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$ZnFe_2O_4$@dimethylglyoxime: Preparation and Catalyst Application in the Synthesis of 2-amino-tetrahydro-4H-chromene-3-carbonitrile Derivatives †

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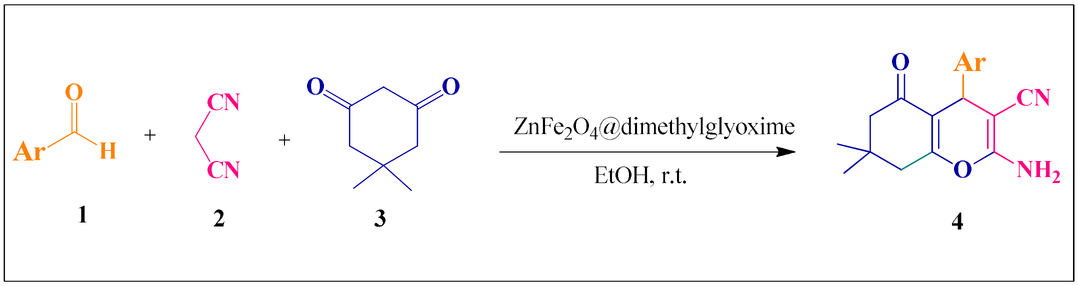
Abstract: Hybrid materials constructed from two or more constituents provide new features and distinctive application which is not found in the single-part material. Spinel ferrites with general formula of AB_2O_4, where A and B represent a divalent metal ion such as Zn(II), Ni(II), Cu(II) and Fe(III) ions, appeared as efficient catalysts for the synthesis of organic compound. These magnetic nanoparticles have both the Lewis acid and the Lewis base sites in their structure. In present study, the $ZnFe_2O_4$ was prepared and modified with dimethylglyoxime to obtain magnetic $ZnFe_2O_4$@dimethylglyoxime hybrid catalyst. Dimethylglyoxime is a dibasic acid substance which has been used as a chelating agent for divalent metal ions due to containing two nitrogen atoms and hydroxyl groups. Surface modification of zinc ferrite with this dibasic acid substance produced bifunctional hybrid catalyst with increased catalytic active sites. In next step, prepared catalyst was applied in the synthesis of 2-amino-tetrahydro-4H-chromene-3-carbonitrile derivatives by condensation of, aromatic aldehydes, malononitrile and dimedone in ethanol at room temperature. The present procedure offers some advantages such as simple procedure, mild reaction condition, short reaction times and retrievable catalyst.

Keywords: Dimethylglyoxime; $ZnFe_2O_4$; multicomponent reaction; hybrid catalyst

1. Introduction

Magnetic catalysts with applicable advantages such as reusability and easy separation from the reaction mixture have attracted great attention [1]. For the production of heterogeneous magnetic catalysts, iron is generally more suitable due to its properties such as abundance in nature, low toxicity and availability [2]. Chemists have found that hybrid materials made from two or more components exhibited different properties than each component and synergistic effects, therefore the design and fabrication of hybrid materials is an effective approach in catalyst chemistry [3]. Ferrites are polycrystalline materials and are made of a large number of tiny crystals with different orientations [4]. Zinc ferrite has been widely used in diverse applications due to its magnetization properties, simple synthesis, low toxicity and good chemical stability, recently [3–5]. Dimethylglyoxime is a dibasic acid substance which has been used for divalent ions due to its special structure and the presence of chelating elements of nitrogen and hydroxyl [6,7]. MCRs are valuable approach in organic chemistry that can produce a variety of biologically active compounds [8–10].The tetrahydro-4H-chromene and its derivatives are important biologically active compounds because of significant medicinal properties such as antispasmodic, anticoagulant and also have effective therapeutic effects in neurological diseases and cancer [11]. In Continues to our research on MCRS and heterocyclic compound, in present work, the modified $ZnFe_2O_4$ prepared by co-precipitation procedure in the presence of dimethylglyoxime as dibasic acid substance to obtain hybrid catalyst with more active site and enhanced catalytic efficiency. Then, the prepared $ZnFe_2O_4$@dimethylglyoxime composite was used as hybrid catalyst for synthesis of 2-amino-tetrahydro-4H-chromene-3-carbonitrile derivatives via one-pot condensation of various aromatic aldehydes, malononitrile and dimedone (Scheme 1).



Scheme 1. The synthesis of 2-amino-tetrahydro-4H-chromene-3-carbonitrile derivatives.

2. Experimental

2.1. General

All consumed chemicals and solvents were bought from Sigma Aldrich and Merck companies. Fourier transform infrared (FT-IR) spectra were recorded using a Shimadzu 8400 S spectrometer. Elemental analysis of prepared sample was carried out by energy-dispersive X-ray (EDX) analysis recorded on Numerix JEOL-JDX 8030 (30 kV, 20 mA). X-ray diffraction (XRD) pattern of the prepared catalyst was recorded on an X-ray diffractometer (Bruker D8 Advance). Melting points were measured with an electrothermal 9100 apparatus.

2.2. Preparation of the $ZnFe_2O_4$@dimethylglyoxime

The $ZnFe_2O_4$@dimethylglyoxime was prepared by co-precipitation of Zn^{2+} and Fe^{3+} aqueous solution in the presence of dimethylglyoxime under alkaline condition. First, $Zn(OAC)_2$. $2H_2O$ (1.6 mmol) and $FeCl_3$. $6H_2O$ (3.2 mmol) were dissolved in 50 mL distilled water. Then dimethylglyoxime (4.5 mmol) was added to prepared solution and dispersed by ultrasonic at room temperature for 15 minutes. In the next step, NaOH (0.25 mmol) was dissolved in 50 mL of distilled water then was added to the contents of the reaction drop by drop. The reaction was completed at 90 °C after 1hour. Finally, resulting precipitate was washed with distilled water several times and dried in an oven at 60 °C.

2.3. General Procedure for the Synthesis of 2-amino-tetrahydro-4H-chromene-3-carbonitrile Derivatives Derivatives

The mixture of aromatic aldehyde (1.0 mmol), malononitrile (1.0 mmol), dimedone (1.0 mmol) and 0.01 g of $ZnFe_2O_4$@dimethylglyoxime catalyst were stirred in EtOH at 80 °C. The completion of the reaction was monitored by thin layer chromatography. After the reaction was complete, the catalyst was separated with a magnet, washed with deionized water and dried. Then pure product was obtained by crystallization of the crude precipitate in ethanol.

3. Results and Discussion

3.1. Characterization of Catalyst

The presence of constituent elements in the $ZnFe_2O_4$@dimethylglyoxime composition was studied by EDX analysis. The results of EDX analysis in Figure 1. The observed peaks are related to the presence of zinc, iron, nitrogen and oxygen, which indicate the existence of components elements in the prepared sample.

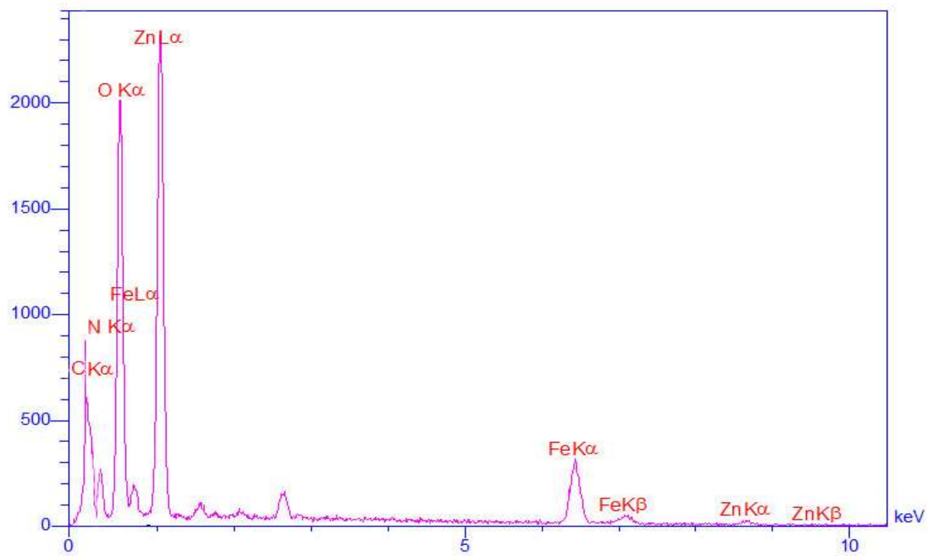


Figure 1. EDX analysis of the $ZnFe_2O_4$@dimethylglyoxime catalyst.

The XRD pattern of $ZnFe_2O_4$@dimethylglyoxime is shown in Figure 2, which compared to standard pattern of $ZnFe_2O_4$. As is observed, the standard pattern of $ZnFe_2O_4$ with card no. JCPDS, 00-022-1020 have characteristic diffraction peaks at 2θ = 18.19°, 29.92°, 35.26°, 42.85°, 56.81° and 62.21°. The prepared catalyst pattern showed similar diffraction peaks at 2θ = 17.40°, 30.13°, 35.23°, 57.1° and 62.22° confirming the existence of crystalline nanoparticles in the catalyst composition. The average crystallite size in the hybrid nanocatalyst was determined to be about 42 nm based on the information of the characteristic diffraction peaks and using Debye-Scherer equation.

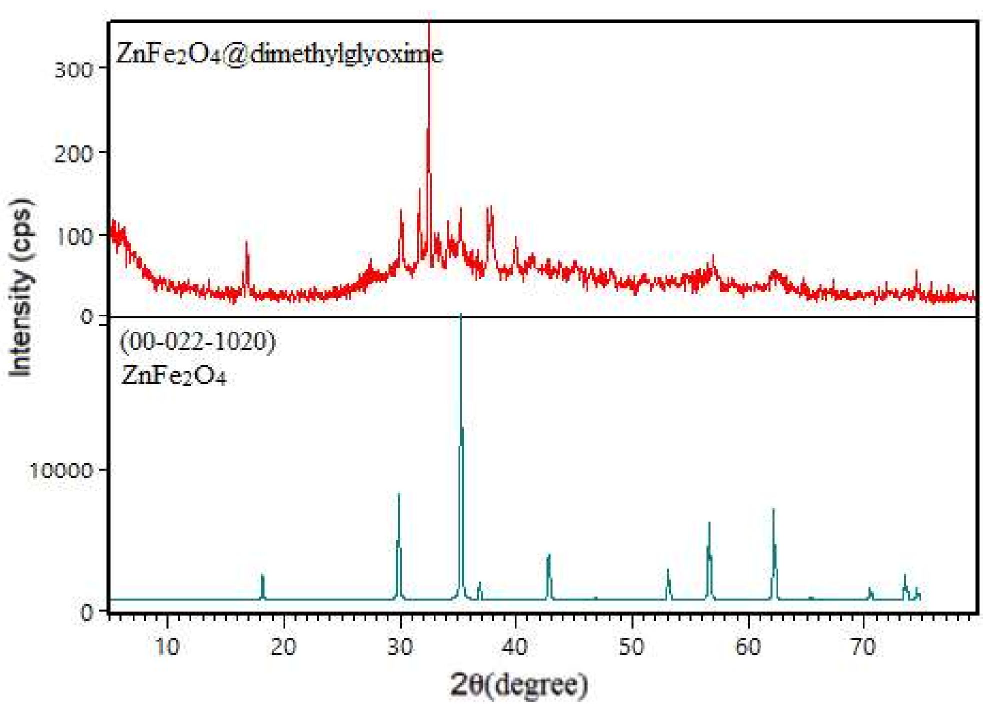


Figure 2. XRD pattern of $ZnFe_2O_4$@dimethylglyoxime catalyst.

The FT-IR analysis was used to identify the functional groups of $ZnFe_2O_4$@dimethylglyoxime catalyst. Figure 3 showed the IR spectrum of $ZnFe_2O_4$@dimethylglyoxime hybrid catalysts in the range of 400–4400 cm^{-1}. The absorption at 415 cm^{-1} is related to the stretching vibration of Zn-O, and the appearing absorption in the range of 520–550 cm^{-1} is related to the stretching vibration of Fe-O[12]. The absorption bands at 1122 and 1050 cm^{-1} is attributed to symmetrical and asymmetrical stretching vibration of N-O bond, respectively. A weak band in 1572 cm^{-1} is ascribed to the starching vibration of C=N bond. Absorption band at 2936 cm^{-1} is related to stretching vibration of C–H bond, the adsorption related to the stretching vibrations of the hydroxyl groups in dimethylglycoxime structure and the $ZnFe_2O_4$ surface, appeared as intensive band in the range of 3400–3600 cm^{-1}.

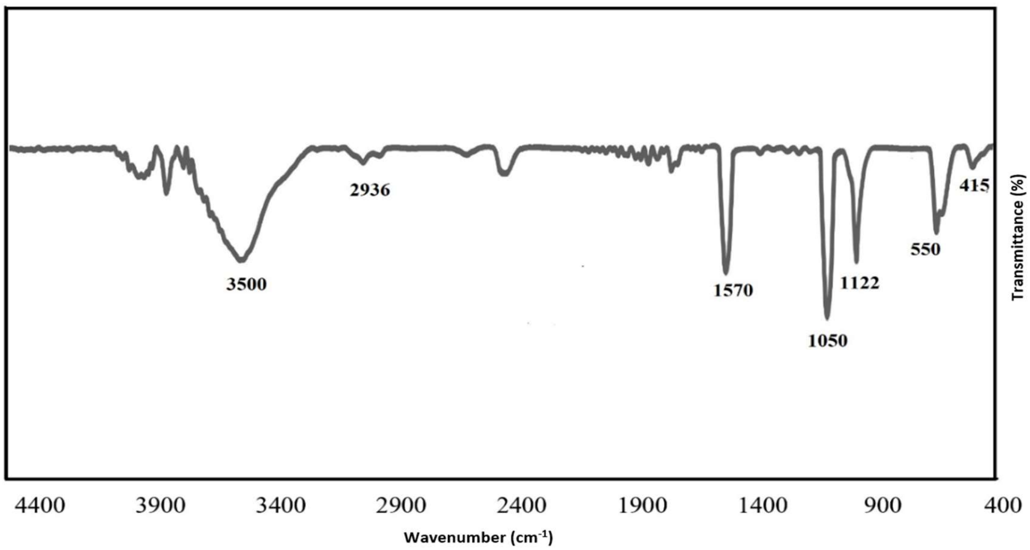


Figure 3. FTIR analysis of the $ZnFe_2O_4$@dimethylglyoxime catalyst.

3.2. *Catalytic Application of $ZnFe_2O_4$@dimethylglyoxime in the Synthesis of 2-amino-tetrahydro-4H-chromene-3-carbonitrile Derivatives*

Synthesis of 2-amino-tetrahydro-4H-chromene-3-carbonitrile derivatives using some aromatic aldehydes was selected under optimal conditions to evaluate the efficiency of the prepared $ZnFe_2O_4$@dimethylglyoxime catalyst. As shown in Table 1, all tested aromatic aldehydes with electron drawing and electron donating groups produced high yield products in a short reaction times.

Table 1. Synthesis of 2-amino-tetrahydro-4H-chromene-3-carbonitrile derivatives.

					Melting point (°C)	
Entry	**Aryl**	**Product**	**Time(min)**	**Yield [a] (%)**	**Observed**	**Literature**
1	4-$NO_2C_6H_4$	**4a**	3	96	180–182	176–182[9]
2	3,4,5-$(MeO)_3C_6H_4$	**4b**	6	90	176–178	175–177[9]
3	3-ClC_6H_4	**4c**	6	92	228–230	229–232[9]
4	4-HOC_6H_4	**4d**	18	82	208–209	208–210[9]
5	4-$MeOC_6H_4$	**4e**	10	88	216–218	217–220[13]
6	2,4-$Cl_2C_6H_4$	**4f**	5	94	119–120	118–120[9]

[a] Isolated yield.

4. Conclusions

$ZnFe_2O_4$@dimethylglyoxime is a recyclable, efficient, cost-effective hybrid catalyst which was used in the synthesis of 2-amino-tetrahydro-4H-chromene-3-carbonitrile derivatives. This procedure provides advantages such as producing high-efficiency products in a short time, easy workup for purification of product, and the ability to reuse the catalyst.

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Reference

1. Aisida, S.O.; Ahmad, I.; Zhao, T.K.; Maaza, M.; Ezema, F.I.. Calcination Effect on the Photoluminescence, Optical, Structural, and Magnetic Properties of Polyvinyl Alcohol Doped $ZnFe_2O_4$ Nanoparticles. *J. Macromol. Sci. Part B* **2020**, *59*, 295–308.
2. Kumar, A.S.; Reddy, M.A.; Knorn, M.; Reiser, O.; Sreedhar, B. Magnetically Recoverable CuFe2O4 Nanoparticles: Catalyzed Synthesis of Aryl Azides and 1, 4-Diaryl-1, 2, 3-triazoles from Boronic Acids in Water. *Eur. J. Org. Chem.* **2013**, *2013*, 4674–4680.
3. Maleki, A.; Varzi, Z.; Hassanzadeh-Afruzi, F. Preparation and characterization of an eco-friendly $ZnFe_2O_4$@ alginic acid nanocomposite catalyst and its application in the synthesis of 2-amino-3-cyano-4H-pyran derivatives. *Polyhedron* **2019**, *171*, 193–202.
4. Andhare, D.; Jadhav, S.; Khedkar, M.; Somvanshi, S.B.; More, S.; Jadhav, K. Self-heating evaluation of superparamagnetic MnFe2O4 nanoparticles for magnetic fluid hyperthermia application towards cancer treatment. *Ceram. Int.* **2020**, *46*, 25576–25583.
5. Chai, L.; Wang, Y.; Zhou, N.; Du, Y.; Zeng, X.; Zhou, S.; He, Q.; Wu, G. In-situ growth of core-shell $ZnFe_2O_4$@ porous hollow carbon microspheres as an efficient microwave absorber. *J. Colloid Interface Sci.* **2020**, *581*, 475–484.
6. Cardoso, W.S.; Dias, V.L.; Costa, W.M.; de Araujo Rodrigues, I.; Marques, E.P.; Sousa, A.G.; Boaventura, J.; Bezerra, C.W.; Song, C.; Zhang, J. Nickel-dimethylglyoxime complex modified graphite and carbon paste electrodes: preparation and catalytic activity towards methanol/ethanol oxidation. *J. Appl. Electrochem.* **2009**, *39*, 55–64.
7. Hassanloie, N.; Noroozi Pesyan, N.; Sheykhaghaei, G. Anchored Ni-dimethylglyoxime complex on Fe_3O_4@ SiO_2 core/shell nanoparticles for the clean catalytical synthesis of dicoumarols. *Appl. Organomet. Chem.* **2020**, *34*, e5242.
8. Hajizadeh, Z.; Hassanzadeh-Afruzi, F.; Jelodar, D.F.; Ahghari, M.R.; Maleki, A. Cu (ii) immobilized on Fe_3O_4@ HNTs–tetrazole (CFHT) nanocomposite: synthesis, characterization, investigation of its catalytic role for the 1,3 dipolar cycloaddition reaction, and antibacterial activity. *RSC Adv.* **2020**, *10*, 26467–26478.
9. Bahrami, S.; Hassanzadeh-Afruzi, F.; Maleki, A. Synthesis and characterization of a novel and green rod-like magnetic ZnS/CuFe2O4/agar organometallic hybrid catalyst for the synthesis of biologically-active 2-amino-tetrahydro-4H-chromene-3-carbonitrile derivatives. *Appl. Organomet. Chem.* **2020**, *34*, e5949.
10. Maleki, A.; Hassanzadeh-Afruzi, F.; Varzi, Z.; Esmaeili, M.S. Magnetic dextrin nanobiomaterial: An organic-inorganic hybrid catalyst for the synthesis of biologically active polyhydroquinoline derivatives by asymmetric Hantzsch reaction. *Mater. Sci. Eng. C* **2020**, *109*, 110502.
11. Paczkowski, I.M.; Guedes, E.P.; Mass, E.B.; de Meneses, E.W.; Marques, L.A.; Mantovani, M.S.; Russowsky, D. Synthesis of hybrid perillyl-4 H-pyrans. Cytotoxicity evaluation against hepatocellular carcinoma HepG2/C3A cell line. *J. Heterocycl. Chem.* **2020**, *57*, 2597–2614.
12. Liang, P.L.; Yuan, L.Y.; Deng, H.; Wang, X.C.; Wang, L.; Li, Z.J.; Shi, W.Q. Photocatalytic reduction of uranium (VI) by magnetic ZnFe2O4 under visible light. *Appl. Catal. B Environ.* **2020**, *267*, 118688.
13. Ponpandian, T.; Muthusubramanian, S. One-pot, catalyst-free synthesis of spirooxindole and 4 h-pyran derivatives. *Synth. Commun.* **2014**, *44*, 868–874.