



Preparation of (MWCNTs)-COOH/CeO₂ Hybrid as an Efficient Catalyst for Claisen-Schmidt Condensation

Tahereh Heidarzadeh, Navabeh Nami^{*}, Daryoush Zareyee

Department of Chemistry, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran

(Received 18 Nov. 2020; Final revised received 19 Feb. 2021)

Abstract

Acid functionalized multi-walled carbon nanotubes/CeO₂ (MWCNTs)-COOH/CeO₂ hybrid was fabricated by the reaction of functionalized (MWCNTs)-COOH and Ce(NO₃)₂.6H₂O in acetic acid. Synthesis of CeO₂ nanoparticles and their conjugation on the surface of (MWCNTs)-COOH have been confirmed by FT-IR, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and Energy-dispersive X-ray spectroscopy (EDX). The modification of MWCNTs-COOH with CeO₂ produced an efficient catalyst for the Claisen-Schmidt condensation, so a large variety of chalcones were obtained in high yield using a catalytic amount of (MWCNTs)-COOH/CeO₂ hybrid (5 mol%).

Keywords: (MWCNTs)-COOH/CeO₂, Nanomaterial, Claisen-Schmidt condensation, Chalcone.

^{*}**Corresponding author:** Navabeh Nami, Department of Chemistry, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran. Email: Navabehnami@yahoo.com.

Introduction

Cerium(IV) oxide, also known as ceria, is an important commercial product of the rare-earth metal cerium. It is a pale yellow-white powder with the chemical formula CeO_2 . It has been mostly used for various applications such as sensors, cells, therapeutics agents, drug delivery carriers, electrical, catalytic, and optical [1-5], due to its unique surface chemistry, high stability, and biocompatibility [6-7]. However, to increase the properties of CeO_2 , it is needed to reduce the particle size to the nanometer and increase the active surface area of metaloxide. Decrease in the particle size enhancing conductivity, sensing, and catalytic properties of nano-materials [8,9], which are significantly different from those of bulk particles. The first kind of carbon nano-tubes were Multi-walled carbon nano-tubes (MWCNTs). They are very attractive and well-known chemical compounds because of their special physical and chemical properties and a wide variety of industrial and biological activities such as drug delivery [10, 11], electronics [12], catalysis [13-15], biosensors [16], biomedical [17], storage [18], and photovoltaic [19] activities.

It has been demonstrated that the MWCNTs properties can be dramatically affected by surface modification with biological and chemical compounds [20,21]. Nano-metal and nano-metal oxide particles immobilized multi-walled carbon nano-tubes (MWNTs) have shown excellent catalytic properties in organic reactions [22]. Many metal oxides have been used to modify the surface of MWCNTs [23–24]. Due to the presence of a very active site on the large surface of MWCNT–COOH/ M_xO_y hybrid, it can be used as an effective catalyst in chemical reactions [25]. On the other hand, Carbon nano-tubes (CNTs) are effective supports for nano-metal particles (NP) like zinc oxide, cadmium oxide, lanthanum oxide, or manganese oxide, and together they represent hybrid structures (NP-CNTs) that combine the unique properties of both [26].

Chalcones are well-known intermediates with an unsaturated side chain and aromatic rings for the synthesis of various organic compounds. Chalcones are found in a variety of plants and are considered to be the precursors of flavonoids. The flexible structure of chalcones makes them have a large number of biological activities including antifungal, antitumor, antimutagenic, antiprotozoal, antimitotic, and antiviral properties [27-33]. They are synthesized by Claisen–Schmidt condensation, which involves cross aldol condensation of appropriate aldehydes and ketones by different catalyzed reactions followed by dehydration.

Because of the reasons above, we proposed that the combination of cerium oxide nano-particles and acid functionalized multi-walled carbon nano-tubes can give raise the catalytic activity for the synthesis of heterocyclic and organic compounds. So in this article, we present a simple synthesis of some chalcone derivatives and Claisen–Schmidt condensation using multi-walled carbon nano-

tubes-COOH/CeO₂ (MWCNTs)-COOH/CeO₂ hybrid as an effective catalyst under mild reaction conditions and good yields.

Experimental

Chemicals and Instrumentation

Solvents and chemicals were purchased from Aldrich and Merck. MWCNTs-COOH/CeO₂ was distinguished by powder X-ray diffraction (XRD) PW 3040/60 X'Pert PRO diffractometer system, using Cu K α radiation with ($\lambda = 1.5418 \text{ \AA}$) in the range of $2\theta = 20\text{--}80^\circ$ at room temperature. The morphology and sizes of NPs were measured using a transmission electron microscope (TEM, 150 kV, and Philips-CM 10) and a scanning electron microscope (SEM) by Day Petronic Company-Iran. FT-IR measurements were recorded on a Shimadzu 8400s spectrometer with KBr plates. The NMR spectra were determined on Bruker XL 400 (400 MHz) instruments. Melting points were obtained on an Electrothermal 9100 without further corrections.

Synthesis and purification of (MWCNTs)-COOH

MWCNT (250 mg) was added to 200 ml concentrated nitric acid and the mixture was refluxed for 8 hours then centrifuged for 30 min at 10000 rpm. The functionalized MWCNTs were added in 500 ml redistilled water and filtered by a cellulose nitrate membrane filter (0.45 μm pore size) using a vacuum filtration assembly. The product was frequently washed with distilled water to neutralize the pH of the filtrate. The filtered compound was dried in a vacuum oven at 80°C for 24h and obtained (MWCNTs)-COOH were characterized using different techniques[34].

Preparation of (MWCNTs)-COOH/CeO₂ hybrid

The functionalize (MWCNTs)-COOH (0.3 g) and Ce(NO₃)₂.6H₂O (0.5 M, 200 ml) were mixed and reacted by ultrasonication at 60°C for 30 min, then hydrazine hydrate (80%, 4 ml) and NaOH (1M, 25 ml) were added in the reaction mixture under constant magnetic stirring at room temperature, stirring was continued for 30 minutes and then placed in the 80 °C water bath for 1 hour. The precipitate was collected by centrifugation and washed with distilled water and ethanol and the product is dried, first in theair and then in a vacuum.

General procedure for Claisen-Schmidt Condensation in the presents of (MWCNTs)-COOH/CeO₂

Aromatic aldehydes (1 mmol), acetophenone derivatives, and (MWCNTs)-COOH/CeO₂(5mol %) were mixed and reacted in ethanol (10 ml) under reflux condition. The completion of the reaction was determined by TLC using *n*-hexane: ethyl acetate (1:1) and appeared by a UV lamp (254 & 366 nm). In the end, the reaction mixture was centrifuged and the catalyst was filtered and washed with

ethanol (3 x 5 ml) and water (3 x 5 ml), dried at 100 °C for 2h, and reused for the same reaction. The rest of the reaction mixture was evaporated, and the crude product was purified by recrystallization from ethanol.

Results and discussion

The present paper reports the results of a research aimed to verify the preparation of the (MWCNT)-COOH/CeO₂ hybrid as an effective catalyst for Claisen-Schmidt condensation.

(MWCNTs)-COOH/CeO₂ characterization

The possible interaction between Ce(NO₃)₂.6H₂O and (MWCNTs)-COOH was investigated using FT-IR spectroscopy, which leads the preparation and stabilization of MWCNTs-COOH/CeO₂. As shown in Table 1, The FT-IR spectra of MWCNTs, MWCNTs-COOH, and MWCNTs-COOH/CeO₂ have been investigated in the frequency range 400–4000 cm⁻¹ (Table 3).

Table 1. FT-IR spectral data for MWCNTs, MWCNTs-COOH, and MWCNTs-COOH/CeO₂.

Entry	Compounds	FT-IR (KBr, ν_{\max} cm ⁻¹)
1	MWCNTs	3031.15(=C-H), 2923.94 (CH), 1633.66 (C=C), 1619.29 (C=C)
2	MWCNTs-COOH	3430.02 (OH), 3042.18 (=C-H), 2923.94 (-CH), 1779.19 (C=O), 1634.21(C=C), 1523.35 (C=C), 1266.68 (C-O), 1024.12 (C-O)
3	MWCNTs-COOH/CeO ₂	3421.72 (OH), 2924.21 (-CH), 2519.35 (C=C), 1798.63 (C=O), 1411.03 (C=C), 1104.40 (C-O), 400-530.51 (Ce-O)

The bands at around 1300-1550 cm⁻¹ are associated with the vibration of the carbon skeleton of the carbon nano-tubes. In Table 1 (Entry 2, 3), the bands at about 1630-1750 and 1000-1300 cm⁻¹ indicate the existence of C=O groups of COOH [33]. The bands at about 2000-2450 cm⁻¹ are belonged to the C=C double bonds stretching vibration of the MWCNTs [34]. The peaks around 3400-3650 cm⁻¹ in Table 1 (Entry 2,3) can be assigned to the stretching vibrations of OH groups [35, 36]. The broad peak observed at about 400-550 cm⁻¹ in Table 1 (Entry 3) are assigned to the formation of Ce-O, in which the range between 400-550 cm⁻¹ corresponds to the literature [37,38]. The peak at about 2300 cm⁻¹ became narrower and the bands around 1630-1750 cm⁻¹ are lower in MWCNTs-COOH than those of pure MWCNTs-COOH/CeO₂ because the surface of (MWCNTs)-COOH has been covered by CeO₂.

X-ray diffraction (XRD) is normally used to study and characterize the crystallization and average size of (MWCNTs)-COOH/CeO₂. In Figure 1, the XRD pattern of MWCNTs-COOH/CeO₂ shows different peaks in the whole spectrum of 2θ values ranging from 5° to 80°. Presence of eight distinct high diffraction peaks at 2θ values of 26.50°, 43.35°, 46.33°, and 54.79° for carbon, 28.75°, 33.13°, 47.30°, and 56.33° for CeO₂ respectively, (JCPDS Number. (MWCNTs)-COOH/ CeO₂: 03-065-5923; CeO₂, 00-026-1079; C) [41,42] confirmed that the MWCNTs-COOH/CeO₂ had been formed. The other diffraction peaks could be due to some chemical compounds and crystals on the surface of the nano-particle. The wide X-ray diffraction peaks around their bases show that the MWCNTs-COOH/CeO₂ is in nano-sizes. With the XRD pattern, the average diameter which can be calculated from Scherrer equation [43] ($D = K\lambda/\beta\cos\theta$, where β is the peak width at half maximum, λ is X-ray wavelength, and K is constant) is obtained about 4.3 nm.

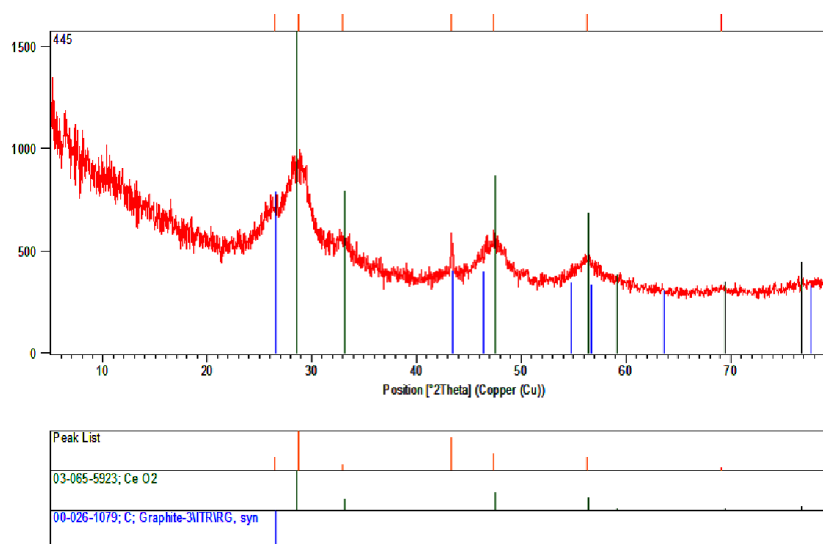


Figure 1. XRD of MWCNTs-COOH/CeO₂ nanocomposite.

The morphology and size of MWCNTs-COOH/CeO₂ were studied using transmission electron microscopy (TEM) in Figure 2. The TEM image indicates that the CeO₂ nano-particles are well bonded to the surface of multi-wall carbon nano-tubes. On the other hand, TEM values are in good agreement with XRD.

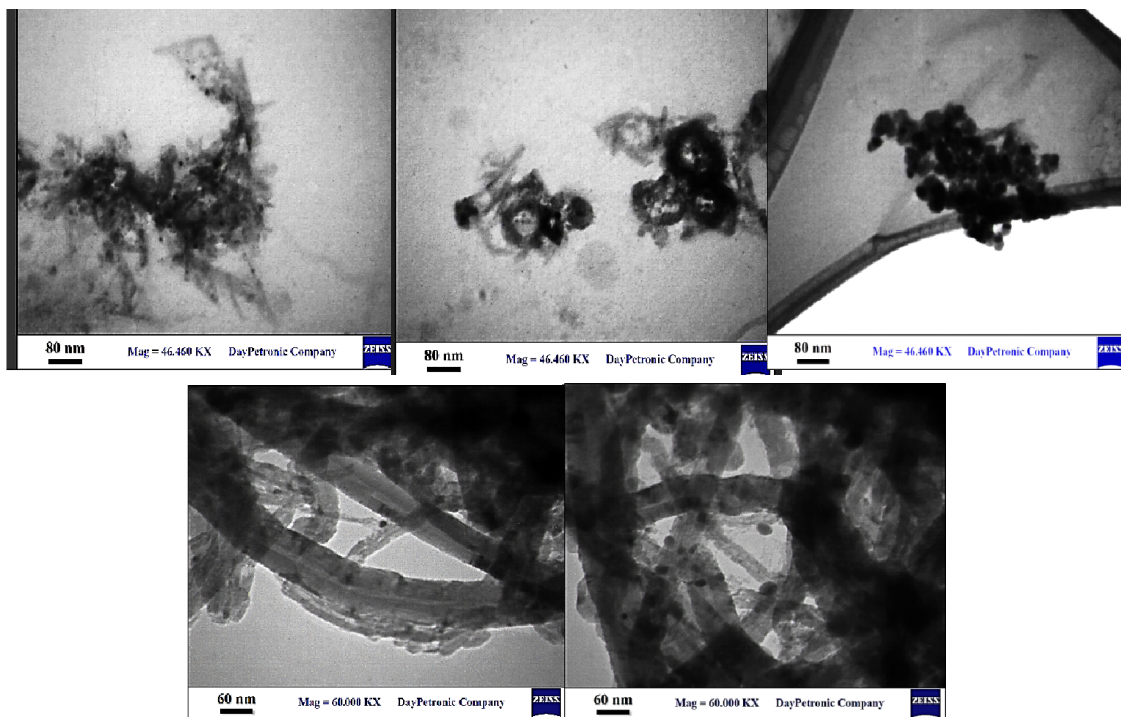


Figure 2. TEM image of MWCNTs-COOH/CeO₂ nanocomposite.

Figure 3 shows the SEM images of (MWCNTs)-COOH/CeO₂. The outside diameter (OD) of (MWCNTs)-COOH was 20-30 nm but after modification, it was changed to 40-50 nm. It is shown that CeO₂ nano-particles have grown as nano-particles on the surface and inside of the (MWCNTs)-COOH.

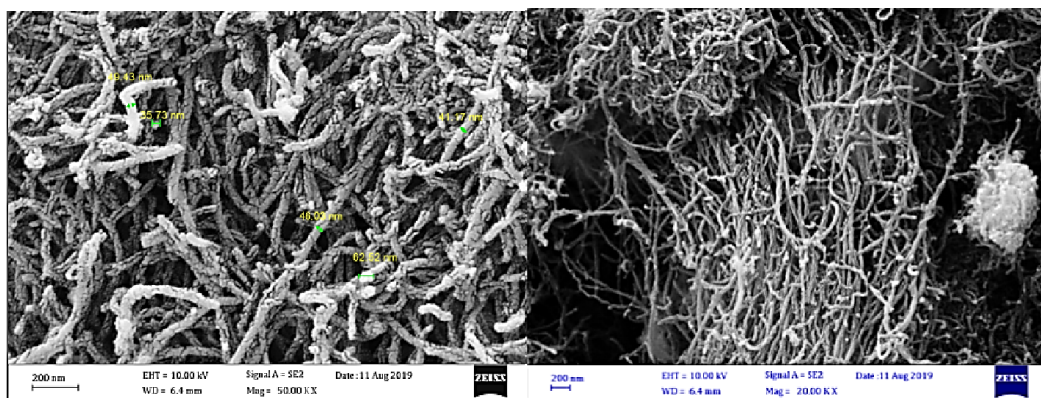


Figure 3. SEM micrograph of MWCNTs-COOH/CeO₂ nanocomposite.

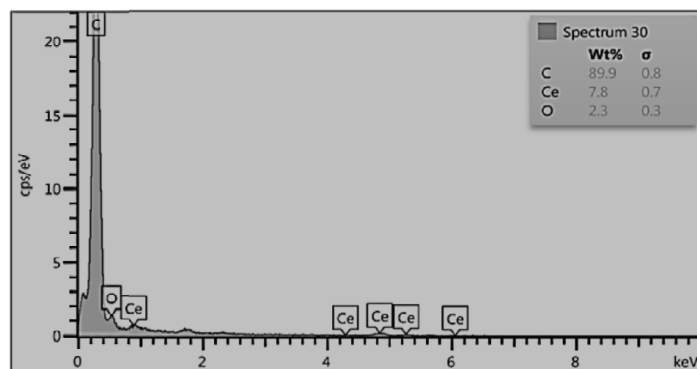
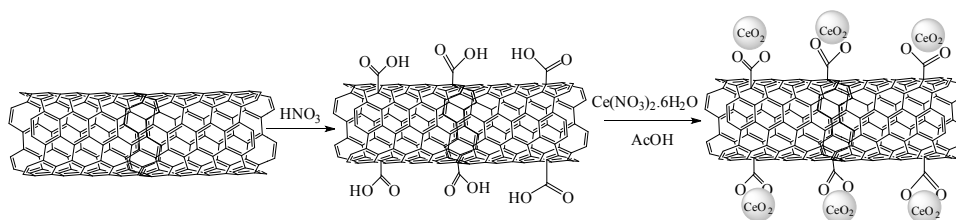


Figure 4. EDX of MWCNTs-COOH/CeO₂ nanocomposite.

In Figure 4, EDX analysis was performed to confirm the elements presented in the resulted MWCNTs-COOH/CeO₂, and the analysis reveals the presence of Ce, O, and C which emphasizes the success of the decoration process with CeO₂ nano-particles.



Scheme 1. Preparation of MWCNTs-COOH/CeO₂ nanocomposite.

Claisen-Schmidt condensation using MWCNTs-COOH/CeO₂

The Claisen-Schmidt condensation as been studied in the absence and presence of different amounts of MWCNTs-COOH/CeO₂ (Table 2 & Figure 5). In the preliminary stage of the investigation, the model reaction of furfural and *p*-nitroacetophenone (Scheme 2) was carried out by using various amounts of NPs in various solvents and solvent-free conditions.

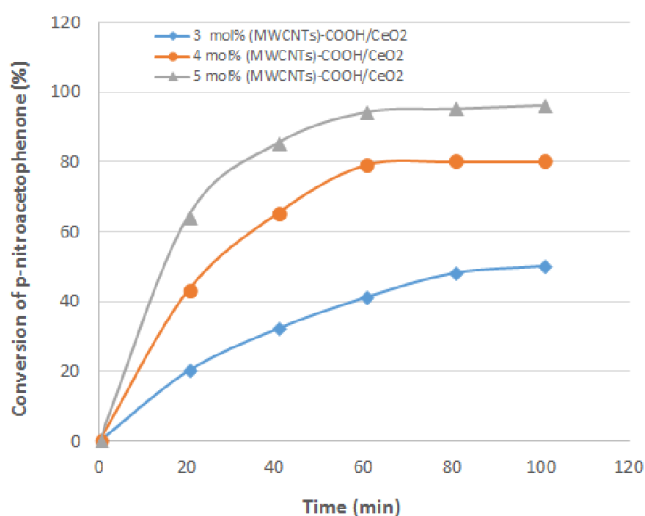


Figure 5. Conversion of *p*-nitroacetophenone in the synthesis of (*E*)-3-(furan-2-yl)-1-(4-nitrophenyl)prop-2-en-1-one in EtOH.

Figure 5 shows the time-dependent conversion plot in the catalyzed Claisen-Schmidt condensation of furfural and *p*-nitroacetophenone to (*E*)-3-(furan-2-yl)-1-(4-nitrophenyl)prop-2-en-1-one. The MWCNTs-COOH/CeO₂(5 mol%) showed fast conversion within 60 min, but later it showed a very slow increase in conversion. Decreasing the amount of catalyst leads to a decrease in the yield of the reaction while increasing the amount of catalysts does not improve the yield of the product any further. The optimum amount of MWCNTs-COOH/CeO₂ was 5 mol%.

Table 2. Reaction of furfural (1 mmol) and *p*-nitroacetophenone (1 mmol) under different conditions.

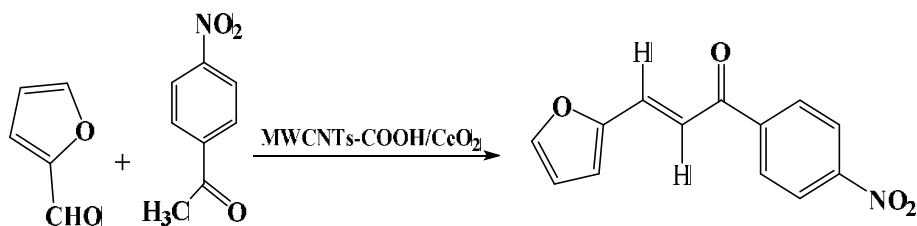
Entry	Solvent	Amount of catalyst MWCNTs-COOH/CeO ₂ (mol%)	Time (min)	Yield ^a (%)
1	THF	-	120	trace
2	THF	3	60	62
3	THF	4	60	73
4	THF	5	60	84
5	THF	7	60	83
6	H ₂ O	-	120	trace
7	H ₂ O	3	60	41
8	H ₂ O	4	60	55
9	H ₂ O	5	60	62
10	H ₂ O	7	60	62
11	EtOH	-	120	trace
12	EtOH	3	60	51
13	EtOH	4	60	79
14	EtOH	5	60	94
15	EtOH	7	60	94
16	CH ₂ Cl ₂	-	120	trace
17	CH ₂ Cl ₂	3	60	34
18	CH ₂ Cl ₂	4	60	47
19	CH ₂ Cl ₂	5	60	62
19	CH ₂ Cl ₂	7	60	62
20	Solvent-free	-	120	trace
21	Solvent-free	3	120	44
22	Solvent-free	4	120	58
23	Solvent-free	5	120	72
24	Solvent-free	7	120	72

^a Isolate Yield.

In the absence of MWCNTs-COOH/CeO₂, the result of the reaction on the TLC plate even after 2h of the reaction wasn't good. The best yield of the product was acquired with 5 mol% of MWCNTs-COOH/CeO₂ in ethanol under mild reaction conditions (Table 2, Entry 14). It is important to note that, under the same conditions, (MWCNTs)-COOH or CeO₂NPs [40] displayed almost no activity. *p*-Methoxyacetophenone did not react with furfural and the yield of *p*-nitroacetophenone with

furfural did not exceed more than 10% even after 12 h. It is clear that modification of (MWCNTs)-COOH with CeO₂ remarkably increased its catalytic activity. MWCNTs-COOH/CeO₂ (5 mol%) was used as an efficient catalyst for Claisen-Schmidt condensation. Because of excellent capacity, the exceedingly simple workup and good yields MWCNTs-COOH/CeO₂ were proved to be a good catalyst for these reactions.

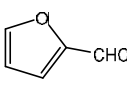
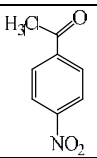
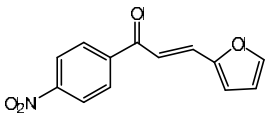
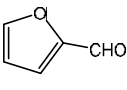
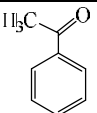
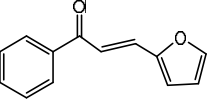
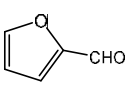
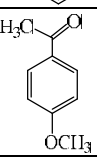
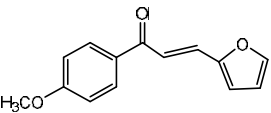
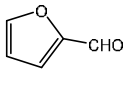
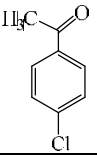
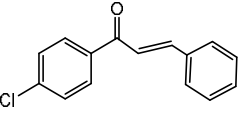
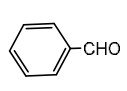
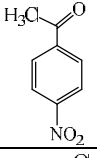
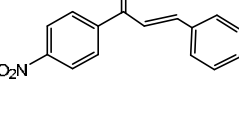
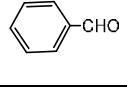
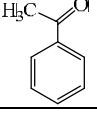
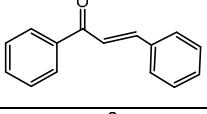
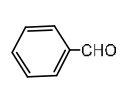
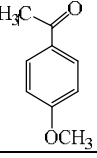
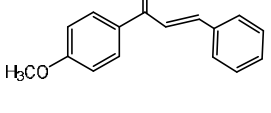
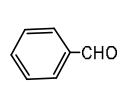
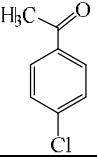
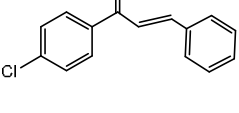
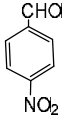
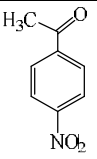
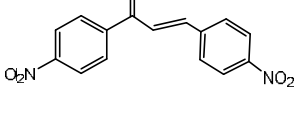
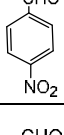
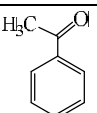
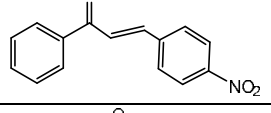
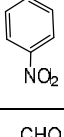
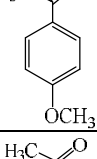
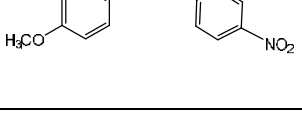
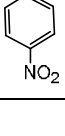
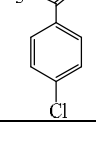
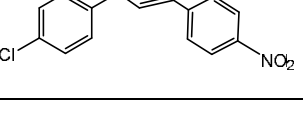
We extended our studies on different aromatic aldehydes with acetophenone derivatives to evaluate the scope and potential limitations of this methodology (Table 3, entries 1–12). In almost all cases, the reactions proceeded smoothly within 60-120 min, providing the corresponding products in good isolated yields. The products were isolated, purified, and analyzed by NMR and IR. The melting points and spectroscopic data were consistent with those reported in the literature [44-50]. For example, the ¹H NMR spectrum of (*E*)-3-(furan-2-yl)-1-(*p*-nitrophenyl)prop-2-en-1-one 1 showed two singlets at 8.36 and 8.17 ppm for CH_{Aro} protons and three signals at 7.59, 6.82, and 6.57 ppm for CH_{Furan} protons. Two CH signals attributed to unsaturated carbon double bonds (-CH=CH-) have appeared at 7.66 and 7.42 ppm, respectively.



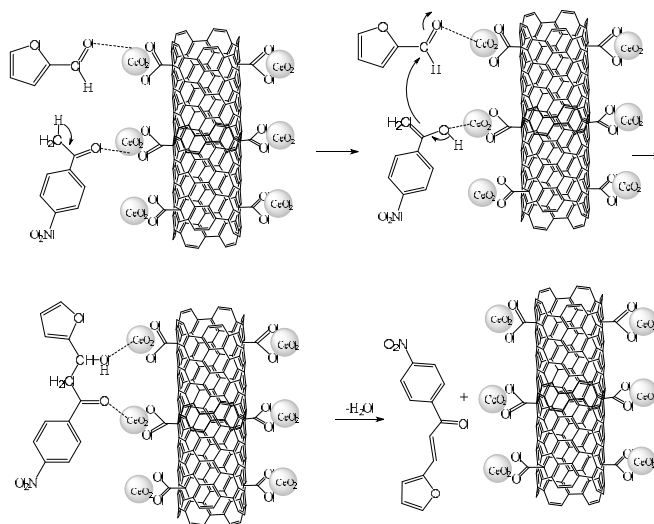
Scheme 2. Synthesis of (*E*)-3-(furan-2-yl)-1-(4-nitrophenyl)prop-2-en-1-one.

Thereafter, we carried out the synthesis of several chalcones with 5 mol% of MWCNTs-COOH/CeO₂ in ethanol (Table 3). Only the *E*-isomers were obtained. The yields were, in general, very high except for the chalcones obtained by condensation of arylaldehydes with *p*-methoxyacetophenone (Table 3, Entry 3 and 7). The low reactivity of this acetophenone due to the presence of an electron-donor group.

Table 3. Claisen-Schmidt condensation with the reaction of aldehydes and acetophenone derivatives using (MWCNT)-COOH/CeO₂.

Entry	Aldehyde	Ketone	Product	Reaction time (min) in ethanol	Yield %
1				60	94
2				90	91
3				120	84
4				90	90
5				90	92
6				120	89
7				120	82
8				90	89
9				60	88
10				60	96
11				90	87
12				60	93

A plausible mechanism for the reaction is investigated in Scheme 3. It is proposed that the carbonyl group of *p*-nitroacetophenone primarily are activated by (MWCNTs)-COOH/CeO₂, and afforded an enol, then the CH₂ of enolate reacts with the carbonyl group of furfural to form a β-hydroxyketone, followed by dehydration to give a conjugated enone.



Scheme 3. A plausible mechanism for synthesis of 3-(furan-2-yl)-1-(4-nitrophenyl)prop-2-en-1-one using (MWCNTs)-COOH/CeO₂.

Recycling of the (MWCNTs)-COOH/CeO₂

The catalyst was simply separated by centrifugation, washed with ethanol and water, and dried at 100 °C for 2 h. The recovered catalyst was then re-entered to a fresh reaction mixture under the same conditions and recycled 5 times without considerable loss of activity (Table 4). More recycling of the nano-catalyst led to a gradual reduction during the recovering and washing steps.

Table 4. Recycling of the (MWCNTs)-COOH/CeO₂.

Number of cycles	Yield ^a (%)
1	94
2	92
3	90
4	89
5	86

To investigate the efficiency of the (MWCNTs)-COOH/CeO₂, we compared some other catalysts for the synthesis of chalcones. Synthesis of chalcones has been formed by various catalysts like NaOH, KF-Al₂O₃, RuCl₃, and NaNO₃/natural phosphate [44, 51-53]. The reported procedures have several disadvantages such as long reaction times, high temperature, and formation of the side products, but using (MWCNTs)-COOH/CeO₂, offers several advantages such as excellent yields,

short reaction times, a simple procedure, reusable heterogeneous catalyst, and using EtOH as a green solvent in contrast with other catalysts.

Conclusions

In conclusion, we demonstrated that (MWCNTs)-COOH/CeO₂ can be prepared under mild reaction condition and used as an efficient catalyst for Claisen-Schmidt condensation. The condensation reactions were carried out in green solvent and the products were gained in high percentage yields without pollution. The rate of the condensation reactions was increased in the presents of the (MWCNTs)-COOH/CeO₂. This heterogeneous and reusable catalyst can be offered for synthesis of some other organic and heterocyclic compounds. This method can also be used as a good template for the synthesis of other nano-materials.

Acknowledgment

The authors wish to thanks Islamic Azad University in Qaemshahr Branch for the institutional support.

References

- [1] M. Faisal, S.B. Khan, M.M. Rahman, A. Jamal, *J. Mater. Sci. Technol.*, 27,594 (2011).
- [2] C. Walkey, S. Das, S. Seal, J. Erlichman, K. Heckman, L. Ghibelli, E. Traversa, J.F. McGinnis, W.T. Self, *Environ. Sci.*, 2, 33 (2015).
- [3] M. Faisal, S.B. Khan, M.M. Rahman, A. Jamal, *Chem. Engineer. J.*, 173,178 (2011).
- [4] T. Kubik, K. Bogunia-Kubik, M. Sugisaka, *Curr. Pharm. Biotechnol.* 6, 17 (2005).
- [5] E.A. Derevyannikova, T. Yu. Kardash, L.S. Kibis, E.M. Slavinskaya, V.A. Svetlichnyi, O.A. Stonkus, A.S. Ivanova, A.I. Boronin, *Phys. Chem. Chem. Phys.*, 19, 31883 (2017).
- [6] S. Das, J.M. Dowding, K.E. Klump, J.F. McGinnis, W. Self, S. Seal, *Nanomed.*, 8,1483 (2013).
- [7] L. He, Y. Su, J. Lanhong, S. Shi, *J. Rare Earths*, 33, 791 (2015).
- [8] F. Meshkani, M. Rezaei, *Powder Tech.*, 199, 144(2010).
- [9] T. Sreethawong, S. Ngamsinlapasathian, S. Yoshikawa, *Mater. Lett.*, 78, 135(2012).
- [10] Y. Lu, G. Yu, X. Wei, C. Zhan, J-W. Jeon, X. Wang, C. Jeffryes, Z. Guo, S. Wei, E.K. Wujcik, *Advanced Composites and Hybrid Materials*, 2, 711(2019).
- [11] M. Roldo, D.G. Fatouros, R. Hallaj, L. Deng, C. Zhu, S. Dong, Y. Zhuo, M.S. Strano, K. Hara, H. Haniu, N. Ogihara, N. Ishigaki, K. Nakamura, H. Kato, M. Kawakubo, Y. Dohi, S. Taruta, Y.A. Kim, M. Endo, H. Ozawa, N. Udagawa, N. Takahashi, N. Saito, *Annual Reports Section "C" (Physical Chemistry)*, 109, 10(2013).
- [12] M. Mehrabi, P. Parvin, A. Reyhani, S.Z. Mortazavi, *Mater. Res. Express*, 4, 095030(2017).

- [13] G. Keru, P.G. Ndungu, V.O. Nyamori, *Int. J. Energy Res.*, 38 1635e1653(2014).
- [14] V. Dalouji, S.M. Elahi, S. Solaymani, A. Ghaderi, *Eur. Phys. J. Plus*, 131, 84(2016).
- [15] W. Bai, Z. Wu, S. Mitra, J.M. Brown, *J. Nanomater.*, 2016, 2159537(2016).
- [16] V.L. Kumar, S.A. Ntim, O. Sae-Khow, C. Janardhana, V. Lakshminarayanan, S. Mitra, *Electrochim. Acta*, 83, 40(2012).
- [17] T.L. Hai, L.C. Hung, T.T.B. Phuong, B.T.T. Ha, B.S. Nguyen, T.D. Hai, V.H. Nguyen, *Microchem. J.*, 153, 104456(2020).
- [18] D. Eder, *Chem. Rev.*, 110, 1348(2010).
- [19] J. Wang, J. Li, X. Xu, B. Zhuoneng, G. Xu, H. Shen, *RSC Adv.*, 6, 42413 (2016).
- [20] E. Rahmanifar, M. Yoosefian, H. Karimi-Maleh, *Curr. Anal. Chem.*, 13, 46 (2017).
- [21] G. Singh, I.P.S. Kapoor, R. Dubey, P. Srivastava, *Mater. Sci. Eng. B*, 176, 121(2020).
- [22] R.N. Bulakhe, C.D. Lokhande, *Sens. Actuators B: Chem.*, 200, 245(2014).
- [23] G. Gulino, A. Compagnini, A. Scalisi, *Chem. Mater.*, 15, 3332(2003).
- [24] R.S. Mane, H.M. Pathan, C.D. Lokhande, *Solar Energy*, 80, 185(2006).
- [25] B. Salehi, S. Mehrabian, M. Ahmadi, *J. Nanobiotechnology*, 12, 26(2014).
- [26] A. Savale, S. Ghotekar, S. Pansambal, O. Pardeshi, *J. Bacteriol. Mycol. Open Access*, 5, 373(2017).
- [27] S.K. Kumar, E. Hager, C. Pettit, H. Gurulingappa, N.E. Davidson, S.R. Khan, *J. Med. Chem.*, 46, 2813 (2003).
- [28] M.R. Ahmad, V.G. Sastry, N. Bano, S. Anwar, *Arab. J. Chem.*, 9, S931 (2016).
- [29] A. Lopez, D.S. Ming, G.H. Neil Towers, *J. Nat. Prod.*, 65, 62 (2002).
- [30] J. Zhang, X-L. Fu, N. Yang, Q-A. Wang, *The Scientific World Journal*, ID 649485 (2013).
- [31] J.H. Wu, X.H. Wang, Y.H. Yi, K.H. Lee, *Bioorganic Med. Chem. Lett.*, 13(10), 1813 (2003).
- [32] M.M. Salemand, K.A. Werbovetz, *J. Nat. Prod.*, 68, 108 (2005).
- [33] M.L. Edwards, D.M. Stemerick, P.S. Sunkara, *J. Med. Chem.*, 33(7), 1948 (1990).
- [34] W. Khan, R. Sharma, P.K. Chaudhury, A.M. Siddiqui, P. Saini, *Int. J. Nanomater. Nanotechnol. Nanomed.*, 2, 025 (2016).
- [35] M. Hamadani, V. Jabbari, M. Shamshiri, M. Asad, I. Mutlay, *J. Taiwan Inst. Chem. Eng.*, 44, 748(2013).
- [36] K-Y. Hwa, B. Subramani, *Biosens. Bioelectron.*, 62, 127 (2014).
- [37] S. Balamurugan, A. R. Balu, K. Usharani, M. Suganya, S. Anitha, D. Prabha, S. Ilangovan, *Pacific Science Review A: Natural Science and Engineering*, 18, 228 (2016).
- [38] M.A. Atieh, O.Y. Bakather, B. Al-Tawbini, A.A. Bukhari, F.A. Abuilawi, M.B. Fettouhi, *Bioinorg. Chem. Appl.*, 2010, 603978 (2010).

- [39] T. Arunachalam, M. Karpagasundaram, N. Rajarathinam, *Mater.Sci-Poland*, 35, 791(2017).
- [40] E.K. Goharshadi, S. Samiee, P. Nancarrow, *J. colloid interface sci.*, 356, 473(2011).
- [41] O.T. Sorensen, *J. Solid State Chem.*, 18, 217 (1976).
- [42] C.E.Holcombe, U.S. AEC Oak Ridge Y-12 Plant, *Report Y 1887* (1973).
- [43] B.E. Warren, X-ray Diffraction, *Courier Corporation*, 1990.
- [44] M. Attarde, A. Vora, A.Varghese, Y. Kachwala, *Organic Chemistry: an Indian Journal*, 10 192(2014).
- [45] T. Budiati, *J. Chem. Pharm. Res.*, 10(8), 132 (2018).
- [46] A. Cetin, A. Cansiz, M.Digrak, *Heteroat. Chem.*,14, 345 (2003).
- [47] M. Cabrera, M. Simoens, G. Falchi, M.L. Lavaggi, O.E. Piro, E.E. Castellano, A. Vidal, A. Azqueta, A. Monge, A. López de Ceráin, G. Sagrera, G. Seoane, H. Cerecetto, M. González, *Bioorg. Med. Chem.*,15, 3356 (2007).
- [48] A.Al Sawas, J.Merza, W. Khalil, A.soliman, *Chem. Mater. Res.*, 10, 30(2018).
- [49] F. Hayat, A. Salahuddin, S. Umar, A. Azam, *Eur. J. Med. Chem.*,45, 4669 (2010).
- [50] K. Kapoor, V.K. Gupta, R. Kant, J.R. Pandya, S.B. Lade, H.S.Joshi, *Acta Cryst., E*, 67, 3185(2011).
- [51] J.T. Li, W.Z. Yang, S.X. Wang, S.H. Li, T.S. Li, *Ultrason.Sonochem.*, 9, 237(2002).
- [52] N. Iranpoor, F. Kazemi, *Tetrahedron*, 54, 9475(1998).
- [53] S. Sebti, A. Solhy, R. Tahir, S. Boulaajaj, J.A. Mayoral, J.M. Fraile, A. Kossir, H. Oumimoun, *Tetrahedron Lett.*, 42, 7953(2001).