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Decoration of multi-walled carbon nanotubes with NiO nanoparticles and investigation on their catalytic activity to synthesize pyrimidinone heterocycles

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Abstract A supported carbon material is shown to be a highly efficient, eco-friendly and recyclable solid acid catalyst for the Biginelli reaction of aldehyde, β -ketoester and urea or thiourea under microwave irradiation in the absence of solvent. This method offers significant advantages such as efficiency, the excellent yield, avoidance of the organic solvents, mild reaction conditions, easy separation and simple operation. In addition, because of employing microwave as heating source and reducing use of organic solvents, this novel method emerges as a greenapproach leading to less harmful residues. Furthermore, a mechanism was proposed to rationalize the reaction and the role of NiO–MWCNTs was also investigated in these transformations.

Keywords NiO–MWCNTs \cdot 3,4-Dihydropyrimidin-2(1*H*)-one \cdot Microwave irradiation \cdot Heterogeneous catalyst \cdot Multi-walled carbon nanotubes

Introduction

Pyrimidinones or dihydropyrimidinones (DHPMs) are well known for wide range of their bioactivities due to their therapeutic and pharmaceutical properties. These cores are regarded as one of the most important groups of drug-like scaffolds [1]. They possess a broad spectrum of

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S. Gandomi-Ravandi e-mail: gandomi_so@yahoo.com pharmacological activities such as calcium channel blocker [2], neuropeptide Y (NPY) antagonists [3], selective α_{1a} receptor antagonists [4, 5] and antihypertensive [6, 7]. Their applications have been stimulated in the field of drug research to develop a wide range of synthetic methods and chemical transformations. Since the first report on the synthesis of DHPMs by Pietro Biginelli in 1893 [8], the most chemists have modified the original Biginelli reaction by changing substrates and also reaction conditions [9–11]. Various catalysts have recently been suggested to improve the reaction by different researchers. Some of these catalysts included Zn_(1-x)Ni_xAl₂O₄ spinels [12], chloroindate ionic liquid (BMI.InCl₄) [13], Iron(III) tosylate [14], Cu/ SiO₂ [15], nanocomposite Fe_{0.2}Al_{0.8}Zn₁O₄ [16], 1,3,5-triazine-2,4,6-trivltrisulfamic acid [17], choline-based ionic liquids [18], melamine sulfonic acid/ZnO nanotube [19] and poly(4-vinylpyridine)-supported copper iodide nanoparticles [20]. The discovery of a new and efficient catalyst has key importance to prepare 3,4-dihydropyrimidine-2-(1H)-ones under mild conditions with high yield.

It is important to develop heterogeneous catalysts in organic synthesis, because of the potential advantages of these materials consist of ease of handling, lack of corrosion, recovery and regeneration [21]. Metal oxide nanoparticles have recently been used as heterogeneous catalyst because of their interesting structure, high catalytic activities and improved selectivity [22–26]. More interest has been focused on cheap transition metal oxides such as nickel oxide (NiO), owing to its p-type semi-conductivity, low toxicity and non-flammable properties which make it safe to handle [27–29]. However, the specific surface area of the pure NiO is not high enough for the practical applications. Carbon nanotubes (CNTs) are cylindrical, regular and symmetric nanostructures made of carbon atoms rolled up with graphene [30]. Owing to inactivity of

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the walls of CNTs, the functionalization processes must be carried out before adsorption experiments to develop the adsorption capacities of CNTs [31]. Also, the useful applications of nanocomposites of metal oxides as catalyst have been improved in organic synthesis owing to their high catalytic activity and the large surface area. Combination of NiO and CNTs with excellent electron transfer rate and large specific surface area is expected to provide a chance for improvement of the durability and performance of pure NiO particles [32]. Consequently, carbon nanotubes decorated with NiO nanoparticles can influence their physical, thermal, mechanical and electrical properties and may give novel properties and promising applications with the combination of features of nanoparticles and carbon nanotubes [33]. However, there is no example of using NiO-MWCNTs as a catalytic system to synthesize DHPMs under microwave irradiation. Therefore, for the first time, we would like to report a simple approach to prepare 3,4dihydropyrimidin-2(1*H*)-ones/thiones (Biginelli reaction) via microwave-activated cyclocondensation of aromatic aldehyde, β -dicarbonyl compound and urea or thiourea in the presence of NiO-MWCNTs as catalyst (Scheme 1). Herein, we also present a sonochemical approach for the fabrication and uniform dispersion of NiO nanoparticles on the surface of multi-walled carbon nanotubes. Ultrasonic irradiation prevents the agglomeration of the nanoparticles and improves the dispersion ability of the coatings' formulation.

Experimental

All chemicals were of research grade obtained from Sigma-Aldrich and were used without any further purification. MWCNTs were purchased from Nanotech Port Co. (Taiwan). These MWCNTs were produced via the chemical vapor deposition (CVD, or sometimes called catalytic pyrolysis) method. The outer diameter of MWCNTs was between 10 and 20 nm. Melting points were determined on an Electrothermal MK3 apparatus using open capillaries and are uncorrected. FT-IR spectra were recorded on a



Scheme 1 Microwave-mediated multi-component synthesis of dihydropyrimidinones (thiones)

Perkin Elmer FT-IR 550 spectrophotometer using KBr pellets. NMR spectra were recorded on a Bruker DRX-400 spectrometer and chemical shifts are expressed in δ ppm downfield from TMS as an internal standard. To characterize NiO-MWCNTs nanocomposites, fourier transform infrared spectroscopy (FT-IR) was employed to analyze the functional groups on the purified MWCNTs. X-ray diffraction (XRD) pattern of the as-synthesized material was obtained using a Holland Philips X-ray diffraction (XRD) diffractometer model X'PertPro (CuK, radiation, $\lambda =$ 0.154056 nm), at a scanning speed of $2^{\circ}/\text{min}$ from 10° to 100° (2 θ). The nanocatalysts were determined also using a TESCAN model VEGA II scanning electron microscope (SEM) operated at a 15-kV accelerating voltage. Recrystallization was carried out in suitable solvent. The Raman spectra were recorded on a Bruker SENTERRA spectrometer with Laser wavenumber 785 nm and spectral range $200-3,500 \text{ cm}^{-1}$. All products were identified through their spectroscopic data and the melting points were confirmed by comparison with those reported in the literature.

Preparation of NiO-supported on the acid-treated MWCNTs

Oxidized carbon nanotubes were prepared by purification in a ratio of 3:1 70 % nitric acid and 98 % sulfuric acid using sonication for 6 h. The purified samples were washed and neutralized by distilled water and were dried at 100 °C for 2 h. Composite material of NiO-MWCNTs was prepared by thermal decomposition of Ni(OH)₂/MWCNTs [34]. In short, 0.06 M NiCl₂·6H₂O was mixed with 0.1 g acid-treated MWCNTs. Then, ammonium hydroxide was dropped into this mixed suspension at pH 8 and was sonicated for 20 min. After that, the suspension was soaked in the solution for 5 h and was separated by centrifugation to achieve intermediate product (Ni(OH)₂/MWCNTs). Indeed, Ni²⁺ ions were enucleated by chelation with carboxyl functional groups on the surface of MWCNTs due to the electrostatic attraction. Then, OH⁻ reacts in situ with the Ni²⁺ and Ni(OH)₂ precipitates were formed on the surface of MWCNTs through electrovalent bonding. Next, the composite material was calcined at 400 °C for 2 h and NiO-MWCNT nanocomposites are achieved after these heat treatments (Fig. 1). Finally, the resulting products were washed with deionized water several times and collected by centrifugation. Now the material is ready to be used as a supported catalyst.

Preparation of the Biginelli compounds

A mixture of (thio) urea (1 mmol), aldehyde (1 mmol) and methyl acetoacetate (1.5 mmol) was irradiated in the presence of NiO–MWCNTs (0.04 g) into microwave oven at





 Table 1 Comparison of the results of the synthesis of 4a using different catalysts under microwave irradiation

Entry	Catalyst	Time (min)	Yield (%)	
1	MWCNTs	10	20	
2	MWCNTs-COOH	10	35	
3	NiO NPs	10	70	
4	NiO	10	60	
5	NiCl ₂	10	49	
6	NiO-MWCNTs	10	98	

 Table 2 Optimization of reaction conditions of 4a using various concentrations of catalyst

Entry	Catalyst (g)	Time (min)	Yield (%)
1	0.01	35	80
2	0.02	30	85
3	0.03	20	90
4	0.04	10	98
5	0.05	15	98

300 W for the appropriate time. After the reaction was completed, hot ethanol was added to mixture and the catalyst was removed by filtration and the filtrate was poured onto crushed ice. The resulting solid was collected by filtration and was recrystallized from ethanol to afford the pure product in high yield.

Results and discussion

Nickel oxide supported on multi-walled carbon nanotubes afforded a valuable catalytic system to promote the synthesis of DHPMs. In addition, the microwave technique represented a better procedure owing to the higher yield, milder reaction conditions, easier workup and green chemistry. The reaction conditions were optimized with the model substrates of benzaldehyde, methyl acetoacetate and urea in the presence of NiO–MWCNTs nanocomposites as heterogenous catalyst under microwave irradiation. At first, we examined the reaction parameters such as amount and type of catalyst, reactant ratios and also reusability of catalyst. Initially, the various catalysts were studied for their activities in the model reaction. As shown in Table 1, NiO–MWCNTs were found to be highly active in term of reaction yield under MW irradiation.

Next, we performed the model reaction with different amounts of NiO–MWCNTs nanocomposite to evaluate the effect of the catalyst. It was found that the highest yield was obtained using 0.04 g catalyst (Table 2). There is no significant improvement in the yield by increasing in the amount of catalyst (Table 2, Entry 4).

Moreover, the recyclability of the supported catalyst is also important. The resulting mixture was washed using hot ethanol and the catalyst was recovered by filtrating of the reaction mixture and was reused after dilution with ethyl acetate for subsequent experiments under similar reaction conditions. It was found from Fig. 2 that there was no significant decrease in activity after four runs using the NiO–MWCNTs.

To investigate the efficiency of microwave irradiation, the model reaction was also examined in conventional conditions. As shown in Table 3, it was apparent that the reaction proceeded better under microwave irradiation.

The same reaction was investigated with different molar ratios of reactants to determine the appropriate molar ratio and the highest yield of the desired product **4a** was obtained with 1:1:1.5 ratios of benzaldehyde, methyl ace-toacetate and urea in the presence of 0.04 g NiO–MWCNTs under microwave irradiation. Afterward, a wide range of aromatic aldehydes carrying either electron-

donating or -withdrawing substituents was investigated under the optimized reaction conditions to study the generality of this process. Most importantly, aromatic aldehydes carrying either substituents reacted very well to give the corresponding dihydropyrimidinones in excellent yields with high purity. The results are summarized in Table 4.



Fig. 2 Reusability of catalyst in the synthesis of 4a under microwave irradiation

Table 3 Synthesis of compound 4a under heating and microwave conditions

Entry	Conditions	Time (min)	Yield (%)	
1 r.t stirring		110	5	
2	Thermal 40 °C	90	20	
3	Thermal 60 °C	70	30	
4	Thermal 80 °C	50	45	
5	Thermal 100 °C	35	60	
6	Thermal 120 °C	30	65	
7	Microwave	10	98	

Catalyst (0.04 g)

Table 4Catalytic synthesis ofdihydropyrimidinones (thiones)catalyzed by NiO–MWCNTsunder microwave conditions

Also, thiourea has been used with similar approach to produce the corresponding thio-derivatives of DHPMs.

Figure 3 presents the typical Scanning Electron microscopy (SEM) images of NiO–MWCNTs nanocomposites. These micrographs show the presence of metal oxide nanoparticles. It can be clearly observed that the NiO nanoparticles were dispersed with the homogeneous distribution on the outside wall of the MWCNTs.

Raman spectroscopy is a powerful and sensitive technique to investigate the structural properties of carbonaceous materials and the extent of disorder in the functionalized CNTs and CNTs based composite materials [40, 41]. Figure 4 compares the Raman spectra of acidtreated MWCNTs and NiO-MWCNTs between 200 and 4.000 cm^{-1} . Two broad bands were located at 1,596 (G bands) and 1,307 (D bands) cm^{-1} region corresponding to the acid-treated MWCNTs, which show the C-C bond vibrations of carbon atoms with sp² electronic configuration in graphene sheet structure and the disordered and imperfect structures of carbon materials, respectively [42]. Attaching NiO nanoparticles led to the red shift of D-band $(1,274 \text{ cm}^{-1})$ and G-band $(1,555 \text{ cm}^{-1})$ peak position relative to oxidized multi-walled carbon nanotubes (Fig. 4b). In addition, it appears a peak at 515 cm^{-1} confirmed to the stretching modes of NiO [43]. The stretching modes of NiO have also been detected at 200–800 cm^{-1} region [44, 45]. The intensity ratio of the I_D/I_G corresponding to integrated intensity ratios was found to be 1.86 for the oxidized MWCNTs samples; however, it was about 1.47 for the NiO-MWCNTs samples.

The XRD patterns of MWCNTs–COOH, nanocrystalline NiO and NiO–MWCNTs composites are presented in Fig. 5. The diffraction peaks at 37.42° , 43.46° , 63.01° , 75.44° and 79.40° correspond to (111), (200), (220), (311) and (222) reflections, respectively, which they are

Entry	R	Х	Product	Mp (°C)		Time (min)	Yield (%)
				Obs.	Lit.		
1	Н	0	4 a	208-210	209–211 [35]	10	98
2	4-Cl	0	4b	204-205	204–206 [36]	15	92
3	4-NO ₂	0	4c	235-237	236–238 [<mark>35</mark>]	15	95
4	2,4-Cl ₂	0	4d	254-255	252–253 [<mark>36</mark>]	20	91
5	3-OMe	0	4e	206-208	207–208 [37]	15	90
6	2-Br	0	4f	240-241	240-242 [38]	10	88
7	3-OMe-4-OH	0	4g	225-226	225 [39]	25	85
8	Н	S	4h	233-235	232–234 [38]	15	93
9	4-OH	S	4i	245-247	245-246 [38]	20	87
10	4-OMe	S	4j	178-180	179–180 [<mark>38</mark>]	20	92
11	4-Br	S	4k	152-154	153–154 [<mark>38</mark>]	15	93
12	4-NMe ₂	S	41	151–153	152–155 [36]	20	89

Fig. 3 SEM images of NiO– MWCNTs





Fig. 4 Raman spectra of \mathbf{a} acid-treated MWCNTs and \mathbf{b} NiO–MWCNTs composite

correlated with NiO in cubic phase. This confirms the crystalline nature and phase purity of NiO nanoparticles. Also, a peak is clearly observed near 26.32° [(002) plane], which is typical for multi-walled CNTs [46]. The XRD result clearly indicates that NiO nanoparticles were decorated on the surface of MWCNTs. The average crystal size of the NiO–MWCNTs was calculated by the Debye–Scherrer formula to be 18.93 nm.

FT-IR spectra of acid-treated MWCNTs, NiO–MWCNTs nanocomposites and recovered NiO–MWCNTs are presented in Fig. 6. In case of oxidized MWCNTs, the presentative peaks observed around 3,438, 1,726 and 1,627 cm⁻¹ are assigned to O–H, C=O and C=C stretching



Fig. 5 XRD patterns of oxidized MWCNTs, nanocrystalline NiO and NiO–MWCNTs

frequencies. The C=O stretching frequency is owing to the presence of carbonyl and carboxylic groups produced during the oxidation of pristine MWCNTs. Also, C=C stretching frequency is owing to the inherent structure of MWCNTs. The significant peaks at 428, 567 and 1,400 cm⁻¹ are assigned to the Ni–O bond stretching vibration mode in FT-IR spectrum of NiO–MWCNTs (Fig. 5b). Also, Fig. 5c shows clearly the recovered nanocomposites.

EDX spectrum is also recorded to determine the chemical composition of NiO–MWCNTs (Fig. 7). The results indicate the presence of carbon, nickel and oxygen elements in the nanocomposites. Results of element content in EDS patterns reveal that the content of Ni is 24.63 W %.



Fig. 6 FT-IR spectra of **a** acid-treated MWCNTs, **b** NiO–MWCNTs catalyst and **c** recovered NiO–MWCNTs composites



Fig. 7 The EDX spectrum of NiO-MWCNTs

The ATR FT-IR spectra of the MWCNT–COOH and NiO–MWCNTs are shown in Fig. 8. A sharp peak was observed for Ni–O stretching vibration mode at 667 cm⁻¹. Also, it is shown that characteristic frequencies correspond to the signature of bands of graphitic carbon materials and the functional groups containing oxygen in carbon frameworks.

Therefore, we have introduced NiO–MWCNTs nanocomposites as a novel and highly effective heterogenous catalyst for the condensation of aldehyde, urea (thiourea) and 1,3-dicarbonyl compound under microwave conditions in excellent yields. All the products were characterized by FT-IR and ¹H NMR analysis and their melting points are like the known compounds reported in the literature.



Fig. 8 The ATR FT-IR spectra of oxidized MWCNTs and NiO-MWCNTs

A reasonable mechanistic pathway of Biginelli condensation via *N*-acylimine intermediate **I** is shown in Scheme 2. This intermediate is formed from the reaction of the aldehyde and urea and then is stabilized by catalyst through coordinate bonds owing to metal empty orbital. Meanwhile, the metal support acts as a Lewis acid and increases the electrophilic character of the carbonyl groups. Then, methyl acetoacetate enolate is stabilized by complexing the two oxygen atoms with metal ion. The iminium ion intermediate **I** interacts with methyl acetoacetate enolate to produce an open chain intermediate ureide **II**. At last, dihydropyrimidinones are afforded during the cyclization and dehydration of intermediate **II**.

Conclusions

In summary, this investigation deals with a novel and practical approach to synthesize 3,4-dihydropyrimidin-2(1H)-ones, which was achieved by applying the Biginelli cyclocondensation reaction in the presence of nickel oxide supported on the multi-walled carbon nanotubes as a heterogenous catalyst. The catalyst is highly efficient, selective, easy to handle and it is easily removed from the reaction mixture. This recyclable heterogeneous catalyst provides a simple strategy to prepare a variety of heterocycles under green conditions. Our interest in environmentally friendly organic synthesis prompted us to investigate the utility of NiO–MWCNTs as a catalyst for the Biginelli reaction under microwave irradiation. A collection of DHPMs has been generated by a parallel

Scheme 2 Plausible mechanism for the Biginelli reaction in the presence of NiO– MWCNTs nanocomposites



synthesis approach. This study will help to develop an easy protocol for the synthesis of many DHPMs derivatives with high yields in an energy-efficient protocol.

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