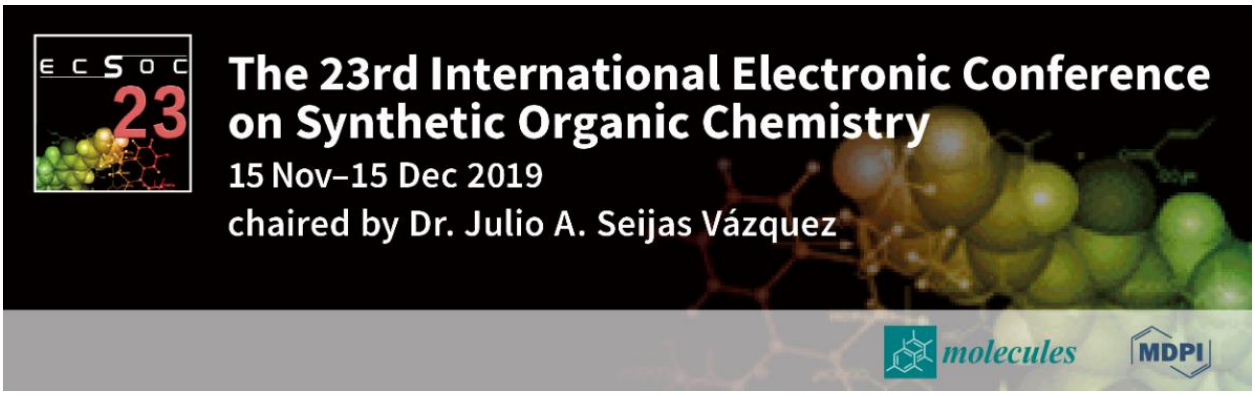


ZnS/$CuFe_2O_4$: magnetic hybrid nanocomposite to catalyze the synthesis of 2,4,5-triaryl-1H-imidazole derivatives

Fereshte Hassanzadeh-Afruzi, Shahrzad Bahrami and Ali Maleki*

Catalysts and Organic Synthesis Research Laboratory, Department of Chemistry, Iran University of Science and Technology, Tehran 16846-13114, Iran

**Corresponding author E-mail: maleki@iust.ac.ir*; Fax: +98-21-73021584; Tel: +98-21-77240540-50

Abstract

Integration of nanomaterials is an entirely new method to synthesis efficient catalysts. These compounds provided new characteristics and distinctive application which is not accessible in the single-particle nanoparticles. Although there is little catalytic activity in each component of the hybrid material, their hybrid displays much higher activity. Indeed, the presence of intermediate

metal oxides and their oxides in the hybrid catalyst framework caused a synergistic effect, thus facilitate the organic reaction more effectively. The extensive biochemical and pharmacological activities of imidazole-containing compounds have required the development of efficient methods for synthesizing these compounds, which is a significant topic in organic chemistry. The imidazole nucleus function as a main scaffold for constructing of biologically important molecules.

The ZnS/$CuFe_2O_4$ magnetic hybrid nanocatalyst was synthesized by a simple co precipitation and characterized successfully. Synthesized nanocomposite was utilized as a magnetic and heterogeneous catalyst for the one-pot synthesis of 2,4,5-triaryl-1H-imidazole derivatives with condensation of various aromatic aldehydes, benzil and ammonium acetate. The presented method shows some advantages such as mild conditions, good yields, and simple separation of products from the reaction mixture and cost-effective catalyst. The observation data showed nanocatalyst ZnS/$CuFe_2O_4$ were easily separated from the reaction using an external magnetic field and use again five times in subsequent reactions without appreciable reduction in catalytic activity.

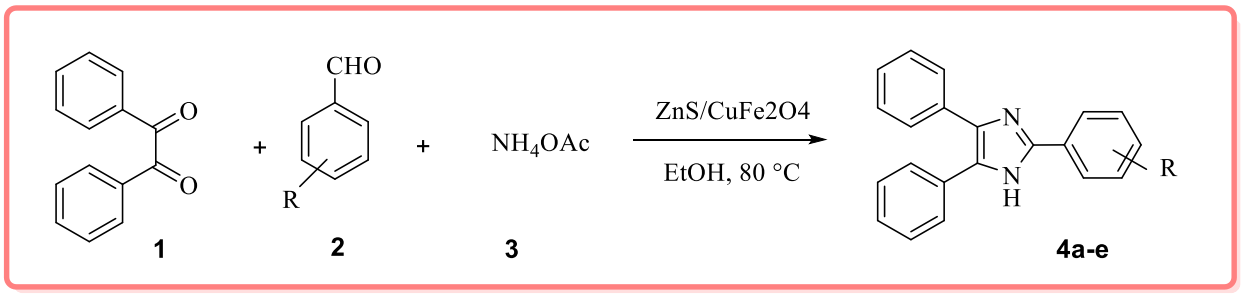
Keywords: Hybrid catalyst, multicomponent reaction, magnetic nanocomposite, imidazole

1. Introduction

Within the last decades nonmagnetic catalysts have gained significant attention since they possess merits of both homogeneous and heterogeneous catalysts like high reactivity and ease of separation from the reaction mixture [1]. For manufacturing magnetic catalyst, iron seems to be the most suitable case because of its more natural abundance, ease of availability, low-cost and less toxicity than other metals with magnetic nature [2]. Nanomaterial combination is a new approach for

effective catalyst synthesis. Such compounds provided new features and distinctive applications that are not present in single-particle nanoparticles [3]. ferrites are important magnetic material with unique features that has wide applications in a variety of fields such as sensors, environmental filtration, magnets and electrical materials, magnetic resonance imaging, ceramic coating. $CuFe_2O_4$ has inverse spinel structure which in that Cu^{2+} cations and half of the Fe^{3+} cations occupy octahedral sites, while the other half of the Fe^{3+} cations occupy tetrahedral sites. Inverse spinel ferrites have been utilized as catalysts in reactions such as azide-alkyne cycloaddition, epoxide ring-opening and the Ullmann coupling [4, 5].

The synthesis of imidazole as main scaffold for constructing of biologically active molecules is a noteworthy topic in organic chemistry. They have diverse medicinal and biological activities like antibacterial, antifungal, reducing inflammation, anti-cancer antiviral, anti-diabetic, anti-allergic, analgesic and herbicidal [6, 7]. In continues to our research on MCRs and nanomaterials and due to the importance of heterocyclic compounds [8-25], in this work, $ZnS/CuFe_2O_4$ was used as a hybrid nanocatalyst in the synthesis of 2,4,5-triaryl-1H-imidazole derivatives via one-pot condensation of various aromatic aldehydes, benzil and ammonium acetate (Scheme 1).



Scheme 1. The synthesis of 2,4,5-triaryl-1H-imidazole

2. Experimental

2.1. General

All solvents and chemicals were purchased from Merck and Aldrich companies. EDX spectra were provided with a Numerix DXP–X10P. FESEM image was provided with Hitachi S-480 instrument. The XRD pattern of the nanocatalyst was recorded with the X′Pert Pro diffractometer operating with (40 mA, 40 kV). Melting points were measured with an Electrothermal 9100 apparatus.

2.2. *Preparation of $ZnS/CuFe_2O_4$*

At first thioacetamide (1.6 mmol) was dissolved in 20 ml distilled water. Then $FeCl_3.6H_2O$ (2 mmol), $CuCl_2.4H_2O$ (1 mmol) and $Zn(NO_3)_2.2H_2O$ (1 mmol) were dissolved in 20 ml distilled water separately , and gradually added to the aqueous solution of thioacetamide. The resulting mixture was first dispersed using ultrasonic and then stirred at room temperature. Next, ammonia was added drop by drop to above mixture and stirring continued at room temperature for 30 minutes. The resulting precipitate was separated from the reaction mixture using magnets, washed several times with distilled water and ethanol, and dried at room temperature for 24 hours to provide a $ZnS/CuFe_2O_4$ magnetic catalyst.

2.3. *General procedure for the synthesis of 2,4,5-triaryl-1H-imidazole derivatives*

The mixture of 4-chlorobenzaldehyde (1 mmol), ammonium acetate (4 mmol), benzil (1 mmol) and $ZnS/CuFe_2O_4$ (0.03 g) as a catalyst were stirred at 80°C in ethanol. The reaction progress was monitored by thin layer chromatography. After completion of the reaction, the crude precipitate

was washed with deionized water and dried. Pure products were obtained by recrystallization from ethanol.

3. Results and discussion

Elemental analysis of the $ZnS/CuFe_2O_4$ nanocatalyst was carried out using EDX to study the chemical composition of the synthesized catalysts. As is observed in Fig. 1 the presence of high-intensity peaks related to Zn, Cu, S, Fe and O elements represent the components of the synthesized catalyst.

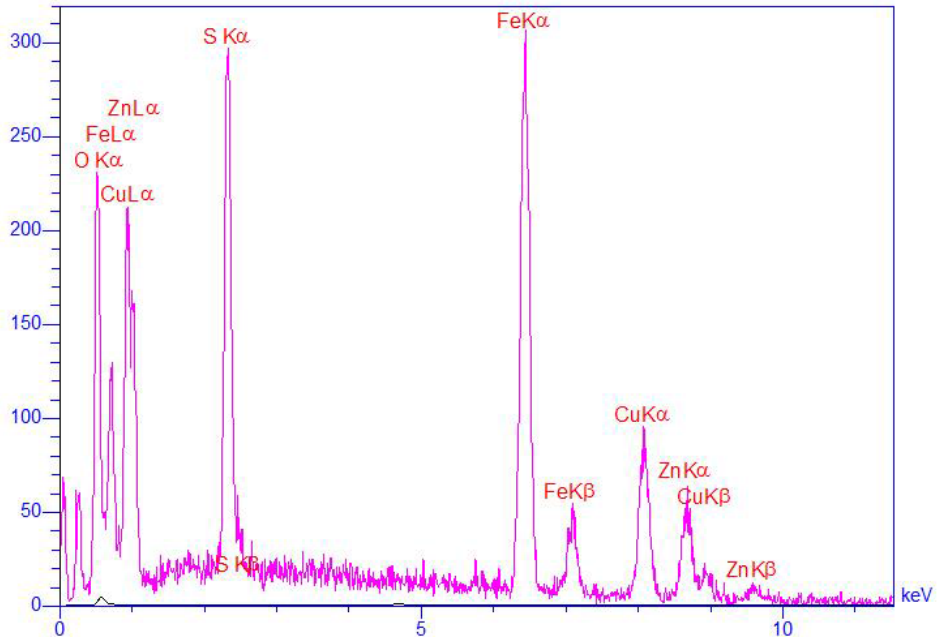


Fig. 1. EDX analysis of the $ZnS/CuFe_2O_4$ catalyst.

FESEM image was used to study morphology and particle size of the synthetic nanocatalyst. Fig. 2 shows spherical like nanoparticles with uniform distribution. The average of particle size in the $ZnS/CuFe_2O_4$ catalyst is less than 20 nm.

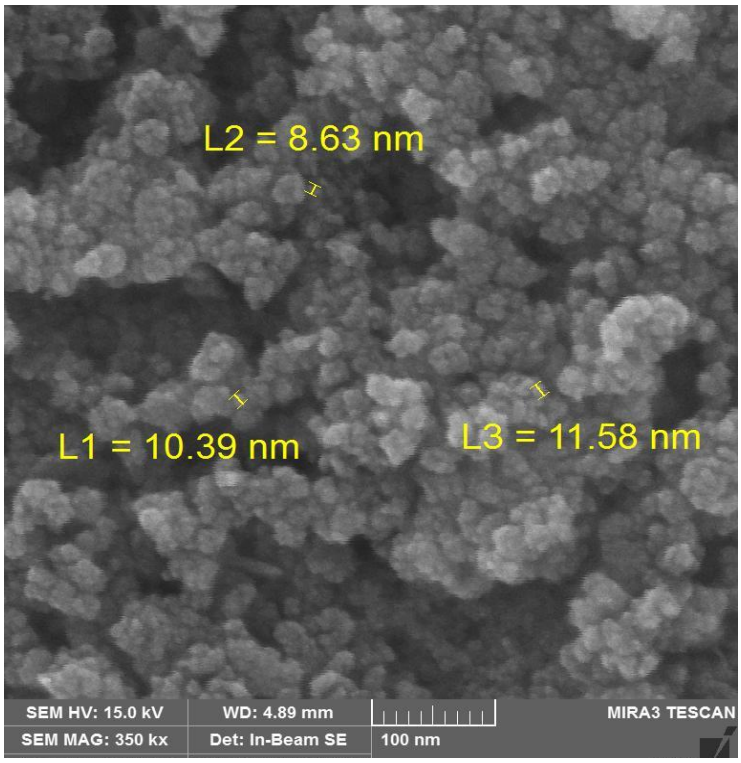


Fig. 2. FESEM analysis of the ZnS/$CuFe_2O_4$ catalyst.

Furthermore, X-ray diffraction analysis to investigate the crystalline nature of catalyst was employed. As is depicted in Fig. 3 the XRD pattern of ZnS/$CuFe_2O_4$ was compared with $CuFe_2O_4$ and ZnS. Prepared nanocatalyst has distinct peaks in 2θ = 29.80°, 32.21°, 35.71°, 43.31°, 48.40°, 57.25°, 59.66°, 63.62° which are consistent with the XRD pattern of ZnS and $CuFe_2O_4$.

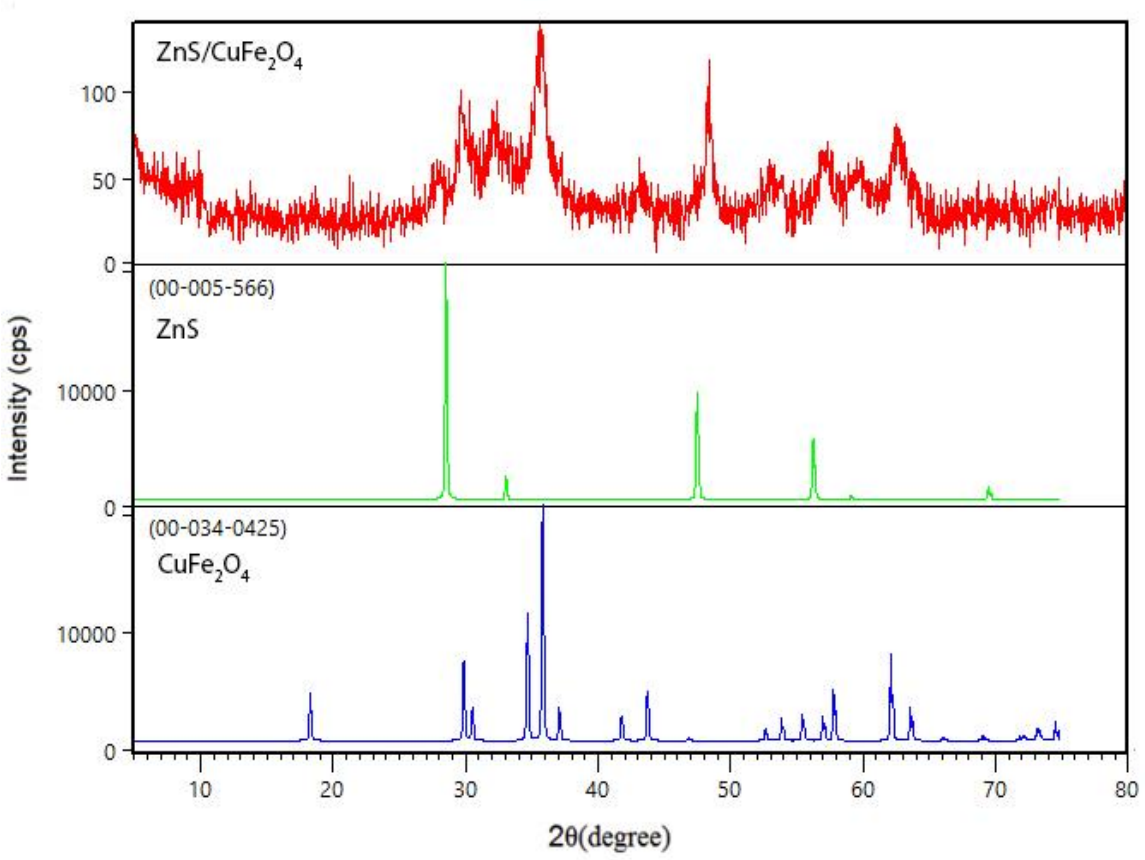


Fig. 3. XRD pattern of $ZnS/CuFe_2O_4$.

Catalytic application of $ZnS/CuFe_2O_4$ *in the synthesis of 2,4,5-triaryl-1H-imidazole derivatives*

Synthesizing of 2,4,5-triaryl-1H-imidazole derivatives using some aromatic aldehydes in optimum condition was studied in order to evaluate generality, applicability and limitation of this protocol. As can be observed in Table 1, all aromatic aldehydes with electron withdrawing and electron donating substitution produced the satisfying corresponding products.

Table 1. Synthesis of 2,4,5-triaryl-1H-imidazole derivatives.

Entry	R	Product	Yield[a] (%)	Mp (°C)
1	4-Cl	**4a**	92	259-261
2	3-NO_2	**4b**	89	264-266
3	4-OMe	**4c**	83	228-230
4	3-OMe	**4d**	89	257-259
5	4-Me	**4e**	82	229-231

[a] Isolated yield.

4. Conclusions

$ZnS/CuFe_2O_4$ nanocomposite was prepared via a convenience procedure and was utilized as cost-effective hybrid heterogeneous catalyst in the synthesis of biologically active 2,4,5-triaryl-1H-imidazole derivatives. This protocol offers some merits such as mild reaction conditions, simple separation of products from the reaction mixture, retrievable catalyst.

Acknowledgements

The authors gratefully acknowledge the partial support from the Research Council of the Iran University of Science and Technology.

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