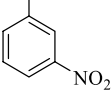
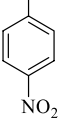
Entry	X	Aldehyde	Product	Time (min.)	Yield (%)	m.p. (°C) [Lit.]
1	CN		4a	10	88	214–216 [35]
2	CN		4b	8	96	212–214 [36]
3	CN		4c	5	91	177–179 [37]
4	CN		4d	5	93	212–214 [38]
5	CN		4e	5	92	203–205 [39]
6	CN		4f	10	85	208–210 [40]
7	CN		4g	10	95	225–226 [39]
8	CN		4h	8	92	228–230 [41]
9	CN		4i	12	90	207–209 [41]
10	CN		4j	15	95	228–230 [42]
11	CN		4k	13	97	231–233 [43]
12	CN		4l	10	94	210–212 [38]

Table 2 (continued)

Entry	X	Aldehyde	Product	Time (min.)	Yield (%)	m.p. (°C) [Lit.]
13	CO ₂ Me		4 m	15	95	173–175 [new]
14	CO ₂ Me		4 n	25	84	134–136 [new]
15	CO ₂ Et		4 o	21	78	183–185 [new]
16	CO ₂ Et		4 p	25	82	182–184 [42]
17	CO ₂ Et		4 q	20	80	180–182 [42]

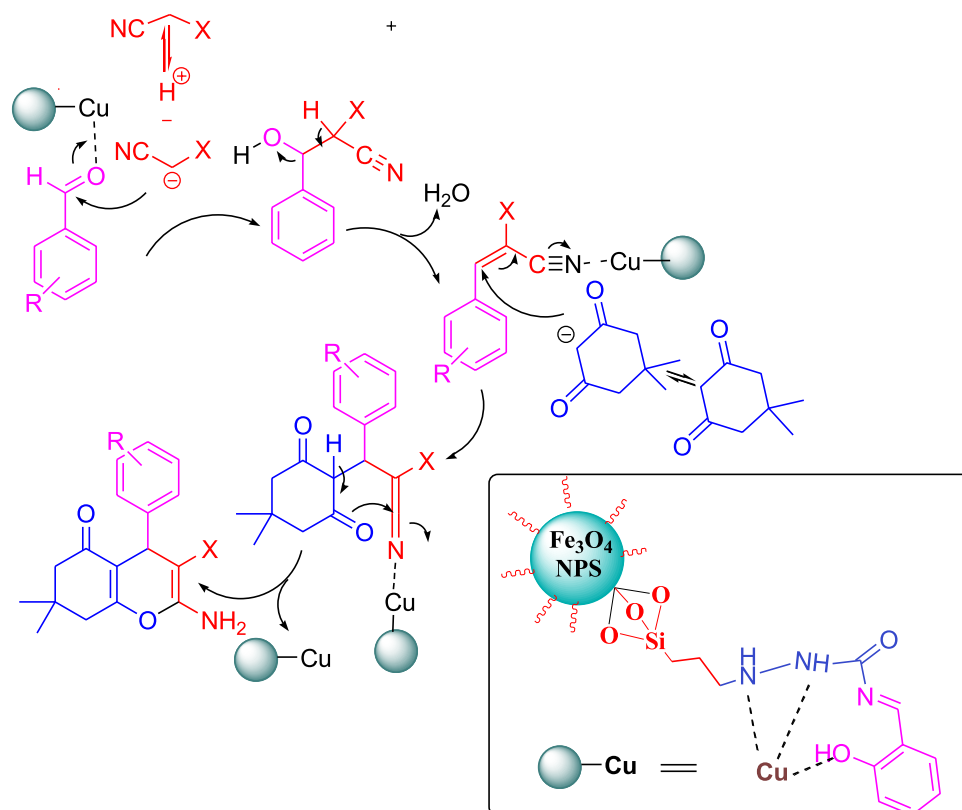
Scheme 2 Suggested mechanism for the synthesis of 2-amino-4H-chromenes using prepared nanocatalyst

Table 3 Comparison of some catalysts effects with Fe₃O₄@Sal@Cu nanocatalyst in the synthesis of **4b**

Entry	Catalyst	Catalyst mol% or mg	Solvent	Condition	Time (min)	Yield (%)	References
1	Bulk-Fe ₃ O ₄	5 mol%	H ₂ O	R.t	60	30	[44]
2	DABCO	10 mol%	H ₂ O	Reflux	120	94	[45]
3	Nano-Fe ₃ O ₄	5 mol%	H ₂ O	R.t	60	51	[44]
4	D,L-proline	20 mol%	H ₂ O/EtOH	R.t	> 30	92	[46]
5	ZnO-β zeolite	100 mg	EtOH	Reflux	50	87	[47]
6	γ-Fe ₂ O ₃ DMNPs	10 mol%	H ₂ O	R.t	60	51	[44]
7	Silica gel-supported polyphosphoric acid	100 mg	H ₂ O	Reflux	8	85	[48]
8	Fe ₂ O ₃ @SiO ₂ @VB ₁	8 mg	H ₂ O/EtOH	Sonication/80 °C	15	93	[49]
9	γ-Fe ₂ O ₃ @Hap-Si-(CH ₂) ₃ -AMP	1.5 mol%	H ₂ O	Reflux	10	84	[50]
10	Fe ₃ O ₄ @Sal@Cu	8 mg	EtOH	Sonication/r.t	5	96	This work

40 mL of above solution, and the color of solution changed from yellow to red. The reaction continues until the yellow color of the solution obtained again. In the following, the resulting solution was poured to 400 mL of water containing 60 mL of ammonium (28%) and followed by sonication for 30 min. Then, the obtained magnetic dispersion was separated by a magnet, washed three times with water and dried under vacuum at 60 °C for 12 h.

Synthesis of 3-Cl-propyl Fe₃O₄

Fe₃O₄ NPs was functionalized with (3-chloropropyl) trimethoxysilane according to the literature [56]. Typically, Fe₃O₄ NPs (2 g) was suspended in toluene (40 mL) and stirred for 15 min by ultrasonic. Then, (3-chloropropyl) trimethoxysilane (2 mL) was introduced and the resulting mixture was refluxed at 111 °C under inert (N₂) atmosphere for 24 h. At the end of the reaction, the resulting brown solid was filtered, washed several times with toluene and dried at 90 °C overnight.

Incorporation of semicarbazide with 3-Cl-propyl Fe₃O₄

Considering the previous reports [51] regarding the reaction of alkyl chloride and semicarbazide, the functionalization of the 3-Cl-propyl Fe₃O₄ with semicarbazide was carried out as follows: 3-Cl-propyl Fe₃O₄ (1 g) was suspended in dry toluene (60 mL). Then, semicarbazide (0.5 g) and catalytic amount (1 mL) of trimethylamine as a catalyst were added to the suspension. Subsequently, the resulting mixture was refluxed at 111 °C for 24 h. Upon completion of the reaction, the solid was filtered off and washed with dry toluene for several times. T-Fe₃O₄- was achieved after drying at 100 °C overnight.

Synthesis of imine functionalized Fe₃O₄ with salicylaldehyde

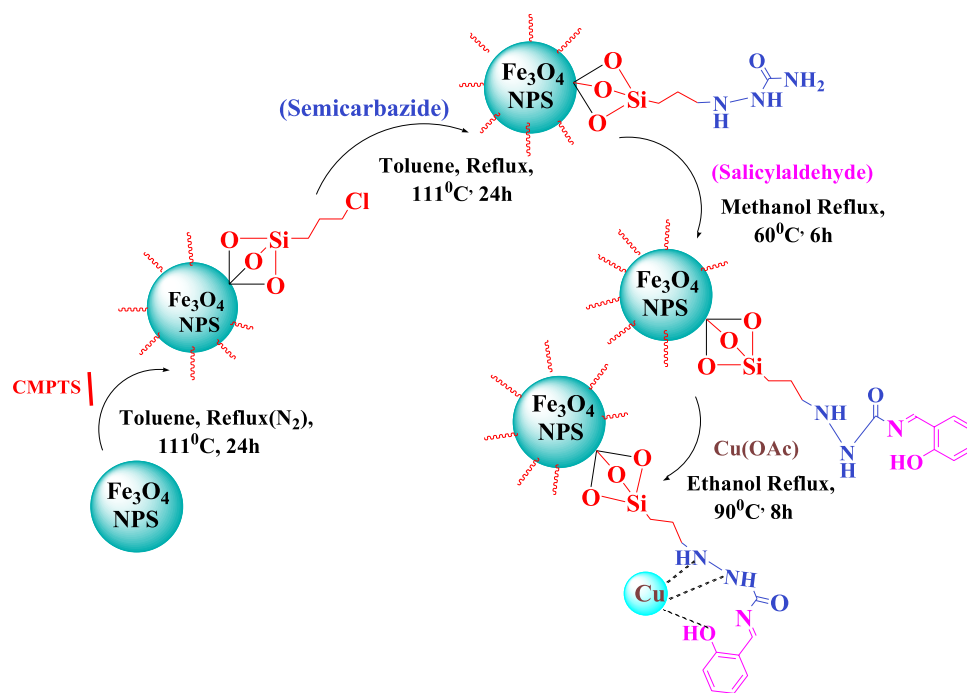
Salicylaldehyde (0.5 mL) was dissolved in of methanol (5 mL) and added dropwise to the suspension of semicarbazide-propyl Fe₃O₄ (1 g) in dried methanol (25 mL). The mixture was subsequently refluxed at 60 °C for 10 h.

Synthesis Fe₃O₄@Sal@Cu

To incorporate copper, dried salicylaldehyde-Fe₃O₄ was suspended in absolute ethanol (20 mL). To this suspension, copper(II) acetate (0.2 g) was added and the resulting mixture was kept under refluxing condition for about 8 h at 90 °C. Upon completion of the reaction, the mixture was cooled to room temperature. Subsequently, the precipitate was filtered and purified by washing with ethanol repeatedly. The final catalyst was obtained after drying at 100 °C for 10 h. The schematic of preparation of Fe₃O₄@Sal@Cu is shown in Fig. 6.

General procedure for the synthesis of 2-amino-4H-chromenes

A mixture of an aromatic aldehyde (1.0 mmol), dimedone (1.0 mmol), malononitrile (1.1 mmol) and nanocatalyst (8 mg) in absolute EtOH (5 ml) was stirred at room temperature. The completion of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, the catalyst was separated easily by an external magnet. The pure products were obtained from the reaction mixture by recrystallization from hot EtOH, and no more purification was required. All the product were known compounds which were identified by characterization of their melting points (as indicated in Table 3) by comparison with those authentic literature samples and also in some cases their FT-IR and ¹H NMR.

Fig. 6 Preparation of $\text{Fe}_3\text{O}_4@$ Sal@Cu

To disclose the worthy and usable of $\text{Fe}_3\text{O}_4@$ Sal@Cu in large scale, we set up reaction with 4-chlorobenzaldehyde (50 mmol, 5.35 g), malononitrile (50 mmol, 3.3 g), dimedone (50 mmol, 7.0 g), $\text{Fe}_3\text{O}_4@$ Sal@Cu (0.4 g) and ethanol (250 ml) in a round flask and then stirred for 5 h at room temperature. The reaction was carried out, and the product was obtained in (93% yield, 11.65 g). Therefore, $\text{Fe}_3\text{O}_4@$ Sal@Cu could be used for the synthesis 2-amino-4H-chromenes in ethanol at room temperature even in large scale.

Table 4 Reusability of the catalyst in the synthesis of **4b**

Entry	Run (s)	Yield %
1	Fresh	96
2	First	95
3	Second	93
4	Third	91
5	Fourth	91

Reusability of the catalyst

To evaluate reusability of the catalyst, after completion of the reaction, the catalyst was removed by external magnet and washed by hot ethanol and dried in 60 °C for 3 h.

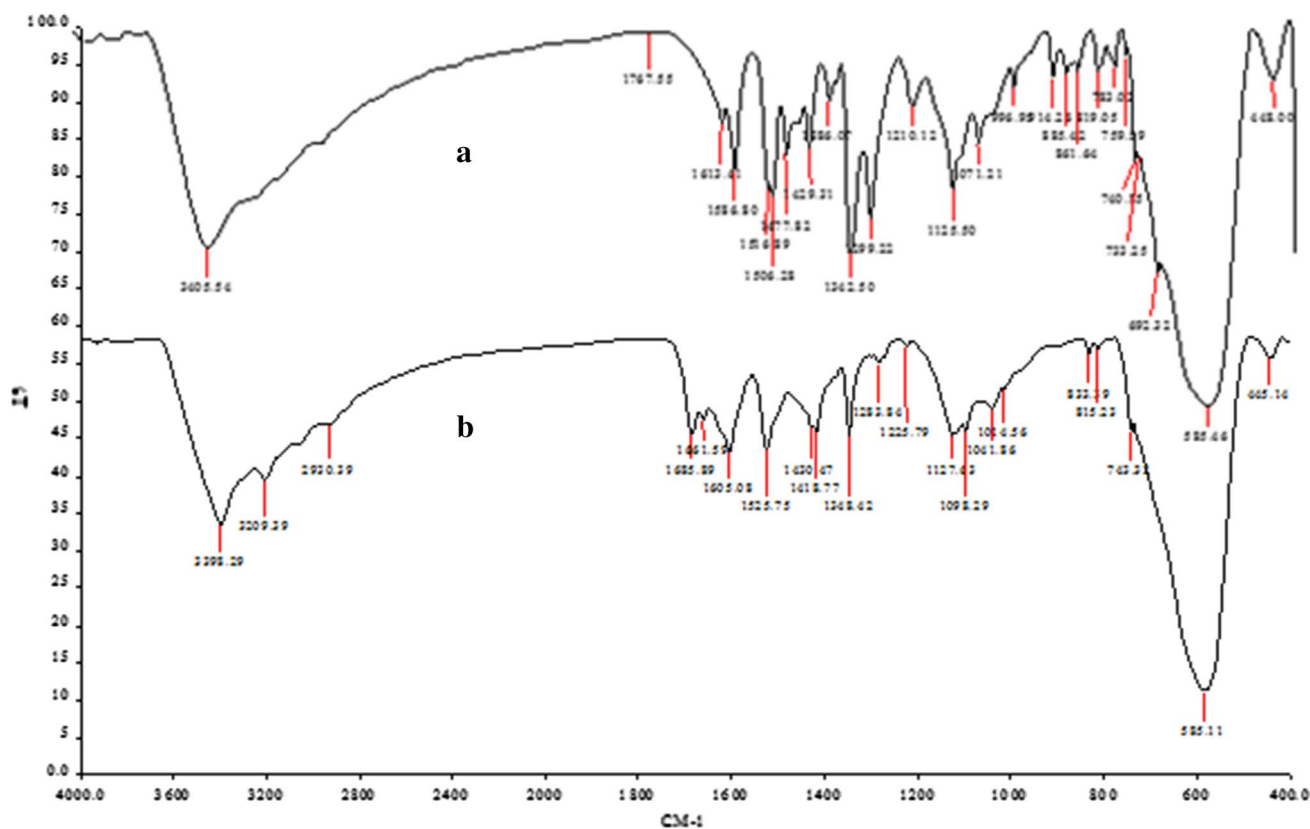


Fig. 7 FTIR spectra of the catalyst: **a** fresh, **b** after 5 runs

Then, the recovered catalyst was used for the synthesis of **4b** for four times. The results in Table 4 depicted that it acts as recovered catalyst as well as fresh catalyst. IR spectra of fresh catalyst and that recovered after five runs are indicated in Fig. 7.

Physical and spectra data for compounds

2-amino-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**4b**)

IR (KBr, cm^{-1}): 3430, 3335, 3200, 2985, 2873, 2187, 1681, 1660, 1601, 1530, 1368, 1350, 1212, 1039, 826, 733. ^1H NMR (300 MHz, DMSO, ppm) δ 7.17–7.66 (m, 4H Ar), 4.40 (s, 1H), 2.5 (bs, NH), 2.26 (d, $J = 16.07$ Hz, 2H), 2.10 (d, $J = 16.04$ Hz, 2H), 1.03 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (75 MHz, DMSO, ppm) δ 195.9, 163.1, 153.1, 150.2, 147.7, 147.0, 134.1, 124.3, 121.3, 119.6, 111.8, 110.1, 100.2, 57.6, 56.2, 44.3, 40.3, 35.6, 28.5, 26.2, 18.4.

Methyl 2-amino-4-(4-hydroxy-3-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carboxylate (**4m**)

IR(KBr, cm^{-1}): 3209, 3028, 2952, 2887, 2835, 1641, 1614, 1582, 1484, 1374, 1312, 1252, 1230, 1096, 1008, 758. ^1H NMR (300 MHz, DMSO, ppm) δ 6.37–6.82 (m, 3H Ar), 3.64 (s, 1H), 3.44–3.55 (m, 3H), 2.75 (br, OH), 2.14–2.35 (m, 3H), 2.05 (br, NH), 1.46 (s, 2H), 1.30 (s, 2H), 1.05 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (75 MHz, DMSO, ppm) δ 206.1, 204.6, 196.9, 165.1, 164.2, 159.1, 147.7, 146.2, 145.3, 124.3, 118.6, 114.8, 110.1, 100.2, 57.6, 44.3, 38.3, 32.6, 27.5, 26.2.

Methyl 2-amino-4-(4-(dimethylamino)phenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carboxylate (**4n**)

IR(KBr, cm^{-1}): 3396, 2955, 2888, 1738.13, 1613, 1520, 1377, 1165, 1065, 934, 816. ^1H NMR (400 MHz, DMSO, ppm) δ 6.52–7.07 (m, 4H Ar), 3.64 (s, 1H), 3.44–3.55 (m,

3H), 2.80 (s, 6H), 2.29 (s, NH), 1.96 (s, 2H), 1.36–1.46 (dd, 2H), 0.9–1.05 (m, 6H). ¹³C NMR (75 MHz, DMSO, ppm) δ 196.9, 164.2, 159.1, 147.7, 147.2, 124.3, 118.9, 75.6, 61.7, 51.6, 44.3, 38.3, 30.6, 26.5, 18.2.

Ethyl 2-amino-7,7-dimethyl-5-oxo-4-(pyridin-4-yl)-5,6,7,8-tetrahydro-4H-chromene-3-carboxylate (4o)

IR (KBr): 3402, 2959, 2871, 1742, 1686, 1597, 1533, 1370, 1243, 1203, 861.

¹H NMR (300 MHz, DMSO, ppm) δ 7.10–7.66 (m, 4H Ar), 4.46 (s, 1H), 3.90–3.94 (m, 2H), 3.30 (s, 4H), 2.27 (bs, NH), 1.08 (m, 3H), 1.02 (s, 3H), 0.95 (s, 3H). ¹³C NMR (75 MHz, DMSO, ppm) δ 195.9, 163.2, 158.1, 147.7, 147.0, 124.3, 113.9, 75.6, 61.7, 51.6, 44.3, 38.3, 30.6, 26.5, 18.2.

Conclusions

In summary, the present research has developed an efficient and simple process for the synthesis of 2-amino-4H-chromenes by of Fe₃O₄@Sal@Cu as a novel, efficient and heterogeneous catalyst via three-component reaction conditions. The simple experimental procedure, short reaction times, easy to handle of the nanocatalyst, high reusability and magnetically separable, and very good yields are the advantages of this method.

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