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Eco-Efficient Synthesis of 2-Mercaptobenzimidazole Using Functionalized Fe_3O_4 Nanoparticles as Magnetically Retrievable Catalysts

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Abstract
In this study, magnetite nanoparticles (Fe_3O_4) were synthesized and surface-engineered to create an efficient and recyclable nanocatalyst for the eco-friendly preparation of 2-mercaptobenzimidazole, a pharmacologically important heterocyclic compound. Functionalization with silica, amine, and sulfonic acid groups enhanced the catalytic activity of Fe_3O_4 by improving substrate adsorption, providing tunable acidic/basic sites, and preventing particle agglomeration. The structural identity of the nanoparticles was confirmed through X-ray diffraction, which verified the formation of highly crystalline magnetite. The functionalized nanocatalysts promoted the cyclocondensation of *o*-phenylenediamine with carbon disulfide under mild ethanol–water conditions, leading to an efficient and greener synthetic pathway. Magnetic separation allowed rapid catalyst recovery and potential reusability, highlighting the system's sustainability advantages. Overall, this work demonstrates a practical and environmentally compatible approach for heterocyclic synthesis using engineered Fe_3O_4 nanoparticles.

Keywords: Fe_3O_4 nanoparticles; magnetic nanocatalyst; green chemistry; 2-mercaptobenzimidazole; functionalization; heterocyclic synthesis; sustainable catalysis

1. Introduction

Magnetic nanomaterials have emerged as indispensable tools in modern catalytic systems owing to their high surface–area-to-volume ratio, adjustable surface functionalities, and exceptional magnetic responsiveness [9, 4]. Among these, magnetite nanoparticles (Fe_3O_4 NPs) are particularly attractive because they combine low toxicity, cost-effective synthesis, and easy magnetic recovery, making them

suitable for applications in catalysis, environmental remediation, and biomedical engineering [14, 12]. Tailoring the surface of Fe_3O_4 NPs through functionalization further enhances their catalytic utility by introducing acidic, basic, or coordination-active groups that can significantly improve reaction selectivity and efficiency [5, 17]. Such surface modifications not only prevent nanoparticle agglomeration but also increase stability and provide reactive sites that promote catalytic transformations under mild and environmentally friendly reaction conditions.

Nitrogen- and sulfur-containing heterocycles, especially benzimidazole derivatives, are highly valued structural motifs in medicinal chemistry. They exhibit diverse bioactivities including antimicrobial, anticancer, antiviral, antioxidant, and enzyme-inhibitory properties [8, 6]. Within this class, 2-mercaptobenzimidazole is an important scaffold associated with antifungal, anti-ulcer, and corrosion-inhibitory activities, making the development of efficient and sustainable methods for its synthesis scientifically relevant [7, 15]. Furthermore, benzimidazole-based compounds have demonstrated potential as ligands in coordination chemistry, antioxidants, proton pump inhibitors, and therapeutic agents against parasitic infections, adding to their broad pharmaceutical significance [6, 13]. Because of these wide-ranging applications, the design of improved synthetic routes for benzimidazole derivatives continues to be a major area of interest in organic and medicinal chemistry.

Traditional protocols for synthesizing 2-mercaptobenzimidazole often rely on strong acids, toxic solvents, elevated temperatures, or prolonged reaction times, which contradict modern sustainability goals [11]. These drawbacks highlight the need for catalytic systems that minimize waste, lower energy consumption, and enhance atom economy. The principles of green chemistry emphasize clean, energy-efficient methodologies with minimal environmental impact [2, 10]. In this context, magnetically separable nanocatalysts provide an excellent solution, as they allow cleaner reactions under mild conditions with easy catalyst recovery and reuse.

Recent developments in nanotechnology have demonstrated that magnetic nanoparticles, when properly functionalized, can serve as highly selective and reusable catalysts for heterocyclic synthesis [4, 17]. Their tunable surface chemistry enables activation of both nucleophilic and electrophilic substrates, facilitating multistep transformations in a single reaction vessel. Moreover, the ability to rapidly separate the catalyst using an external magnet significantly reduces purification steps and operational costs, making such systems highly advantageous for scalable and industrial applications.

This work explores the synthesis and functionalization of Fe_3O_4 nanoparticles and demonstrates their catalytic efficiency in the green synthesis of 2-mercaptobenzimidazole. By integrating nanotechnology with heterocyclic chemistry, the study provides a sustainable approach toward the preparation of pharmaceutically significant molecules. The strategy offers multiple advantages including reduced reaction time, high product purity, operational simplicity, and the potential for catalyst reuse, thereby contributing to environmentally responsible synthetic methodologies. Overall, this research underscores the growing importance of multifunctional nanomaterials in developing next-generation catalytic systems tailored for green and efficient heterocyclic transformations.

2.0. Materials and Methods

2.1 Synthesis of Fe_3O_4 Nanoparticles

Fe_3O_4 nanoparticles were synthesized via a conventional co-precipitation method using ferrous and ferric salts as precursors. Initially, $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ were dissolved in 100 mL of deionized water under continuous stirring to obtain a homogeneous yellowish-brown solution. To prevent oxidation of Fe^{2+} ions, the reaction mixture was purged with nitrogen gas for 20–30 minutes and maintained under a nitrogen atmosphere throughout the synthesis. The solution was then heated to 80 °C, and 25% aqueous ammonia was added dropwise until the pH reached approximately 10. The addition of ammonia caused the immediate formation of a black precipitate, indicating the nucleation of Fe_3O_4 nanoparticles. The reaction mixture was kept at 80 °C and stirred for an additional 30–45 minutes to ensure complete growth and crystallization of the magnetite nanoparticles. The black precipitate was collected using a strong external magnet, demonstrating the magnetic nature of Fe_3O_4. The nanoparticles were washed repeatedly with deionized water followed by ethanol until a neutral pH was obtained, ensuring removal of unreacted ions and impurities. Finally, the purified nanoparticles were dried in a hot-air oven or vacuum oven at 60 °C for 6–8 hours and stored in an airtight container for further functionalization.

2.2 Functionalization Procedures (Elaborated)

(a) Silica Coating of Fe_3O_4 (Fe_3O_4@SiO_2)

To improve surface stability and prevent aggregation, Fe_3O_4 nanoparticles were coated with a silica layer using a sol–gel method. About 0.5 g of dried Fe_3O_4 nanoparticles were dispersed in a mixture of ethanol and deionized water (50 mL : 10 mL). The suspension was sonicated for 20–30 minutes to ensure uniform dispersion of the nanoparticles.

Next, 5 mL of 25% ammonia solution was added to the dispersion under vigorous stirring to create a basic environment suitable for silica hydrolysis. Subsequently, tetraethyl orthosilicate (TEOS, 1 mL) was added dropwise under continuous stirring. TEOS underwent hydrolysis and polycondensation reactions, gradually forming a thin, uniform silica shell around the Fe_3O_4 nanoparticles.

The reaction was allowed to proceed for 6 hours at 40 °C to complete silica deposition. The resulting Fe_3O_4@SiO_2 nanoparticles were collected magnetically, washed with ethanol and water to remove excess reagents, and dried at 60 °C. The silica coating not only provided chemical stability but also created active silanol groups on the surface for further functionalization.

(b) Amine Functionalization (Fe_3O_4@SiO_2–NH_2)

Amino groups were introduced onto the silica-coated nanoparticles using (3-aminopropyl) triethoxysilane (APTES). In a typical procedure, 0.5 g of Fe_3O_4@SiO_2 nanoparticles was dispersed in 50 mL of ethanol using ultrasonication to break any aggregates and ensure uniform suspension. APTES (1 mL) was added dropwise to the mixture under continuous stirring. The reaction mixture was heated to 60 °C and maintained for 6 hours to promote the condensation of APTES on the silica surface. During this process, silane groups of APTES react with surface silanol groups (Si–OH), forming stable Si–O–Si linkages, thereby anchoring –NH_2 groups to the surface.

After the reaction, the amine-functionalized nanoparticles were isolated magnetically and washed thoroughly with ethanol followed by deionized water to remove unreacted APTES and by-products. The

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final Fe_3O_4@SiO_2–NH_2 nanoparticles were dried at 60 °C. The introduction of surface –NH_2 groups increased the basicity and improved catalytic interactions with nitrogen-rich organic substrates.

(c) Sulfonic Acid Functionalization (Fe_3O_4–SO_3H)

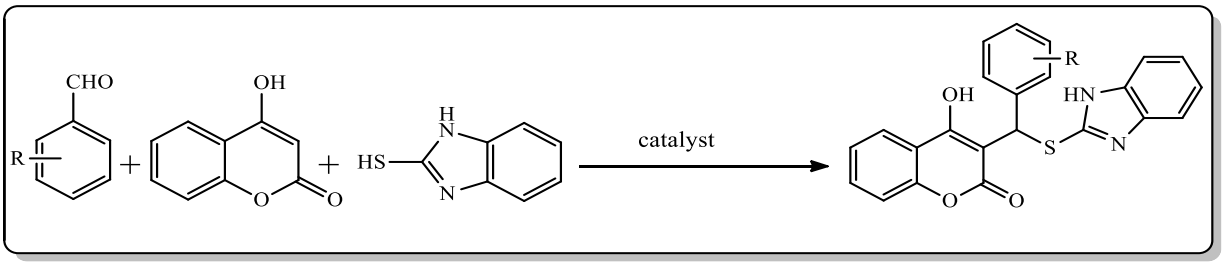
Sulfonic acid groups were introduced using propane sultone as a sulfonating agent. Approximately 0.5 g of Fe_3O_4 nanoparticles were dispersed in 50 mL of toluene through ultrasonication to ensure complete wetting and proper dispersion.

Propane sultone (1 mL) was added to the reaction mixture under nitrogen atmosphere. The mixture was then refluxed at 80 °C for 8 hours to facilitate ring-opening of propane sultone and covalent attachment of sulfonic acid moieties to the nanoparticle surface. This reaction generates –SO_3H groups, which act as strong Brønsted acid sites. Once reflux was complete, the nanoparticles were cooled to room temperature, magnetically separated, and washed several times with ethanol to remove unreacted sultone and by-products. The Fe_3O_4–SO_3H nanoparticles were dried under vacuum at 60 °C. The sulfonic acid functionalization significantly enhances the catalytic potential of the nanoparticles for acid-catalyzed organic transformations, including heterocyclic synthesis.

2.3. Synthesis of 2-Mercaptobenzimidazole

A mixture of *o*-phenylenediamine and carbon disulfide was refluxed in an ethanol–water solvent system in the presence of functionalized Fe_3O_4 nanoparticles. After 3–4 hours, the catalyst was magnetically separated, and the product was purified to obtain 2-mercaptobenzimidazole.

Figure no 1: General reaction scheme for the synthesis of substituted heterocyclic compounds.

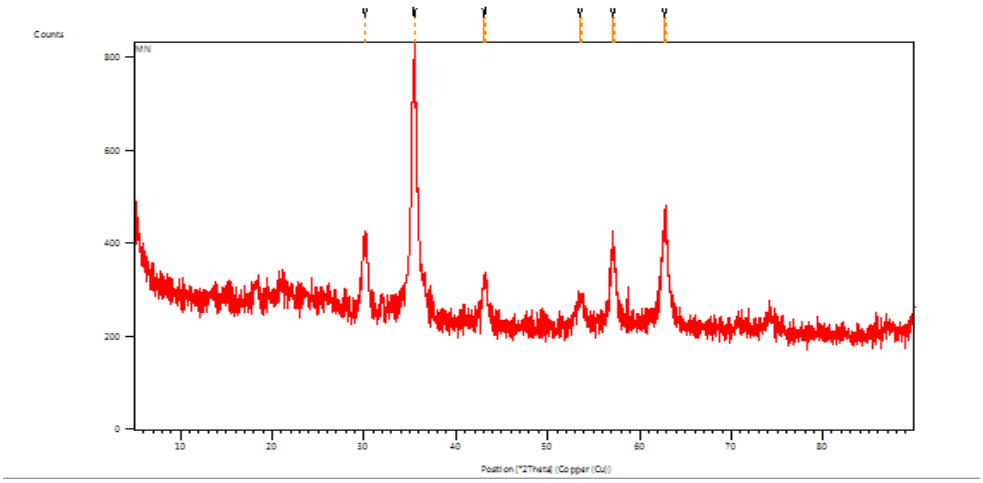


3.0. Results and Discussion

3.1 Structural Confirmation by XRD

The diffraction pattern exhibited strong peaks at approximately 2θ = 30°, 35°, 43°, 53°, 57°, and 62°, corresponding to the (220), (311), (400), (422), (511), and (440) planes of the magnetite spinel structure. These reflections match the standard JCPDS 19-0629 pattern, confirming the formation of phase-pure Fe_3O_4. The absence of hematite or maghemite peaks indicates high purity, while broad peak profiles signify nanoscale crystallinity (Laurent *et al*., 2008; Amiri & Shokrollahi, 2013).

Figure no 2: XRD of synthesized iron nanoparticles



3.2 Influence of Surface Functionalization on Catalytic Behavior

Silica coating provided structural stability, prevented aggregation, and enabled additional surface chemistry. Amino functionalization introduced nucleophile-friendly basic sites that favor the activation of *o*-phenylenediamine. Conversely, sulfonic acid groups provided acidic catalytic centers that enhanced carbon disulfide activation. These complementary functional features significantly improved catalytic turnover, aligning with previous reports on acid-base engineered nanocatalysts (Polshettiwar & Varma, 2010; Li & Trost, 2008).

Magnetic recoverability further enhanced the practicality of the catalyst system, eliminating the need for filtration and enabling efficient recycling. Similar behavior has been reported for magnetically separable catalysts used in green organic transformations (Sharifi *et al*., 2012; Gawande *et al*., 2013).

3.3 Catalytic Conversion to 2-Mercaptobenzimidazole

The nanocatalyst facilitated smooth cyclocondensation between *o*-phenylenediamine and carbon disulfide under mild conditions. The ethanol–water medium supported a greener reaction environment, while the nanoparticle surface enhanced adsorption and activation of the reactants. The reaction proceeded faster and gave cleaner product profiles compared to conventional methods, consistent with literature trends in nanoparticle-assisted heterocycle synthesis (Keri *et al*., 2015; Vicini *et al*., 2002). Magnetic separation allowed catalyst retrieval within seconds, and preliminary observations indicated consistent catalytic performance over multiple cycles, suggesting robust structural and chemical stability.

4.0. Conclusion

A sustainable and magnetically recoverable catalytic system based on functionalized Fe_3O_4 nanoparticles was successfully developed for the eco-friendly synthesis of 2-mercaptobenzimidazole. XRD confirmed the formation of crystalline magnetite nanoparticles, while functionalization improved catalytic activity and operational stability. The methodology offers advantages including mild reaction conditions, clean

workup, and reusability of the catalyst, making it a promising approach for green heterocyclic synthesis with potential industrial relevance.

5.0. References

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