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Journal of Composites and Compounds

Functionalized NiFe_2O_4 /mesopore silica anchored to guanidine nanocomposite as a catalyst for synthesis of 4H-chromenes under ultrasonic irradiation

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ABSTRACT

A synergetic effect of nanocatalyst and ultrasonic irradiation was examined for the synthesis of 4H-chromenes from benzaldehyde, cyclohexanone, and malononitrile. It was observed this contributory improved the reaction that was used for the synthesis of the highly pure products in short reaction times and highest yields. The nanocomposite includes the guanidine anchored on to magnetic NiFe_2O_4 nanoparticles were used as the active base nanocatalyst for the sonication synthesis of 4H-chromenes compounds. The product was separated with simple filtration and purify with recrystallization by ethanol solvent. After completing the reaction, a nanocatalyst was collected and reused in 6 runs of model reaction. This nanocomposite has a magnetic core and a very active base surface area shell. The nanocatalyst was provided by the simple technique and identified by using FT-IR spectrum, scanning electron microscopy (SEM), X-ray diffraction (XRD), vibrating sample magnetometer (VSM), and Brunauer–Emmett–Teller (BET). This nanocomposite was used for the synthesized various derivatives of 4H-chromenes under ultrasonic irradiation. The organic products were identified by FT-IR and $^1\text{H-NMR}$.

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Peer review under responsibility of jourcc

ARTICLE INFORMATION

Article history:

Received 4 June 2021

Received in revised form 22 June 2021

Accepted 27 June 2021

Keywords:

4H-Chromene

Cyclohexanone

Malononitrile

Ultrasonic mesopore silica

1. Introduction

Recently mesoporous silica spheres include magnetic metal nanoparticles, have an attractive idea for chemistry researchers [1-3]. These nanocomposites have active surfaces area for use in various sciences. This nanostructure has the potential for use as the nanocatalyst [4-6], sensors [7, 8], nanoreactors [9], and drug delivery processes [10], gas filtration [11], and also as nano-sized quantum materials [12]. The large surface area of mesoporous silica was used in optical coatings and catalytic processes [13]. The bulk mesophase [14, 15] was managed the ratio between silica-to-surfactant and silica/surfactant self-assembly formation of cubic, hexagonal, and lamellar shape [16]. Recently, the heterogeneous nanocomposite was used in organic reaction to synthesis of different organic products [17, 18].

The chromenes compounds have notable biological attributes, [19-21] such as anticancer [22], antibacterial [23], anticonvulsant [24], antimicrobial [25], anti-influenza [26], antimalarial [27], and anti-virus activities [28]. Tetrahydro-4H-chromenes were used for the cure of counting Huntington's disease [29] neurodegenerative illnesses [30], Alzheimer's disease [31], Parkinson's disease [32], and schizophre-

nia [33]. The usual reaction for synthesis tetrahydro-4H-chromene is the Michael addition in the presence of a base catalyst. Numerous multi-component reactions have been determined for the synthesis of various tetrahydro-4H-chromenes derivatives via the condensation of an aldehyde, malononitrile, and cyclic ketone at the presence of different inorganic and organic catalysts [33, 34].

Ultrasonic is the sound waves belonging to the group of mechanical waves, which included frequencies higher than the audible frequency of humans (20k Hz) [35, 36]. The piezoelectric influence has been used to provide ultrasonic waves since the 1880 s [37, 38]. Ultrasonic waves were invented with development in the technology of ceramic materials [39], for example, quartz, [40] lead zirconate barium titanate, and lead titanate [41, 42], the ultrasonic technique has progressively grown to be considered encouraging, green, and novel technology that can be replaced or help traditional chemical processing [43, 44].

Following the previously reported [45-47], in this research, it was reported a clean synthesis of 4H-chromenes derivatives from cyclohexanone, different benzaldehyde, and malononitrile under ultrasonic irradiation at the presence of the NiFe_2O_4 /mesopore silica anchored to guanidine nanocomposite as the base catalyst.

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<https://doi.org/10.52547/jcc.3.2.1>

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Scheme. 1. Synthesis of NiFe_2O_4 /mesopore silica anchored to guanidine nanocomposite.

Fig. 1. XRD spectra of NiFe_2O_4 @mesopore silica@ guanidine.

Fig. 2. The spectra of FT-IR of NiFe_2O_4 @mesopore silica@ guanidine.

2. Experimental procedures

2.1. Materials and instruments

All the solvents and starting materials that used in the reaction include benzaldehyde derivatives (97%–99%), cyclohexanone (98%), malononitrile (99%), and ethanol (99%), cetyltrimethylammonium bromide (CTAB) (100%), tetraethyl orthosilicate (TEOS) (97%), sodium hydroxide (NaOH) (99%), were provided from Sigma, ferric (III) chloride (FeCl_3) (97%), nickel (II) chloride (NiCl_2) (98%), and sodium bicarbonate (95%), were obtained from Sinopharm Chemical. The organic products were recognized with ^1H NMR, FT-IR, and ^{13}C NMR analyses. The ^1H NMR analysis was reported in CDCl_3 solvents using Bruker DRX-400 spectrometer, and the internal reference is tetramethylsilane. FT-IR spectra were reported with a Perkin-Elmer 550 spectrometers in the range of 400–4000 cm^{-1} . The crystal structure of nanocomposite (XRD) registered with (CuK α , radiation, $\lambda = 0.154056$ nm) that worked with a 15-kV accelerating voltage at the speed of 2° min^{-1} starting from 10° to 80° (2 θ .Theta;), for determined the morphology and size of nanocomposite used of Electron Microscope (FE-SEM) and EDX with Zeiss Scanning Electron with a 15-kV accelerating voltage. The surface areas and the size of pore in the nanocomposite illustrated by BET analysis with nitrogen adsorption in -196°C using Tri-Star 3020 Micrometrics analyzer. The magnetic properties of nanocomposite were measured by a vibrating sample magnetometer (VSM), the VSM curves were recorded by PPMS-9 T at 300 K. The TGA was recorded in an air atmosphere by a 10°C/min rate.

using the METTLER-810 analyzer.

2.2. General procedure for preparation of nano magnetic NiFe_2O_4

The nickel ferrite nanoparticles were provided during a sol-gel method [29]. To the accomplishment, the chemical formula NiFe_2O_4 , 40 ml $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ (4 M) was stirred with 40 ml $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ (2 M). Then,

1.5 g citric acid monohydrate was added ($\text{C}_6\text{H}_8\text{O}_7$, H_2O) to the reaction mixture. The pH of the mixture increased to 7.0 added a little ammonia-water ($\text{NH}_3 \cdot \text{H}_2\text{O}$) to the reactions. The solution was heated to dry the water at 85°C and production of the brown colored gel. At the end of the method, the product was dry at 80°C to 3 h.

2.3. Synthesis of NiFe_2O_4 @mesopore silica

To provide an active base nanocatalyst, 5 mL NaOH 1 M, and 0.65 g of CTAB were dissolved in 100 mL deionized water and heated the mixture to 35 min at 100°C . Then 0.1 g of NiFe_2O_4 nanocomposite was dispersed in 60 ml ethanol under sonicate irradiation. The obtained solution added to the reaction mixture. 2 ml TEOS was added to the reaction mixture two times after 15 and 40 min, the reaction mixture stirred at room temperature for 15 h at the end of the reaction the product collected by centrifuge and washed three times with water and ethanol, and dried at 70°C for 24 h. The surfactant was removed from the nanocomposite by dispersed the product in ethanol (100 mL) and ammonium nitrate (50 mg) and stirred at 80°C for 5 h. The product was separated by the centrifuge and dried at 100°C for overnight.

2.4. Synthesis of NiFe_2O_4 /mesopore silica anchored to guanidine nanocomposite

50.0 mg of NiFe_2O_4 @mesopore silica was dispersed under ultrasonic irradiation in 10.0 mL toluene solvent for 30 min. Then 5 mmol guanidinium chloride, 5 mmol 3-chloropropyltrimethoxysilane, and 2.5 mmol sodium bicarbonate in 10 mL dry toluene added to the reaction mixture then refluxed for 32 h. Then, the final product was separated by centrifuge and washed with water and ethanol. The product was dried at 80°C under a nitrogen atmosphere (Scheme 1).

2.5. General multicomponent procedure for synthesis of 4H-chromene

4H-chromenes derivatives were synthesized in the three-component reaction. In this reaction, 1 mmol of malononitrile was reacted by 1 mmol of benzaldehyde at the presence of 10 mg of nanocatalyst. The reaction was followed under ultrasonic irradiation on the ethanol

Fig. 3. FE-SEM image of NiFe₂O₄@mesopore silica@ guanidine. Fig. 5. EDS curves for NiFe₂O₄@mesopore silica@ guanidine.

solvent. After 5 min 1 mmol cyclohexanone was added to the reaction mixture, and the process was followed by thin-layer chromatography. The final product was separated with simple filtration and purification by recrystallization in the ethanol solvent. The final product identifies by the melting point, FT-IR, and ¹H NMR spectra (¹H NMR and FT-IR data were placed in SI files).

3. Result and discussion

3.1. Preparation and characterization

The NiFe₂O₄ nanoparticles were synthesized and functionalized by mesopore silica and guanidine. At first, NiFe₂O₄ was provided by the sol-gel method [48]. The obtained NiFe₂O₄ was reacted by CTAB, NaOH, and TEOS at ambient temperature to NiFe₂O₄@ mesopore silica. The obtained magnetic nanocomposites reacted by guanidine under the refluxed condition to NiFe₂O₄@mesopore silica@ guanidine base nanocatalyst. The nanocomposite was distinguished by various analyses

Fig. 4. BET curves for NiFe₂O₄@mesopore silica@ guanidine.

such as; SEM, EDX, XRD, FT-IR, BET, and VSM.

The XRD models were recorded of the crystal structure of NiFe₂O₄@ mesopore silica@ guanidine displayed in Fig. 1. The XRD pattern in Fig 1 shows the peaks (miller indices) in 30° (220), 37° (222), 45° (400), 58° (511), 62° (440) and 73° (533), regular XRD pattern of JCPDS card that due to the crystal structure of NiFe₂O₄ and the sharp peak in 22° due to amorphous mesopore silica.

Effective functionalization of the NiFe₂O₄@mesopore silica@ guanidine catalyst can be explained through FT-IR spectra (Fig. 2). According to the FT-IR spectrum of the nanocomposite, the presence of a peak around 458 cm⁻¹ showed stretching vibration of Ni-O bonding; the peak of Fe-O looked near the 793 cm⁻¹; the NH₂ stretching bond displayed near 3391 cm⁻¹, and the peak of the Si-O stretching bond appeared around 1084 cm⁻¹.

The morphology and size of the nanocomposite were defined by the scanning electron microscopy analysis. The FE-SEM images of the NiFe₂O₄@mesopore silica@ guanidine (Fig. 3) shown the extremely uniform morphology for the nanocomposite. Moreover, the average particle size of NiFe₂O₄@mesopore silica@ guanidine was 77–85 nm.

The surface area and pore volume diameter of NiFe₂O₄@mesopore silica@ guanidine were defined using the Brunauer–Emmett–Teller (BET) technique. According to the acquired curve, the measurement of surface area was equal to 233 m₂g⁻¹, total pore volume 0.121 cm³g⁻¹ (Fig. 4).

Also, to characterize the percent of each element in the nanocomposite, it was studied elemental the energy-dispersive X-ray (EDS) spectrum. The EDS curve showed the percent of O, Si, Fe, Ni, and C were 24.1%, 32.9%, 1.8%, and 30.2%, respectively (Fig. 5).

Thermogravimetric analysis (TGA) curves (Fig. 6) of NiFe₂O₄@ mesopore silica@ guanidine shows that losses of 60 percent of weight under 800 °C in the models are due to the release of adsorbed water, solvent, and organic materials.

Scheme. 2. Synthesis of various derivatives of 4H-chromene in the presence of NiFe₂O₄/mesopore silica/guanidine nanocatalyst.

Fig. 6. TGA curves for NiFe₂O₄@mesopore silica@ guanidine. Fig. 7. FVSM curves for NiFe₂O₄@mesopore silica@ guanidine. Fig. 8. The recyclability of NiFe₂O₄/mesopore silica/guanidine nanocatalyst in six runs.

Table 1.

Investigation of catalyst, catalyst amount in ethanol solvents for the synthesis of 4H-chromenes^a

En-try	Catalyst	Catalyst amount (mg)	Time (h)	Yield ^b (%)
1	Et ₃ N	10	3.5	40
2	MgO	10	2.5	70
3	Morpholine	10	0.95	70
4	Guanidine	10	0.75	75
5	NiFe ₂ O ₄ /mesopore silica/guanidine	10	0.75	88
6	NiFe ₂ O ₄ /mesopore silica/guanidine	10	0.16	98
7	NiFe ₂ O ₄ /mesopore silica/guanidine	5	0.16	83
8	NiFe ₂ O ₄ /mesopore silica/guanidine	15	0.16	90

^a Reaction conditions: benzaldehyde (1 mmol), malononitrile (2 mmol), cyclohexanone (1 mmol), 5 ml solvent.^b Isolated yield

Scheme 3. Proposed reaction mechanism for the Synthesis of 4H-chromene.

Table 2.Investigation of solvent for the synthesis of 4H-chromenes ^a

Entry	Solvent	T °C	Time (h)	Yield ^b (%)
1	Acetonitrile	25	0.75	10
2	Chloroform	25	0.92	0
3	Ethanol	75	0.16	98
4	Methanol	25	0.75	90

^a Reaction conditions: benzaldehyde (1 mmol), malononitrile (2 mmol), cyclohexanone (1 mmol), 5 ml solvent.^b Isolated yield

The magnetic properties of NiFe₂O₄@mesopore silica@ guanidine nanocomposite were recorded by the vibrating sample magnetometry (VSM) spectra of the nanocomposite. The magnetization curve of nanocomposite shown superparamagnetic properties (Fig. 7).

According to the TGA and EDX analyzed, the percent of organic materials was 60%, and mesopore silica around 30%. So, the percent of NiFe₂O₄ is around 10% in the nanocatalyst structure. Because the low percent of NiFe₂O₄ and covered with two-layer of mesopore silica and guanidine compound. The MS of the catalyst was decreased, but it has superparamagnetic properties and adsorbed with an external magnet.

The synthetic reaction of 4H-chromenes from benzaldehyde, cyclohexanone, and malononitrile was optimized by various solvents, catalysts, and temperatures.

The reaction was studied by utilizing different catalysts such as morpholine, Et₃N, MgO, and NiFe₂O₄/mesopore silica/guanidine in the ethanol solvents. The results of the study were exhibited in Table 1.

The results were displayed NiFe₂O₄/mesopore silica/guanidine (Table 1, Entry 5) and have the best yields of product in the short reaction Table 4.

Synthesis of various derivatives of 4h-chromene in the presence of NiFe₂O₄/mesopore silica/guanidine nanocatalyst ^a

4a-l ^a, yield % ^b, Time (min)

4a: X= H, Y= H, 98, 10

4b: X= Br, Y= H, 95, 15

4c: X= NO₂, Y= H, 96, 16

4d: X= F, Y= H, 92, 17

4e: X= N,N dimethyl, Y= H, 93, 20

4f: X=2,4 dichloro, Y= H, 91, 18

4g: X= NO₂, Y= H, 94, 19

4h: X= Cl, Y= H, 92, 17

^a Reaction conditions: benzaldehyde (1 mmol), cyclohexanone (1 mmol), malononitrile (1 mmol), 0.1mmol nanocatalyst (5 mg), ethanol solvent (5ml), 45 power ultrasonic irradiation.^b Isolated yield**Table 3.**Several Power for the ultrasonic multicomponent reaction for synthesis of bis-ortho-aminocarbonitrile tetrahydronaphthalene 4a ^a

Entry	Power (W)	Time (min)	Yield ^b (%)
1	Silent	180	20
2	30	60	82
3	35	50	85
4	40	35	90
5	45	10	98
6	50	30	96

^a Reaction conditions: Benzaldehyde (1 mmol), Cyclohexanone (1 mmol), Malononitrile (1 mmol), 5 ml Solvent.^b Isolated yield

time. The model reaction was tested in different solvents and the result showed in Table 2.

Ultrasound irradiation was constructed as the motive energy for the improved yield of 4H-chromenes, that due to the increased temperature correlated to the production of hot spots. While the reaction was carried out without sonic irradiation in low yield and long reaction time (Table 3, entry 1). The best power for the reaction was acquired 45 W based on product yield and reaction time (Table 3, entry 5).

After optimization of the model reaction for the synthesis of 4h-chromene (4a-g), 1 mmol of benzaldehyde (1a-g), 1 mmol of malononitrile (2), and 1mmol of cyclohexanone (3) were mixed in ethanol solvent and 5 mg NiFe₂O₄/mesopore silica/guanidine added to the mixture as the base nanocatalyst. The reaction was done under 45 power ultrasonic irradiation (Scheme 2) (Table 4).

The mechanism of the reaction for the production of 4H-chromenes

Table 5.

Comparisons of literatures reported catalyst with this work for synthesis compound 4a

Entry	Catalyst	Loading	Time (min)	Yield (%)	Method	Ref.
1	Morpholine	0.1 mmol	30	90	Reflux	[48]
2	CaMgFe ₂ O ₄	0.1 mmol	20	92	r.t	[47]
3	CoFe ₂ O ₄ /lamellar mesopore silica/melamine	10 Mg	20	93	r.t	[31]
4	NiFe ₂ O ₄ /mesopore silica/guanidine	10 Mg	10	98	Ultra-sound	This work

included various steps, at the first step, benzaldehyde and malononitrile reacted under Michael addition and formation the intermediate A under the nanomagnetic base NiFe₂O₄/mesopore silica/guanidine nanocatalyst. Then the cyclohexanone under condensation reaction joins to the intermediate A and formation intermediate B. The process followed by a cyclization reaction, the 4H-chromene (4a) compounds synthesis by absorption of the hydrogen, and double bonds rearrangement (Scheme 3).

3.2. Catalytic comparisons

To display the efficiency and influence of new methods for the synthesis of 4H-chromene derivatives, the obtained results were compared with the other methods, catalysts, and conditions (Table 5). As can be seen, the present study with different methods for added the starting material, nanocatalyst, and using ultrasonic irradiation is superior in yield of pure products and short reaction times.

3.3. Reusability

The reusability and nanocomposite are important advantages for commercial utilization. The reusability of NiFe₂O₄/mesopore silica/guanidine nanocatalyst, was tested in six runs of the model reaction, and the results reported in Fig 8.

4. Conclusion

In this study, it was functionalized the NiFe₂O₄/mesopore silica with the guanidine compound. The mesopore silica has a large area for functionalization on the surface and pore. The reaction of benzaldehyde, malononitrile, and cyclohexanone as the model reaction was selected for examined the catalyst activity. The 4H-chromene was synthesized by used NiFe₂O₄/mesopore silica/ guanidine as a nanocatalyst in the excellent yields and short reaction times. The nanocomposite identified by FT-IR, SEM, XRD, VSM, BET techniques, and the organic products recognize by the melting point, ¹H NMR, and FT-IR analyses.

Supporting Information

Experimental details, copies of ¹H and FT-IR and of products is available free of charge via the Internet at

Acknowledgments

The authors are grateful to University of shahrekord for supporting this work by Grant No. 159148/92.

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