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ZnO/Fe_3O_4 MNPs promoted green synthesis of imidazoline under solvent-free Conditios

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Abstract: A one-pot synthesis of imidazolin from dialkyl acetylenedicarboxylates and thiourea in the presence of catalytic amounts of ZnO/Fe_3O_4 MNPs at room temperature in good yields is described. In this research, the Fe_3O_4/ZnO magnetic core–shell nanoparticles (Fe_3O_4/ZnO MCNPs) were synthesized through a green method using Petasites hybridus rhizome water extract as a reducing and stabilizing agent. The morphology and size of the Fe_3O_4/ZnO MCNPs was identified utilizing XRD, SEM and EDX analysis.

Keywords: Imidazoline, ZnO/Fe_3O_4 MNPs, Dialkyl acetylenedicarboxylates.

Introduction

imidazoline and their derivatives possess remarkable biological activities such as antibacterial, antitumour, insecticidal and fungicidal [1-3]. These are also known as anti-radiation agents and used as radiation-sickness drugs [4]. Furthermore, the antibiotic activity of cephalosporins is due to the presence of 1,3-thiazine nucleus [5]. As regards chemical viewpoint, 1,3-thiazines are important synthetic intermediates in organic syntheses [6]. Transformation of 1,3-thiazines into 6-alkyluracils and dihydropyrimidines has also been reported [1b, 7]. Owing to their chemical and biological interest, syntheses of various 1,3-thiazine derivatives have been reported [1, 8-18]. Also, water is an ideal solvent and reagent for biochemical transformations. In the past, water was not used as a solvent for synthetic organic chemistry due to the poor solubility and, in some cases, the instability of organic reagents in aqueous solutions.

Now, it has been recognized that chemical reactions in mixed aqueous solutions or two-phase systems often give better results than in organic solvents and often the insolubility of the final products facilitates their isolation [19, 20]. It can refer to the formation of nanoparticle structures which capped by organic materials from living organisms or plants [21-22]. This method is a cheap, bio friendly, safe and green procedure [23]. These plants extract show some phytochemicals properties that play in both decreasing capping and stabilization agent. Recently, nanoparticles have become the subject of important research, since they have shown to be potential in many applications [24-26]. Commonly, several various chemical and physical methods have been applied so far for the preparation Fe_3O_4/ZnO MNPs. The Fe_3O_4 encapsulated with ZnO nanoparticles gives better results in biomedicine because ZnO is biocompatible (non-toxic) and easy to penetrate cells [27]. Gordon et al. in 2011 [28] synthesized Fe_3O_4/ZnO MNPs and studied its antimicro-bial activity. Li et al. in 2016 [29]

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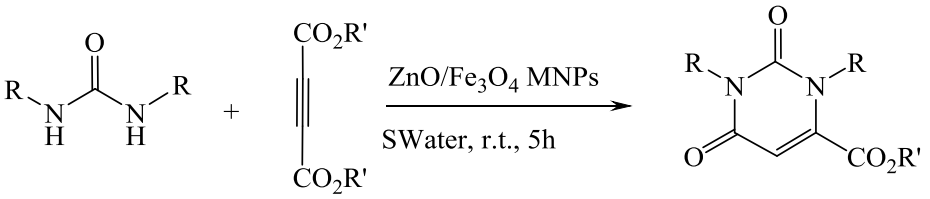
prepared Fe_3O_4/ZnO MNPs used as a nanoprobe for fluorescent chemosensor. Roeinfard et al [30] in 2017 synthesized Fe_3O_4/ZnO MNPs sol-gel method and investigated its cytotoxicity against breast cancer cells.Diverse physical and chemical methods are employed for the preparation of Fe_3O_4 and Fe_3O_4/ZnO MNPs such as co-precipitation, hydrothermal, microemulsion and biosynthesis [31]. As part of our current studies on the development of new routes in heterocyclic synthesis, we report a simple and environmentally benign strategy for the synthesis of functionalized 3,4-dihydro-2*H*-1,3-imidazoline. Thus, the reaction of dialkylthioureas **1** with activated acetylenic esters **2**, in the presence of Fe_3O_4/ZnO MNPs in water at room temperature, produced functionalized imidazoline **3** in good yields (Scheme **1**).

Results and discussion

The structures of compounds **3a**–**3f** were assigned by a consideration of their IR, ^{1}H NMR, ^{13}C NMR spectroscopic and mass spectrometric data. For example, the ^{1}H NMR spectrum of **3a** exhibited three singlets for methyl proton at δ = 3.17, 3.19, and 3.75 ppm, together with characteristic signal for the methine protons at δ = 6.77 ppm. In the ^{13}C NMR spectrum of **3a**, the signals corresponding to carbonyl and thionyl groups were observed at δ = 150.6, 164.6, and 166.2 ppm. The mass spectrum of **3a** displayed the molecular ion peak at *m*/*z* = 214.

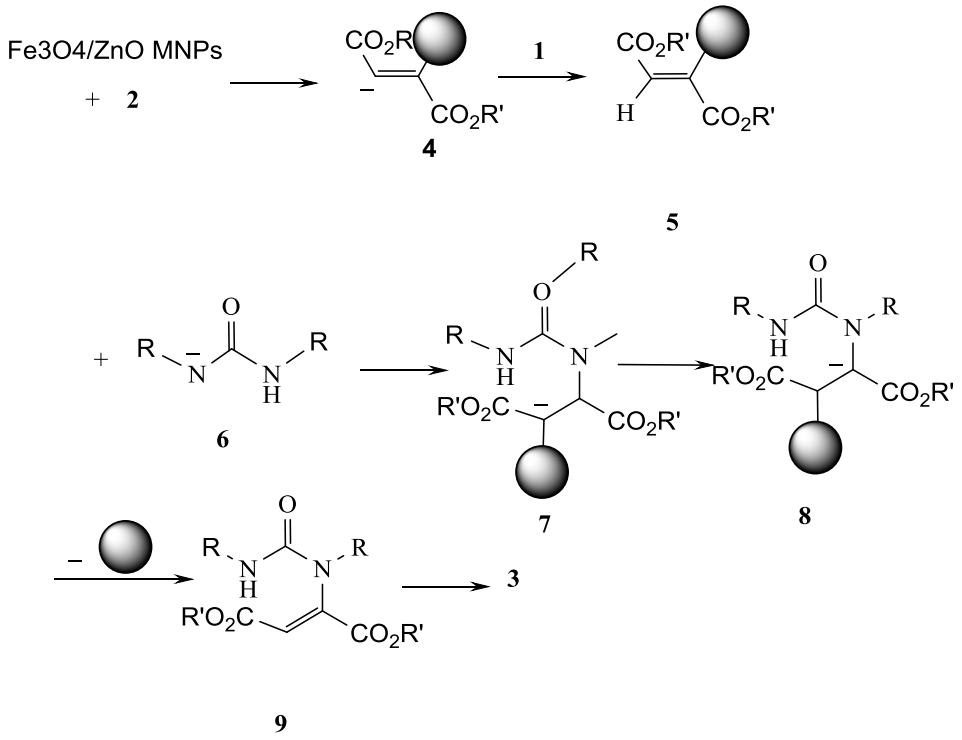
Although the mechanistic details of the reaction are not known, a plausible rationalization may be advanced to explain the product formation. Presumably, the reaction involves the initial formation of a 1:1 zwitterionic intermediate **4** between the activated acetylenes **2** and Fe_3O_4/ZnO MNPs**,** which undergoes reaction with **1** to produce **5**. This intermediate is attacked by anion **6** to produce **7**. Intermediate **7** is converted to product **3** via elimination of Fe_3O_4/ZnO MNPs and cyclization (Scheme **2**).



1 **2** **3**

3	R	R'	Yield/ % of **3**
a	Me	Me	95
b	Me	Et	90
c	Et	Me	92
d	Et	Et	95
e	Ph	Me	93
f	Ph	Et	90

Scheme 1: Reaction of activated acetylenes and Fe_3O_4/ZnO



Scheme 2: Proposed mechanism for the formation of **3.**

The shape of Fe_3O_4-MNPs (Figure 3a), ZnO-NPs (Figure 3b) and Fe_3O_4/ZnO-MCNPs (Figure 3c) was confirmed by giving SEM image.

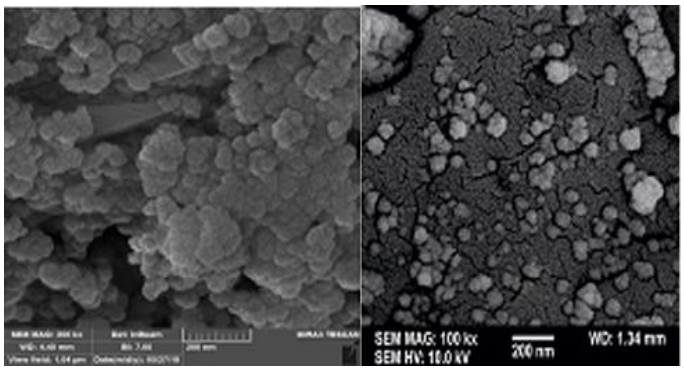


Figure 3a. SEM image of **3a**) ZnO-NPs; **3b**) SEM image of Fe_3O_4-MCNPs

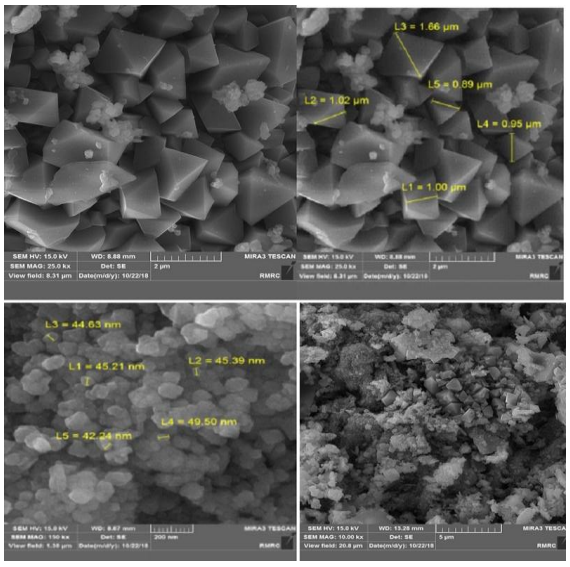


Figure 3c. SEM image of Fe_3O_4/ZnO MCNPs

The XRD pattern of the Fe_3O_4-MCNPs (Figure 4b), ZnO-NPs (Figure 4a) and Fe_3O_4/ZnO-MCNPs (Figure 4c) confirmed the nanoscale of catalyst. The average crystal size for Fe_3O_4/ZnO MCNPs is about 45 nm. For the prepared Fe_3O_4 nanoparticles the diffraction peaks

appear at ~ 30.3◦, 35.5◦, 43.2◦, 57.2◦and 62.7◦which are indexed to (220), (311), (400), (511) and (440) planes. It was confirmed to cubic inverse spinel structure compared well with the JCPDS card no. 19–0629. For Fe_3O_4/ZnO MNPs, the diffraction peaks indexed as (100), (002), (101), (102), (110), (103), (112) and (202) planes which correspond to the hexagonal crystal structure of ZnO nanoparticles and are well matched with JCPDS card no. 36–1451.

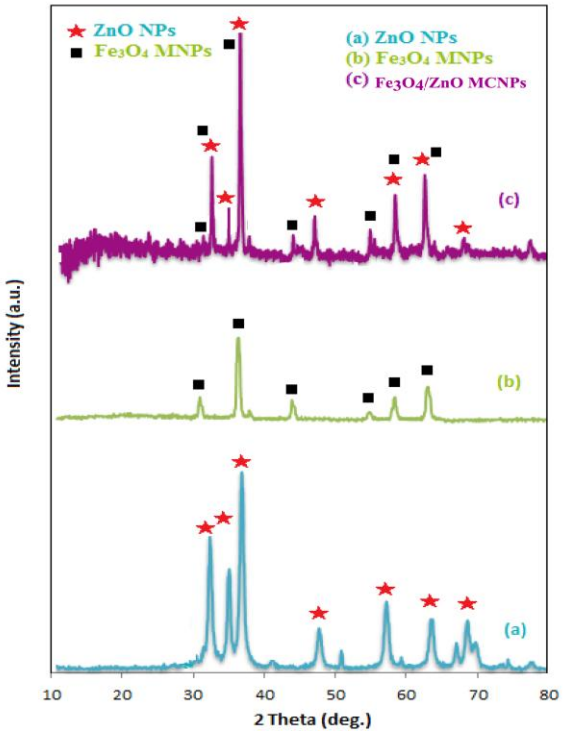


Figure 4. XRD spectra of a) ZnO-NPs; b) Fe_3O_4 MNPs; c) Fe_3O_4/ZnO MCNPs

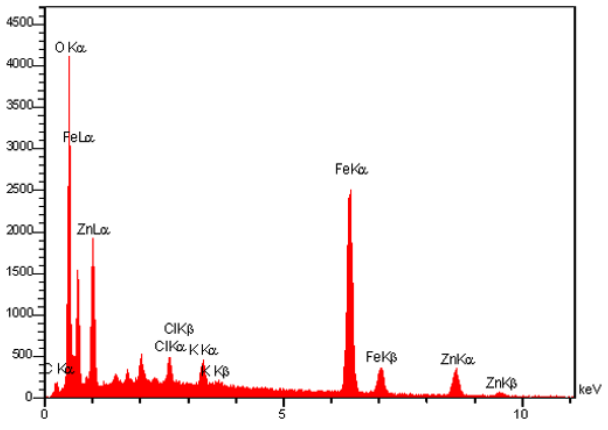


Figure 5. EDX spectra of Bio-Fe_3O_4/ZnO MCNPs

EDX spectrum of Bio-Fe_3O_4/ZnO MCNPs for the sample indicates the clear presence of Fe, O and Fe, Zn, O compo-nents in Figure 5. There is no impurity peak is observed in the EDX spectra and this confirms that the prepared samples are pure form and also shows the uniform distribution of constituent elements.

To obtain a clear size, shape and structural image of the nanoparticles the sample was analyzed using transmission electron microscopy (Figure 6). Transmission electron microscope image reveals the size of the synthesized Fe_3O_4/ZnO-MCNPs to be less than 40 nm.

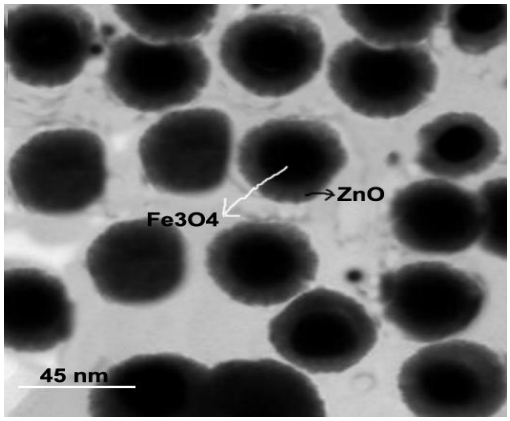


Figure 6. TEM image of the green Fe_3O_4/ZnO-MCNPs

Conclusion

In conclusion, conclusion, the reaction between Fe_3O_4/ZnO-MCNPs and electron-deficient acetylenic esters, in the presence of thiourea leads to functionalized imidazolines in good yields. This procedure has the advantage that the reaction is performed under neutral conditions, and the starting materials can be used without any pre activation or modification.

Experimental

Chemicals were purchased from Fluka and used without further purification. Melting points were measured on an Electrothermal 9100 aparatus. Elemental analyses for the C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. The results agreed favorably with the calculated values. Mass spectra were recorded on a FINNIGAN-MATT 8430 spectrometer operating at an ionization potential of 70 eV. IR

spectra were measured on a Shimadzu IR-460 spectrometer. ^{1}H-, and ^{13}C-NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500.1 and 125.8 MHz.

Preparation of Bio-Fe_3O_4/ZnO MNPs [51]

Dried *Petasites hybridus* rhizome (10 g) was poured in 100 mL water in two-neck round bottom flask (250 mL) under reflux condition. After 2 h, the mixture was filtered and water extract was applied for preparation of Fe_3O_4/ZnO-MNPs as following. $Zn(OAC)_2$ (1.5 g) and $FeCl_2.4H_2O$ (1.5 g) was solved in deionized water (10 mL). Then, *Petasites hybridus* rhizome water extract (30 mL) was added to previous mixture gently at 85 ^{o}C in round bottom flask for 8h. Then it was cooled to room temperature, sonicated for 10 min and were centrifuged at 7000 rpm for about 10 min for removing the unwanted organic matters and then were filtered. The precipitate was collected by filtration and washed with distilled water and ethanol (96%) for several times. The samples were then heated at 500 °C for 1 h. Bio-Fe_3O_4/ZnO MCNPs was dried in the air at room temprature during 24 h.

General procedure for preparation of compounds 3

To a stirred mixture of **1** (2 mmol) and **2** (2 mmol) was added Fe_3O_4/ZnO-MNPs (0.02 g) at r.t. After completion of the reaction (1-3 h) as indicated by TLC (*n*-hexane/EtOAc 8:1), the resulting solid was filtered and dried.

Methyl 3-methyl-2-(methylimino)-4-oxo-3,4-dihydro-2H-1,3-thiazine-6-carboxylate (3a)

Pale yellow powder, yield: 0.37 g (87%), m.p. 98-100°C. IR (KBr) (ν_{max}/cm^{-1}): 1717, 1695, 1658, 1621, 1433, 1331, and 1211 cm^{-1}; EI-MS: 214 (M^+, 25); 199 (45); 186 (62); 155 (70); 144 (75); 69 (100); ^{1}H NMR: 3.17 (3 H, s, MeN), 3.19 (3 H, s, MeN), 3.75 (3 H, s, MeO), 6.77 (1 H, s, CH) ppm. ^{13}C NMR: 28.9 (MeN), 30.7 (MeN), 52.3 (MeO), 115.1 (CH), 141.1 (C), 150.6 (C=O), 164.6 (C=O), 166.2 (C=S) ppm. Anal.Calcd (%) for $C_8H_{10}N_2O_3S$ (214.24): C, 44.85, H, 4.70, N, 13.08. Found: C, 44.79, H, 4.63, N, 12.88.

Ethyl 3-methyl-2-(methylimino)-4-oxo-3,4-dihydro-2H-1,3-thiazine-6-carboxylate (3b)

Pale yellow powder, yield: 0.37 g (85%), m.p. 112-114°C. IR (KBr) (ν_{max}/cm^{-1}): 1714, 1692, 1657, 1613, 1423, and 1197 cm^{-1}; EI-MS: 228 (M^+, 15); 199 (68); 185 (76); 158 (68); 70 (100); 29 (65); ^{1}H NMR: 1.34 (3 H, t, ^{3}J = 7.2 Hz, Me), 3.28 (3 H, s, MeN), 3.29 (3 H, s, MeN), 4.30 (2 H, q, ^{3}J = 7.2 Hz, CH_2O), 6.89 (1 H, s, CH) ppm. ^{13}C NMR: 14.2 (Me), 29.1 (MeN), 38.9 (MeN), 61.6 (CH_2O), 115.8 (CH), 140.9 (C), 1150.9 (C=O), 164.9 (C=O), 166.0 (C=S) ppm. Anal. Calcd (%) for $C_9H_{12}N_2O_3S$ (228.26): C, 47.36, H, 5.30, N, 12.27. Found: C, 47.28, H, 5.12, N, 12.07.

Methyl 3-ethyl-2-(ethylimino)-4-oxo-3,4-dihydro 2H-1,3-thiazine-6-carboxylate (3c)

White powder, yield: 0.43 g (90%), m.p. 125-127°C. IR (KBr) (ν_{max}/cm^{-1}): 1712, 1643, 1610, 1434, 1392, and 1317 cm^{-1}; EI-MS: 242 (M^+, 10); 227 (56); 198 (56); 158 (68); 84 (100); 44 (58); ^{1}H NMR: 1.20 (3 H, t, ^{3}J = 7.3 Hz, Me), 1.24 (3 H, t, ^{3}J = 7.4 Hz, Me), 3.46 (2 H, q, ^{3}J = 7.3 Hz, CH_2N), 3.83 (3 H, s, MeO), 3.86 (2 H, q, ^{3}J = 7.4 Hz, CH_2N), 6.84 (1 H, s, CH) ppm. ^{13}C NMR: 12.6 (Me), 15.8 (Me), 37.9 (MeN), 47.3 (MeN), 52.3 (MeO), 114.8 (CH), 141.7 (C), 147.8 (C=O), 164.5 (C=O), 166.4 (C=S) ppm.

Ethyl 3-ethyl-2-(ethylimino)-4-oxo-3,4-dihydro-2H-1,3-thiazine-6-carboxylate (3d)

White powder, yield: 0.42 g (83%), m.p. 137-139°C. IR (KBr) (ν_{max}/cm^{-1}): 1718, 1693, 1643, 1434, 1313, and 1193 cm^{-1}; EI-MS: 256 (M^+, 15); 227 (66); 168 (68); 88 (100); 45 (88); ^{1}H NMR: 1.14 (3 H, t, ^{3}J = 7.2 Hz, Me), 1.19 (3 H, t, ^{3}J = 7.4 Hz, Me), 1.26 (3 H, t, ^{3}J = 7.3 Hz, Me), 3.40 (2 H, q, ^{3}J = 7.3 Hz, CH_2N), 3.80 (2 H, q, ^{3}J = 7.4 Hz, CH_2N), 4.20 (2 H, q, ^{3}J = 7.4 Hz, CH_2O), 6.77 (1 H, s, CH) ppm. ^{13}C NMR: 12.6 (Me), 14.1 (Me), 15.8 (Me), 37.8 (MeN), 47.2 (CH_2N), 61.4 (CH_2O), 115.3 (CH), 141.3 (C), 148.1 (C=O), 164.5 (C=O), 165.9 (C=S) ppm.

Methyl 3-phenyl-2-(phenylimino)-4-oxo-3,4-dihydro-2H-1,3-thiazine-6-carboxylate (3e)

Pale yellow powder, yield: 0.62 g (92%), m.p. 150-152°C. IR (KBr) (ν_{max}/cm^{-1}): 1714, 1692, 1657, 1612, 1424, 1323, and 1196 cm^{-1}; EI-MS:

338 (M^+, 10); 323 (45); 279 (65); 206 (68); 132 (100); 59 (88); ^{1}H NMR: 3.83 (3 H, s, MeO), 7.34 (2 H, t, ^{3}J = 7.2 Hz, 2 CH_m), 7.56 (1 H, t, ^{3}J = 7.2 Hz, CH_p), 6.94 (2 H, d, ^{3}J = 7.2 Hz, 2 CH_o), 7.01 (1 H, s, CH) ppm. ^{13}C NMR: 52.6 (MeO), 127.9 (C), 129.4 (CH), 134.0 (CH), 141.4 (CH), 147.3 (C), 151.6 (C=O), 164.6 (C=S), 166.4 (C=O) ppm. Anal.Calcd (%) for $C_{18}H_{14}N_2O_3S$ (338.38): C, 63.89, H, 4.17, N, 8.28. Found: C, 63.78, H, 4.13, N, 8.19.

Ethyl 3-phenyl-2-(phenylimino)-4-oxo-3,4-dihydro-2H-1,3-thiazine-6-carboxylate (3f)

Pale yellow powder, yield: 0.63 g (89%), m.p. 148-150°C. IR (KBr) (ν_{max}/cm^{-1}): 1728, 1691, 1612, 1590, 1489, and 1192 cm^{-1}; EI-MS: 352 (M^+, 15); 323 (68); 279 (52); 220 (68); 118 (100); 45 (88); ^{1}H NMR: 1.33 (3 H, t, ^{3}J = 7.2 Hz, Me), 4.30 (2 H, q, ^{3}J = 7.2 Hz, CH_2O), 6.94 (1 H, d, ^{3}J = 7.2 Hz, 2 CH_o), 7.01 (1 H, s, CH), 7.23 (2 H, t, ^{3}J = 7.2 Hz, 2 CH_m), 7.34 (1 H, t, ^{3}J = 7.2 Hz, CH_p) ppm. ^{13}C NMR: 14.2 (Me), 61.8 (CH_2O), 120.6 (CH), 127.9 (C), 115.3 (2 CH), 117.1 (2 CH), 125.3 (CH), 147.4 (C=O), 164.7 (C=S), 166.0 (C=O) ppm.

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