



**Fe₃O₄-CNTs nanocomposites: a novel and excellent catalyst
in the synthesis of diarylpyrimidinones using grindstone
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ARTICLE

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We investigated the possibility of developing Fe₃O₄-CNTs as an efficient and recyclable catalyst system for the synthesis of 4,6-diaryl-3,4-dihydropyrimidine-2(1*H*)-ones under solvent-free conditions via grinding. The procedure is efficient, high-yielding, time-saving and environmentally friendly and has simplicity in the experimental procedure. The structures and purity of these compounds were confirmed by Mp, IR and (¹H & ¹³C) NMR spectral analysis.

Introduction

Recently, the use of other active methylene compounds in addition to β-ketoester in classic Biginelli reaction has emerged as one of the hot research areas to prepare various novel dihydropyrimidinones. The first Biginelli-like reaction was reported by Wang et al.¹ was conducted in CH₃CN by using aldehydes, ketones (instead of 1,3-dicarbonyl compounds) and urea as substrates and FeCl₃·6H₂O and TMSCl as catalysts, which remarkably broadened the Biginelli reaction. Since then, the Biginelli-like reaction has been applied and improved by several authors.²⁻⁴ Various active methylene compounds applied in the Biginelli-like reaction are consist of 5,5-dimethyl-1,3-cyclohexanedione,⁵ 1,3-cyclohexanedione,⁶ 1-tetralone,^{1-3,5,7} acetophenone,¹⁻³ aliphatic aldehydes,⁸ β-oxodithioesters,⁹ and cyclopentanone,¹⁰. Just as the Biginelli reaction operates in the presence of acidic reagents,^{11,12} the Biginelli-like reactions were also developed to prepare novel dihydropyrimidinone derivatives in the presence of acidic catalysts.

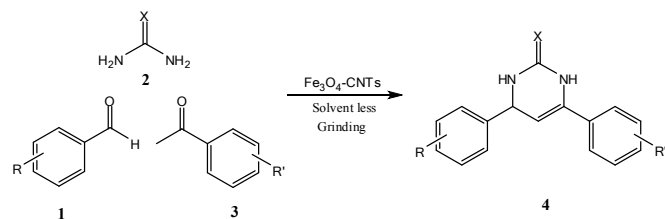
In recent years, more attention has been paid to the functionalization of carbon nanotubes (CNTs) with many types of active inorganic components for further improving their properties and extending their applications in various fields of technology.¹³⁻¹⁷ For example, metal oxides have been successfully decorated on CNTs.^{18,19} Among these multifunctional composites, magnetic CNT composites have been attracting great attention owing to their potential applications in fields such as magnetic data storage, catalysis, electronic devices, magnetic resonance imaging, toners and inks for xerography, electrochemical biosensing, magnetically guided drug delivery systems, magnetic force microscopy as nano probes, and biomedicine.²⁰⁻²⁹ Magnetite Fe₃O₄ is the most useful among them from the applied point of view and

have considered being potentially on research and practical applications. Various techniques have been used to load iron oxide nanoparticles on the outer surface of CNTs.²⁸⁻³¹

Green chemistry focuses on research that attempts to develop economically simple and environmentally safe methods in the synthetic organic chemistry. Green chemistry offers significant potential for clean synthesis, high atom efficiency, selectivity, elimination of toxic waste, reduction in energy costs and mild reaction conditions.³² Solid-state chemistry has been developed rapidly as an efficient and selective method, since molecules in the crystals has been arranged tightly and regularly.³³ One of the methods belonging to this protocol is a simple grinding method called grindstone (mechanochemical) method which reactants are ground simply by mortar and pestle. Grinding is interesting because it is performed in the absence of solvent, leading to safe and environmentally friendly synthesis.³⁴ Furthermore, the proposed technique does not require external heating, leading to energy-efficient synthesis and may be regarded as more economical and ecologically favourable procedure in chemistry.³⁵ Mechanical-induced breaking of molecular bonds, reduction of particle size, increase in surface area, formation of defects and local melting occur due to the kinetic energy supplied during grinding in solvent-free organic reactions based on grinding.^{36,37} The transfer of very small amounts of energy through friction in this process leads to more efficient mixing and close contact between the starting materials on a molecular scale.³⁸⁻⁴⁰

However, despite the extensive studies on the Biginelli-type reactions reported in the literature, to the best of our knowledge, there is no report focusing on the development of one pot Biginelli-type reaction in the presence of Fe₃O₄-CNT nanocomposites as catalyst under solvent-free grinding. To support this process, we investigated the efficiency of our procedure using the Fe₃O₄-CNTs catalytic system under

mechanochemical grinding through three-component cyclocondensation of an aldehyde, acetophenone and urea (Biginelli-like reaction), which is an efficient and environmentally friendly preparation of 4,6-diaryl-3,4-dihydropyrimidine-2(1*H*)-ones (Scheme 1).



Scheme 1. Ketone instead of 1,3-dicarbonyl compounds employed in the Biginelli reaction under grindstone method

Results and discussion

In order to synthesize dihydropyrimidinone derivatives, we focused our attention on Biginelli-type cyclocondensation of aromatic aldehydes with urea and aromatic ketones. For the first time, an easily accessible and stable catalytic system has been used efficiently in the present procedure for Biginelli-type condensation via grinding at room temperature. The benzaldehyde, urea, and acetophenone were selected as the test substrates to get the optimum conditions in this synthesis. The optimum molar concentration of catalyst was determined on the formation of **4a** (Table 1). The reaction was optimized with test substrates in the ratio of 1:1.5:1 in the presence of Fe₃O₄-CNTs (0.05 g). In order to examine the substrate scope of Biginelli-like reaction, we examined the reaction of aromatic aldehyde, ketone, and urea under the above optimized reaction condition. The results are summarized in Table 2. It is observed that, aromatic aldehydes with both electron withdrawing and electron-donating substituent reacted efficiently with urea and acetophenone in the presence of catalytic amounts of Fe₃O₄-CNTs (0.05 g) in a grinding process to get the corresponding DHPMs with high yields (85–98 %). However, satisfactory results were obtained when the reactions were carried out in the presence of this catalytic system.

Table 1. Effects of varied molar concentrations of the catalyst in the formation of **4a** on grinding

Entry	Catalyst (g)	Time (min)	Yield (%)
1	0.00	12	15
2	0.02	12	81
3	0.03	12	90
4	0.05	12	98
5	0.06	12	98

Table 2. Synthesis of 4,6-diaryl-3,4-dihydropyrimidine-2(1*H*)-ones in the presence of catalyst under solvent-free grinding conditions

Entry	R	R'	X	Product	Time (min)	Yield (%)	M.p (°C)	
							Found	Reported
1	H	H	O	4a	12	98	229–231	228–230 ³
2	2-OMe	H	O	4b	15	93	265–267	266–267 ³
3	2,6-Cl ₂	H	O	4c	23	87	275–277	274–276 ³
4	4-OH	H	O	4d	25	89	256–258	257–258 ⁴¹
5	4-Cl	H	O	4e	15	90	268–269	267–269 ⁴¹
6	3-OMe	H	O	4f	20	91	257–259	257–258 ³
7	4-Me	H	O	4g	25	86	249–251	248–250 ³
8	3-Br	H	O	4h	14	88	256–258	258–259 ⁴¹
9	2-Cl	H	O	4i	17	90	261–263	264–265 ³
10	3-OMe-4-OH	H	O	4j	30	85	267–269	267–268 ³

Also, it is noteworthy that the catalyst can be easily recyclable without significant loss of activity. For this purpose, the solid catalyst was separated by an external magnet, was rinsed in ethyl acetate and was dried at 100 °C for 1 h, and finally was reused for the same reaction process. Even after five runs for the reaction, the catalytic activity was almost like the catalyst was used freshly. The results were presented in Figure 1. In all cases, the three components one-pot reactions proceeded smoothly and rapidly to afford the corresponding 4,6-diaryl-3,4-dihydropyrimidine-2(1*H*)-one derivatives in excellent yields. In summary, we report here green and high yielding synthesis of 4,6-diaryl-3,4-dihydropyrimidine-2(1*H*)-ones from readily available aldehydes, acetophenone, and urea in the presence of Fe₃O₄-CNTs by grinding under solvent-free conditions. The conditions are mild and a wide range of functional groups can be tolerated. This procedure is much simpler and faster than the protocols published to date. It is also consistent with a green chemistry approach since no solvent is needed (except for recrystallization).

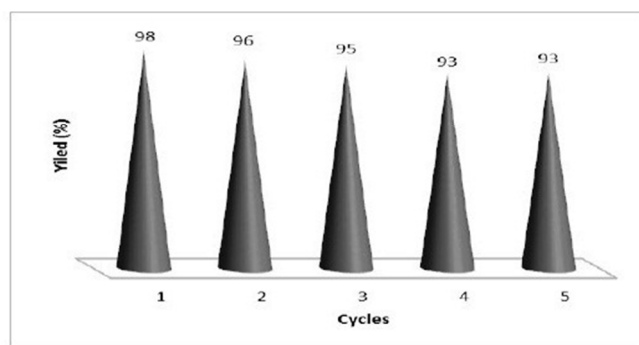


Figure 1. Reusability of the catalyst in the model reaction

The XRD patterns of oxidized MWCNTs and Fe₃O₄/MWCNTs nanocomposites are illustrated in Figure 2. As shown in Figure 2a, the diffraction peaks at 2θ = 25.92° and 43.24° are estimated to the graphite structure (002) and (100) planes of the MWCNTs. According to Figure 2b seven characteristic peaks for Fe₃O₄ nanoparticles (NPs) in 2θ = 30.54°, 35.87°, 43.65°, 54.03°, 57.61° and 63.12°, 74.74° can be assigned to d(220), d(311), d(400), d(422), d(511), d(440), and d(533) crystal planes of magnetic phase, respectively. The peak broadening of Fe₃O₄ in the XRD pattern indicates that the prepared magnetite crystallites in the composite are

significantly small (13.02 nm), which these results were calculated by the Scherrer equation. Diffraction peaks assigned to both acid treated MWCNTs and nanocrystalline Fe_3O_4 can be clearly seen in the XRD curve of $\text{Fe}_3\text{O}_4/\text{MWCNT}$ nanocomposites, indicating the presence of MWCNT structure and Fe_3O_4 nanoparticles.

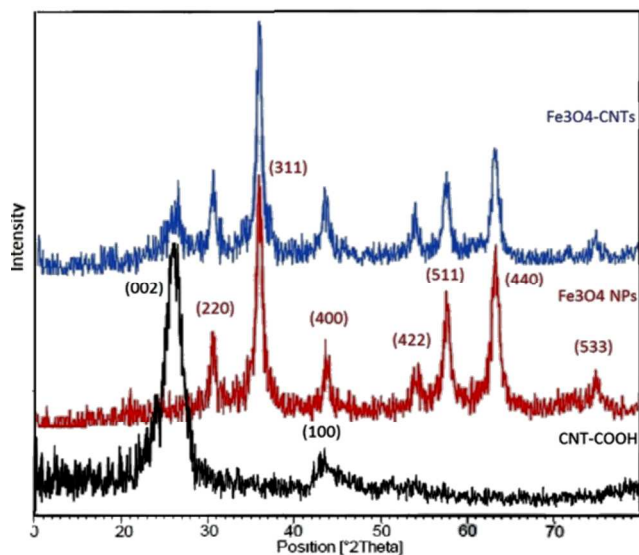


Fig 2. X-ray diffraction patterns of (a) acid treated MWCNTs, (b) Fe_3O_4 NPs, and (c) $\text{Fe}_3\text{O}_4/\text{MWCNTs}$

Figure 3 illustrates the SEM images of the acid treated CNTs and CNT/nano- Fe_3O_4 composites. The SEM images clearly show the uniform distribution of Fe_3O_4 nanoparticles on the surface of the CNTs. The SEM images of catalyst indicate that magnetite nanoparticles are regularly attached on the outside wall of CNTs. Therefore, the interactions between the functional groups of MWCNTs and the iron oxide nanoparticles lead to stable composite materials.

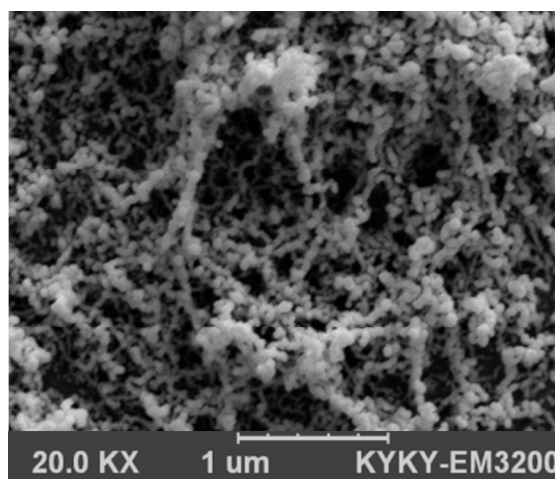
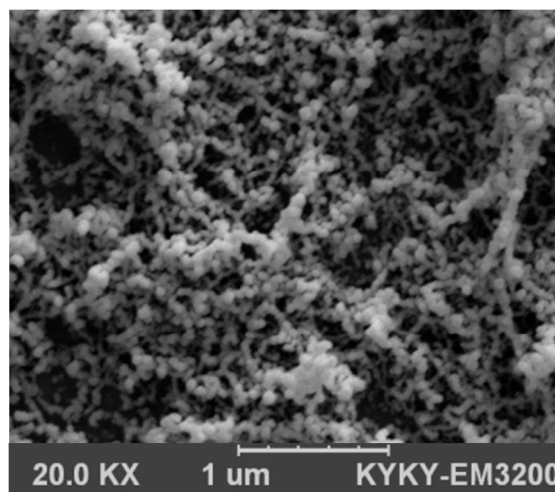
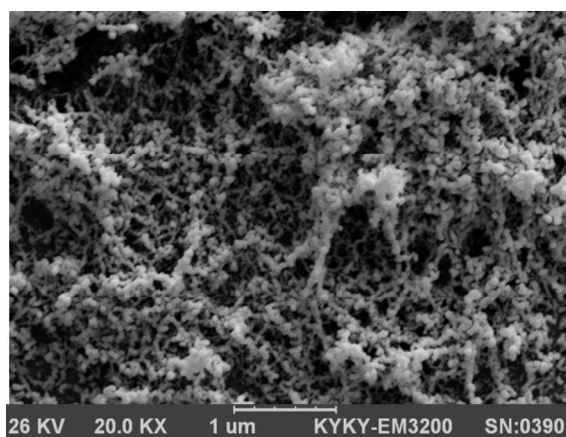


Figure 3. SEM images of $\text{Fe}_3\text{O}_4/\text{CNTs}$ nanocomposites

We analyzed the composite for the presence of Fe via energy dispersive X-ray (EDX) analysis. Figure 4 shows the presence of Fe, O and C elements in the composites. These results confirmed that Fe was efficiently attached on the CNTs surface and the content of Fe is 13.66 w% in the nanocomposites. Due to the presence of OH groups in the functionalized carbon nanotubes, the atomic ratio of Fe and O could not be calculated from EDX analysis.

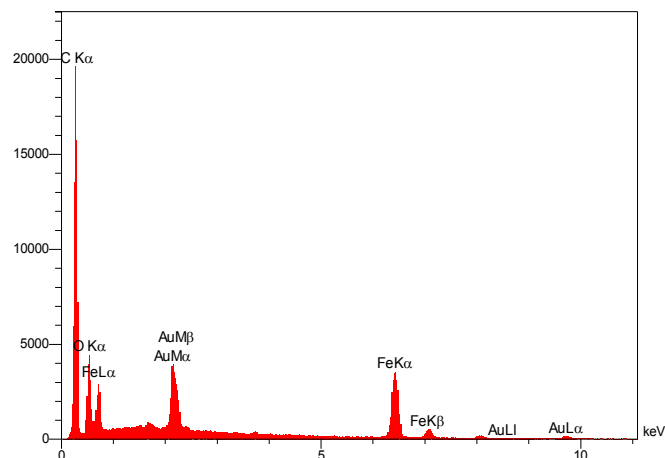
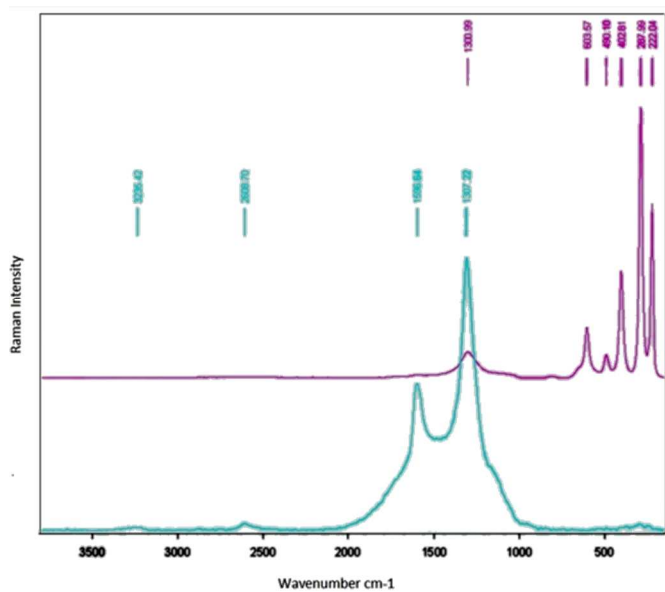


Figure 4. EDX spectrum of Fe_3O_4 -CNTs nanocomposites

Figure 5 clearly shows the Raman spectra of acid treated MWNTs and Fe_3O_4 /MWNTs nanocomposites. Some extra peaks were observed at lower wavenumbers about 222.04, 287.92, 402.81, 490.10, and 603.57 cm^{-1} indicating vibration modes of Fe–O bonds of Fe_3O_4 nanoparticles and Fe–C bonds Fe_3O_4 /MWNTs nanocomposites. This confirms the formation of Fe_3O_4 nanoparticles on the outer wall of MWNTs.⁴² Also, a small shift in G band and D band peaks was observed in the Raman spectroscopic analysis of the Fe_3O_4 /MWNTs nanocomposites. The Raman spectrum of treated MWNTs showed the higher intensity of G band (1596.64 cm^{-1}) in comparison to D band (1307.22 cm^{-1}) corresponding to the purity, regular structure and defects of MWNTs with the IG/ID ratio of 1.22.⁴³

**Figure 5.** Raman spectra of the acid treated MWCNTs and Fe_3O_4 /MWCNTs nanocomposites

The magnetic behaviour of Fe_3O_4 /CNTs nanocomposites and pure Fe_3O_4 nanoparticles prepared under the same reaction conditions has been characterized by vibrating sample magnetometer (VSM). It can be observed from Figure 6 that the saturation magnetization value of Fe_3O_4 /CNTs is 24.72 emu g^{-1} , which is comparatively lower than the pure Fe_3O_4 NPs (49.26 emu g^{-1}). The existence of carbon nanotubes leads to magnetic dead layer and low contents of Fe_3O_4 nanoparticles in the nanocomposites, which results decrease of the saturated magnetization.

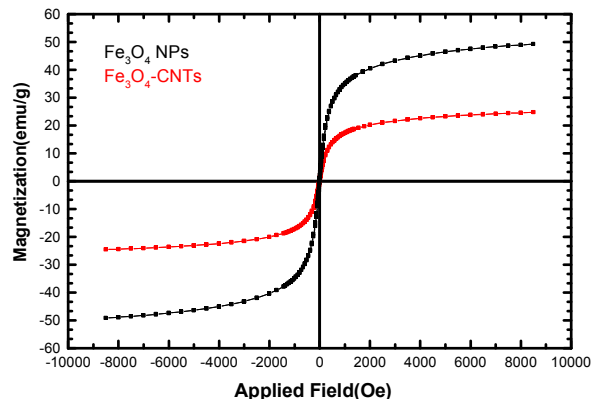
**Figure 6.** Magnetization curves and Fe_3O_4 nanoparticles and Fe_3O_4 /MWCNTs nanocomposites

Figure 7 shows the Fourier transform-infrared spectra (FT-IR) of oxidized MWCNTs, Fe_3O_4 nanoparticles, and CNT/ Fe_3O_4 composites. The broad absorption appearing at around 3436 cm^{-1} and its characteristic absorption at 591 cm^{-1} are attributed to the O–H stretching vibrations. A peak at 1720 cm^{-1} is assigned to C=O stretching vibrations which indicates the attachment of the carboxylic groups to the surface of carbon nanotubes. The absorption band at 2920 cm^{-1} and 2852 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations of methylene (CH_2). A sharp absorption at 1627 cm^{-1} is attributed to the stretching vibration of C=C of CNTs. The bond at 1158 cm^{-1} originates from the graphitic component of MWCNTs. Compared to the oxidized CNTs an absorption band can be seen at 582 cm^{-1} for the composites, which is owing to the stretching vibrations of Fe–O.

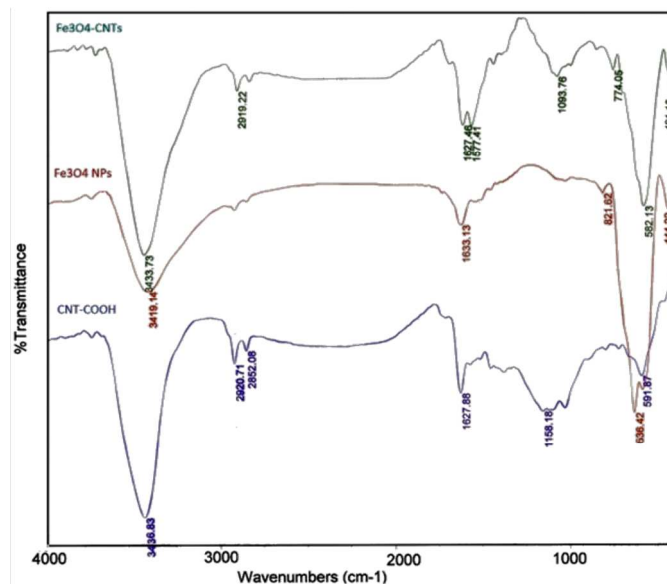
**Figure 7.** FT-IR measurements of acid treated MWCNTs and Fe_3O_4 -CNT composites

Figure 8 shows the ATR FT-IR absorption spectra of oxidized CNTs and CNTs/ Fe_3O_4 nanocomposites. The characteristic absorption peaks of f-MWCNTs are originated from the graphitic component of

carbon nanotubes and vibration of carboxyl and hydroxyl groups. Moreover, the Figure 8b reveals typical Fe₃O₄/CNT characterized by a band corresponding to Fe-O vibrations.

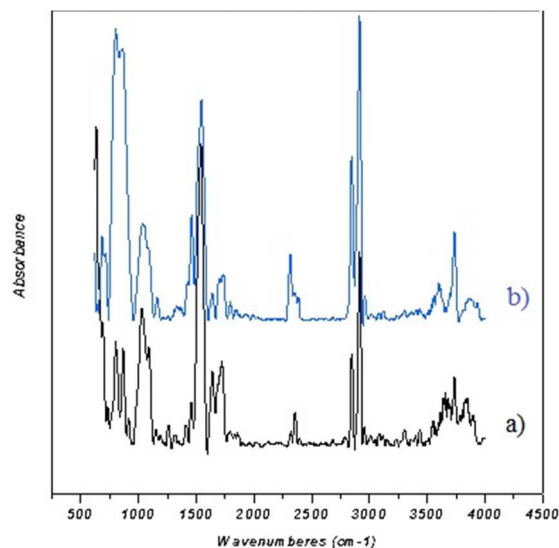
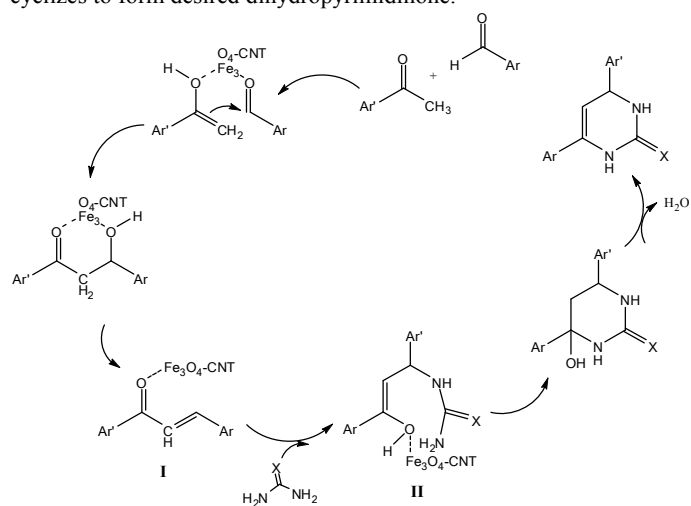


Figure 8. ATR FT-IR spectra of a) acid treated MWCNTs and b) Fe₃O₄-CNT composites

The plausible mechanism of the reaction is illustrated in Scheme 2. In this process, the metal cation acts as Lewis acid and plays a significant role in increasing the electrophilic character of the electrophiles. The first step of the present reaction is cross-aldol condensation of aldehyde with ketone to afford the respective chalcone **I** which then is stabilized by coordination with metal cation. After that the Michael addition of urea to chalcone **I** produces an open chain ureide **II**, which subsequently eliminates water and cyclizes to form desired dihydropyrimidinone.



Scheme 2. Suggested mechanism for the three components condensation of aldehyde, ketone and urea

Experimental

Chemical substances were purchased from Merck, Fluka and Aldrich. MWNTs with outer diameter between 10 and 20 nm were purchased from Nanotech Port Co. (Taiwan). These MWNTs were produced via the chemical vapor deposition

(CVD, or sometimes called catalytic pyrolysis) method. Melting points were determined using an Electrothermal MK3 apparatus and are uncorrected. The IR spectra were measured on Perkin-Elmer FT-IR 550 spectrophotometer. ¹H and ¹³C NMR spectra were recorded on a Bruker DRX-400 spectrometer and chemical shifts are reported in ppm downfield from TMS. The reactions were monitored qualitatively by TLC. Products were all known compounds and were identified by the comparison of their physical and spectra data with those reported in literature. KYKY scanning electron microscope (SEM) spectrometer (model EM3200, operated at a 25 kV) was applied to observe the surface morphology of the nanocomposites. Also, the phase structure of the as-prepared CNTs/Fe₃O₄ nanocomposites were characterized by X-ray diffraction (XRD) a Bruker D8 Advance X-ray diffraction (XRD) diffractometer (CuK, radiation, λ= 0.154056 nm and 40 kV voltage), at a scanning speed of 2°/min from 10° to 100° (2θ). The Raman spectra were measured on a Bruker SENTERRA spectrometer with spectral range: 200-3500cm⁻¹ and Laser wavenumber 785nm.

Preparation of Fe₃O₄/CNTs catalyst

Fe₃O₄-CNTs were synthesized according to the previous report.⁴⁴ Briefly, MWCNTs were stirred in concentrated HNO₃ at 60 °C for 12 h to functionalize the outer surfaces with hydrophilic groups such as -OH, -CO, and -COOH and for removal of the impurities. Then, the purified MWCNTs were recovered by centrifuge, were washed with deionized water to pH 7.0 and were dried at 100 °C for 2 h in an oven. The CNT/Fe₃O₄ nanoparticle composites were prepared by chemical coprecipitation of Fe²⁺ and Fe³⁺ in alkaline solution in the presence of functionalized CNTs. Therefore, 90 mg purified CNTs were suspended in 20 mL of aqueous solution containing 157 mg (0.4 mmol) (NH₄)₂Fe(SO₄)₂·6H₂O and 386 mg (0.8 mmol) NH₄Fe(SO₄)₂·12H₂O at 50 °C. The molar ratio of Fe²⁺:Fe³⁺ was 1:2. Then, the mixture was sonicated for 10 min. Next, 5 mL of 5 M NH₄OH aqueous solution was added to precipitate the iron oxides in pH 11–12 while the mixture solution was sonicated. The reaction was continued at 50 °C for 30 min under mechanical stirring. Afterwards, the as-synthesized samples were separated magnetically from the suspension and were washed three times with doubly distilled water to remove the impurities and were dried in a vacuum oven at 100 °C for 24 h (Figure 9).

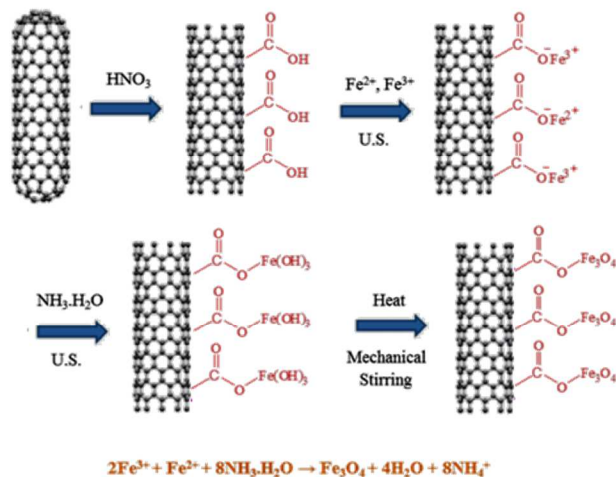


Figure 9. Schematic of the synthesis route for Fe₃O₄-CNTs nanocomposites

General procedure for the three-component synthesis of Biginelli-type compounds

In a typical grinding procedure, benzaldehyde (1 mmol, 0.15 g), urea (1.5 mmol, 0.09 g) and acetophenone (1 mmol, 0.12 g) were mixed thoroughly and were ground in a mortar under solvent-free conditions at room temperature. The grinding processes were continued further following by adding a catalytic amount of Fe₃O₄-CNTs (0.05 g) for an appropriate time period to be completed reaction as was indicated by TLC. After that, the catalyst separated using an external magnet without filtration and all potential iron is separated from the product. The separated solid product was poured into crushed ice, and was stirred for several minutes, and then was filtered and recrystallized from ethanol to afford the pure product in 98% yield.

Conclusions

In this paper, we introduced Fe₃O₄-CNT as a highly efficient and economically viable catalyst for the one-pot synthesis of 4,6-diaryl-3,4-dihydropyrimidin-2(1H)-one derivatives from aldehydes, urea and acetophenone by mechanical grinding. The use of ketones gave us the opportunity to prepare corresponding 5-unsubstituted 3,4-dihydropyrimidin-2(1H)-one derivatives. The method is simple, green, efficient, and is expected to be a useful synthetic protocol for the synthesis of a wide range of novel drug-like dihydropyrimidinones. The procedure is not only advantageous from the environmental point of view but also offers increased rate and high yields and reduced time. Another useful aspect of this procedure is high efficiency from point of view on energy. These make grindstone technology economically useful and environmentally benign for organic synthesis. This new method for the synthesis of Biginelli-like scaffolds makes this ring system accessible for inclusion into pharmacologically important agents. Also, our approach provides support for practical application of Fe₃O₄/CNT nanocomposites as catalyst.

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Notes and references

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