ECC
Eurasian Chemical Communications
Original Research Article
http:// echemcom.com

$CoFe_2O_4$ as green and efficient catalyst for synthesis of multisubstituted imidazoles

Fatemeh Mostaghni*, Fereshteh Taat

Department of Chemistry, Payame Noor University, P.O. BOX 19395-4697 Tehran, Iran

Received: 16 July 2019, Accepted: 24 November 2019, Published: 12 December 2019

Abstract

In this study, $CoFe_2O_4$ as a highly efficient and eco-friendly catalyst has been developed for three component one-pot synthesis of lophine as the representative of multisubstituted imidazoles. The present methodology offers several advantages such as excellent yields (99%), short reaction times (10 min) and environmentally mild reaction conditions (500C). Moreover, the catalyst was separated easily by an external magnet and reused several times without significant loss of catalytic properties.

Keywords: Green catalyst; nano cobaltferrit; heterocycles; one-pot tricomponent synthesis; 2, 4, 5-triarylimidazoles; lophine.

Introduction

Metal oxide catalysts as solid catalysts are good candidates in the fields of materials science and synthesis [1-4]. In addition, mixed metal oxides were found to be better than the ordinary oxides in terms of catalytic activity in different reactions, nature of active sites, and high surface area [5-9]. Mixedoxides, due to having remarkable tunable surface properties are the ideal choices for many organic transformations such as oxidation, cycloaddition, and acid-base reactions [10-12].

N-Heterocyclic compounds such as imidazoles are one of the most important heterocyclic compounds witch found in a wide range of natural products. Multisubstituted imidazoles are biologically active compounds which play important roles in biological process. Numerous activity of multisubstituted imidazoles were reported in literatures. For example these compounds can act as therapeutic agents [13], ionic liquids [14-16], anti-inflammatory [17,18], and antimicrobial reagent [19-22].

In recent years, various methods have been reported for synthesis of these compounds [23,24]. However, most of these methods have one or more disadvantages, such as long reaction times, low yields, the use of dangerous reagents or expensive equipments, and often difficult work-up. Among these, one-pot multi-component reactions (MCRs) are the valuable strategy.

MCRs are attractive due to their simplicity, high efficiency, short reaction time, and the reduction of side products. [25-29]. In this reaction, several

*Corresponding author: Fatemeh Mostaghni
Tel: +98 (071) 44354067, Fax: +98 (071) 44354071
E-mail: mostaghnif@yahoo.com

available compounds simultaneously react in one container to produce a product that contains most of the atoms of the raw materials. This reaction has been carried out at the presence of various catalysts including, sulfamic acid [30], catalyst-free conditions [31], $[TBA]_2[W_6O_{19}]$ [32], SiO_2-$OSbCl_2$ [33], N-Bromosuccinimide [34], urea/hydrogen peroxide [35], ionic liquid 1-n-butyl imidazolium tetrafluoroborate ($[Hbim]BF_4$) [36], iodine molecule [37], recyclable g-C_3N_4 nanocomposite [38], Tetrabutylammonium bromide (TBAB) in isopropanol [39], and $BiFeO_3$/$CuWO_4$ [40].

We used magnetic nanocatalyst cobalt ferrite as a heterogeneous mixed oxide catalyst due to its efficient catalytic properties, high available catalytic surface, and easy separability from the reaction mixture [41-45].

Many preparation methods for $CoFe_2O_4$ nanoparticles have been reported, such as the ball milling, co-precipitation, hydrothermal synthesis, sol-gel, and reaction in a micro-emulsion [46,47]. In this study, $CoFe_2O_4$ nanoparticles was synthesized using the co-precipitation technique. The synthesized material was used as green catalyst for one-pot three component synthesis of lophine as the representative of multisubstituted imidazoles and compared with the reported results from other catalysts. The results revealed that, lophine was produced in high yields and short reaction time. The catalyst was separated easily using an external magnet. In addition, the recycled catalyst was reused several times without significant loss of catalytic properties.

Experimental

General

All the chemicals were analytical grade and used without purification. Crystal structure of nanocatalyst was evaluated using a Bruker make diffractometer, Cu-Kα X-rays of wavelength (λ=1.5406 Å). The XRD patterns were recorded in the 2θ range of 10–90^o with a step width of 0.02 s^{-1}. Melting point was measured using an Electrothermal-9200 melting point apparatus. IR spectra were measured on FTIR-6300 spectrometer (KBr). ^{1}HNMR spectra were recorded on Bruker ADVANC DRX 400 spectrometer, using DMSO as solvent.

Synthesis of magnetite nanocatalyst

$CoFe_2O_4$ were prepared using the coprecipitation method. In a typical reaction, $Co(NO_3)_2.4H_2O$ and $FeCl_3.6H_2O$ with the molar ratio of 1:2 were dissolved in deionized water (100 mL) and stirred at room temperature for 30 min. In addition, polyethylene glycol (average molecular weight: 4000, Qualigen) as a surfactant poured into the above mixture. Finally, the ammonia solution (25%) was added dropwise and mixed with high stirring. The final pH of the mixture was about 8. The mixture was kept under vigorous stirring at 60 ^{o}C for 1 h. The obtained precipitate were dried at 80 ^{o}C and calcined at 450 ^{o}C for 3 h. The structure of the magnetic nanoparticles was studied using the X-ray diffraction (XRD) analysis.

Synthesis of lophine

A mixture of benzaldehyde (1 mmol), benzoin bis-aryl diketone (1 mmol) and ammonium acetate (4 mmol) in ethanol (10 mL) in the presence of (0, 2, 5, 7) mol% $CoFe_2O_4$ nanocatalyst was stirred at rome temperature, 50 °C, and 80 °C. The progress of the reaction was monitored by TLC (n-Hexan: Ethyl acetate 4:1). After the reaction completed, the catalyst was separated using an external magnet. Then, 50 mL cold water was added to the reaction mixture and collects the precipitate by filtration. The crude product was dried and recrystalized from acetone: water (9:1).

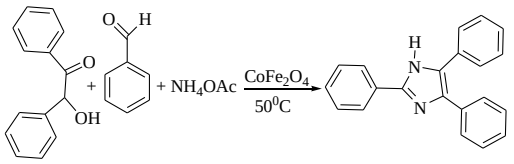

Figure 1. Synthesis of lophine

The white crystals (Figure 1) were characterized using the FTIR and ^{1}HNMR spectroscopy. Yield 99%; purity > 98%; mp: 278 °C (275-276 °C [22]). Elemental analysis for $C_{21}H_{16}N_2$ (296.372) (%): calcd. C 85.10, H 5.55, N 9.34; found C 85.11, H 5.44, N 9.45.

IR bands (KBr) ν=3445, 3082, 2853, 1641, 1504, 1462, 1398, 1128, 1070, 966, 766, 698 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d6): δ=7.22 (t, 1H, J=7.2 Hz), 7.34 (t, 2H, J= 7.2 Hz), 7.39 (t, 2H, J=7.2 Hz), 7.44–7.51 (m, 6H), 7.59 (d, 2H, J=7.6 Hz), 8.10 (d, 2H, J=7.2 Hz), 12.71 (1H, br) ppm.

Results and discussion

The X-ray diffraction pattern of synthesized $CoFe_2O_4$ treated in 450 °C is demonstrated in Figure 2. The XRD pattern exhibited strong diffraction peaks at 25.25°, 37.76°, 48.00°, 54.38°, 57.22°, 62.85°, and 74.32° corresponding to the 220, 311, 400, 422, 511, 440, and 533 lattice planes. It is observed that all the peaks perfectly matched with the standard pattern (ICSD-00-022-1086). This confirmed the formation of single phase and pure $CoFe_2O_4$ with the expected cubic inverse spinel structure with Fd3m space group and without any impurity phase.

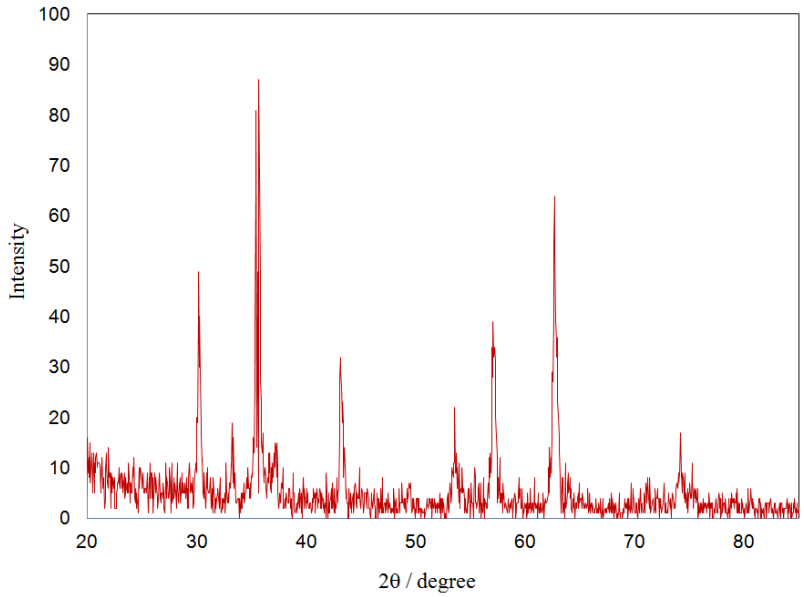

Figure 2. XRD pattern of synthesized $CoFe_2O_4$

The crystallite size of the nanoparticles was calculated using the modified Debye-Scherrer equations [48]. The crystallite size of the nano-particles was found to be 10 nm.

We have used $CoFe_2O_4$ nano catalyst to synthesize lophine trough one pot three component condensation of benzoin, benzaldehydes and ammonium acetate. The pure product was obtained by simple filtration of the cooled reaction mixture. The structure of the synthesized lophine was ascertained using melting point (mp), Fourier transform-infrared spectra (FTIR), and ^{1}H Nuclear magnetic resonance (NMR) spectral techniques. The results were in good agreement with the previous literature reports. To get accurate results, we arranged further experiments to determine the effect of the catalyst amount and temperature on

the rate and efficiency of the reaction. The results are presented in Table 1.

Table 1. $CoFe_2O_4$ catalyzed synthesis of lophine

Entry	Catalyst (mol%)	T (°C)	Time	Yield (%)
1	None	r.t	10 h	-
2	None	50	10 h	trace
3	None	80	10 h	19
4	2	r.t	5 h	35.5
5	2	50	10 min	53
6	2	80	10 min	49
7	5	r.t	5 h	83.5
8	5	50	10 min	98
9	5	80	10 min	78.5
10	7	r.t	5 h	84
11	7	50	10 min	99
12	7	80	10 min	73

As seen in Table 1, increasing the temperature reduced the yields. This can be duo to formation of the undesirable side products. Moreover, it is observed that, higher amount of catalyst facilitated the reaction, led to higher yield. As can be seen in Table 1, 5 mol% catalyst exhibited the highest yield. It should be noted that, further increase in the amount of the catalyst did not have any significant effect on reaction time and yield. Therefore, the best amount of catalyst was 5 mol%.

Table 2. Synthesis of Lophine using different catalysts and reaction conditions

Catalyst	Temprature	time	m.p	yield	Ref
NH_2SO_3H	80	240	277-279	93	30
No catalyst	60	240	275	97	31
$[TBA]_2[W_6O_{19}]$	140	5	275-276	87	32
SiO_2-$OSbCl_2$	80	15	272-273	97	33
NBS	120	45	274-275	92	34
Urea/H_2O_2	Reflux	240	267	78	35
$[Hbim]BF_4$	100	60	269	95	36
I_2	75	15	272-273	99	37
Fe_3O_4@g-C_3N_4	78	120	272	97	38
n-Bu_4NBr	82	20	272	95	39
$BiFeO_3/CuWO_4$	120	10	270-271	93	40
$CoFe_2O_4$	50	10	278	99	This work

Table 2 compares the recent method with reported methods in the literature [30-40]. As shown in Table 2, this catalyst produced the purest product with the highest efficiency in the least time and temperature of reaction, making this method a useful and attractive strategy in view of economic and environmental.

Conclusion

In this work, cobalt ferrite nanoparticles were successfully synthesized using the co-precipitation method and thermally treated at 450 ºC for 3 h. XRD analysis revealed that, $CoFe_2O_4$ nano composite formed into pure and single phase cubic spinel structure. The novelty of this research study was using the $CoFe_2O_4$ as a cheap, nontoxic, and readily separable catalyst that leads to high product yields (99%) under the mild reaction conditions (50 ºC) at the reaction times 10 min. The method offer several advantages, including the mild conditions, short reaction time, high purity (>98%) of product, Easy recoverability of the catalyst and the possibility of reusing on several times.

Acknowledgments

The authors are grateful to the Payame Noor University for its support and encouragements.

References

[1] M. Sadeghi, S. Yekta, *Iran. Chem. Commun*., **2016**, *4*, 21-41.
[2] J. Shi, *Chem. Rev*., **2013**, *113*, 2139-2181.
[3] A.U. Itodo, O.M. Itodo, E. Iornumbe, M.O. Fayomi, *Prog. Chem. Biochem. Res*., **2019**, *01*, 50-59.

[4] B.S. Mohan, D. Ramadevi, K. Basavaiah, *Prog. Chem. Biochem. Res*., **2019**, *02*, 64-67.
[5] K.K. Gangu, S. Maddila, S.N. Maddila, S.B. Jonnalagadda, *Molecules*., **2016**, *21*, 1281-1296.
[6] K.K. Gangu, S. Maddila, S.N. Maddila, S.B. Jonnalagadda, *J. Alloys Comp.*, **2017**, *690*, 817–824.
[7] H. Saeidian, F. Moradnia, *Iran. Chem. Commun*., **2017**, *5*, 252-261.
[8] I.E. Wachs, K. Routray, *ACS Catal*., **2012**, *2*, 1235-1246.
[9] G. Aguila, D. Salinas, R. Jiménez, S. Guerrero, P. Araya, *J. Chil. Chem. Soc*., **2016**, *61*, 3233-3238.
[10] A.R. Moosavi-Zare, H. Goudarziafshar, Z. Jalilian, *Prog. Chem. Biochem. Res*., **2019**, *02*, 59-63.
[11] M. Aghazadeh, *Prog. Chem. Biochem. Res*., **2019**, *02*, 34-39.
[12] K.K. Alisher, T.S. Khamza, Y.S. Ikbol, *Prog. Chem. Biochem. Res*., **2019**, *02*, 1-5.
[13] K.S. Niralwad, B.B. Shingate, M.S. Shingare, *J. Heterocycl. Chem*., **2011**, *48*, 742-754.
[14] A. Zare, A. Hasaninejad, A. Khalafi-Nezhad, A.R. Moosavi-Zare, M.H. Beyzavi, F. Khedri, F. Asadi, N. Hayati, A. Asifi, *J. Iran Chem. Soc*., **2010**, *7*, 461-469.
[15] D.W. Seo, Y.D. Lim, S.H. Lee, S.C. Ur, W.G. Kim, *Bull. Korean Chem. Soc*., **2011**, *32*, 2633-2636.
[16] H. Li, J. Liu, J. Zhu, H. Wang, *J. Korean Chem. Soc.*, **2011**, *55*, 685-690.
[17] M. Amir, I. Ahsan, W. Akhtar, S.A. Khan, I. Ali, *Indian J. Chem*., **2011**, *50B*, 207-213.
[18] A. Husain, S. Drabu, N. Kumar, M.M. Alam, S. Bawa, *J. Pharm. Bioallied. Sci*., **2013**, *5*, 154-161.
[19] A.K. Jain, R.K. Agrawal, V. Ravichandran, S. Sisodiya, *Asian Pac. J. Trop. Med*., **2010**, *7*, 271-274.
[20] A.M. Vijesh, M. Arun, S. Telkar, S.K. Peethambar, S. Rai, N. Isloor, *European J. Med. Chem*., **2011**, *46*, 3531-3536.
[21] V. Padmavathi, C. Prema kumara, B.C. Venkatesh, A. Padmaja, *European J. Med. Chem*., **2011**, *46*, 5317-5326.
[22] R. Ramachandran, M. Rani, S. Senthan, S. Kabilan, *European J. Med. Chem*., **2011**, *46*, 1926-1934.
[23] M. Gorsd, G. Sathicq, G. Romanelli, L. Pizzio, M. Blanco, *J. Mol. Catal. A: Chem*., **2016**, *420*, 294-302.
[24] J.F. Zhou, G.X. Gong, H.Q. Zhu, F.X. Zhu, *Chinese Chem. Lett*., **2009**, *20*, 1198-1200.
[25] J.F. Zhou, G.X. Gong, X.J. Sun, Y.L. Zhu, *Synth. Commun*., **2010**, *40*, 1134-1141.
[26] S. Samai, G.C. Nandi, P. Singh, M.S. Singh, *Tetrahedron*, **2009**, *65*, 10155-10161.
[27] A. Khorramabadi-zad, M. Azadmanesh, S. Mohammadi, *S. Afr. J. Chem.*, **2013**, *66*, 244-247.
[28] B.H. Rotstein, S. Zaretsky, V. Rai, A.K. Yudin, *Chem. Rev*., **2014**, *114*, 8323-8359.
[29] R.S. Joshi, P.G. Mandhane, M.U. Shaikh, R.P. Kale, C.H. Gill, *Chinese Chem. Lett*., **2010**, *21*, 429-432.
[30] N.H. Peng, X.M. Peng, D.G. Zheng, F. Yu, M. Rao, *Heterocycl. Comm*., **2011**, *17*, 223-226.
[31] N. Azizi, N. Dado, A.K. Amiri, *Can. J. Chem.*, **2012**, *90*, 195-198.
[32] M. Ashrafi, A. Davoodnia, F. Tavakoli-Hoseini, *Bull. Korean Chem. Soc*., **2013**, *34*, 1508-1512.
[33] J. Safari, Z. Zarnegar, S. Naseh, Z. Akbari, *Iranian J. Catal*., **2014**, *4*, 125-132.
[34] B. Maleki, SS. Sedigh Ashrafi, *J. Mex. Chem. Soc*., **2014**, *58*, 76-81.
[35] A. Maleki, Z. Alirezvani, *J. Chil. Chem. Soc.*, **2016**, *61(3)*, 3116-3119.
[36] S.A. Siddiqui, U.C. Narkhede, S.S. Palimkar, T. Daniel, R.J. Loholi, K.V. Srinivasan, *Tetrahedron*, **2005**, *61*, 3539-3546.

[37] M. Kidwai, P. Mothsra, V. Bansal, R.K. Somvanshi, A.S. Ethayathulla, S. Dey, T.P. Singh, *J. Mol. Catal. A: Chem*., **2007**, *265*, 177-182.
[38] T.S. Ahooie, N. Azizi, I. Yavari, M.M. Hashemi, *J. Iran. Chem. Soc*., **2018**, *15*, 855-862.
[39] M.V. Chary, N.C. Keerthysri, K.V. Srinivasu, *Catal. Comm*., **2008**, *9*, 2013-2017.
[40] H. Ramezanalizadeh, *Iran. Chem. Commun*., **2018**, *6*, 192-208.
[41] M. KarimKoshteh, M. Bagheri, *J. Mex. Chem. Soc*., **2017**, *61*, 28-34.
[42] N.H. Hong, A.T. Raghavender, O. Ciftja, M.H. Phan, K. Stojak, H. Srikanth, Y.H. Zhang, *Appl. Phys. A*., **2013**, *112*, 323-327.
[43] N. Sanpo, C.C. Berndt, C. Wen, J. Wang, *Acta Biomater*., **2013**, *9*, 5830-5837.
[44] M. Mahdavi, F. Namvar, M.B. Ahmad, R. Mohamad, *Molecules*, **2013**, *18*, 5954-5964.
[45] A.M. Awwad, N.M. Salem, *J. Nanosci. Nanotechnol*., **2012**, *2*, 208-213.
[46] Y. Zhang, Z. Yang, B.P. Zhu, W. Yu, S. Chen, X.F. Yang, F. Jin, J. Ou-Yang, *Ceram. Int*., **2014**, *40*, 3439-3443.
[47] S.P. Dubey, M. Lahtinen, M. Sillanpaa, *Process Biochem*., **2010**, *45*, 1065-1071.
[48] M.W. Mushtaq, F. Kanwal, A. Batool, T. Jamil, M. Zia-ul-Haq, B. Ijaz, Q. Huang, Z. Ullah, *J. Mater. Sci*., **2017**, *52*, 9282-9293.

How to cite this manuscript: Fatemeh Mostaghni, Fereshteh Taat. $CoFe_2O_4$ as green and efficient catalyst for synthesis of multisubstituted imidazoles. *Eurasian Chemical Communications*, 2020, 2(4), 427-432.