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Review: Using Metal Oxide Nanoparticles as Catalyst in Benzimidazoles Synthesis

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Abstract

Heterocyclic compounds, such as benzimidazole derivatives, are a type of heterocyclic chemicals. Benzimidazole consists of a 6-atom benzene ring fused to the five-atom imidazole ring, which is an important structural property of this compound. A powerful inhibitor of various enzymes was used to investigate several pharmacological residences. Heterocyclic compounds, including benzimidazoles, are interested in being very effective compounds and are used in the preparation of many medicines, including as antiviral, anticancer, antiparasitic, antimicrobial, antihistamine, analgesic and as effective treatments for diabetes. Because of their stability, bioavailability, and have large organic activity, benzimidazole derivatives have multiple activities. Using various azole moieties, modifications to a few organic polymers was achieved. This article will discuss some of the current methodologies of synthesizing benzimidazoles and their pharmacological properties, as well as a variety of derivatives.

1. Introduction

Compounds based on benzimidazole or 1H-1,3-benzodiazole, Figure 1, are structurally similar to nucleotides, such as the adenine base of DNA [1-3]. Natural and synthesized benzimidazoles are vital heterocyclic compounds. These compounds are widely used as antifungals [4,5], anthelmintic [6], anti-inflammatory [7-10] and

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antipsychotic medications [11], while others have been found to have interesting bioactivities [12,13].

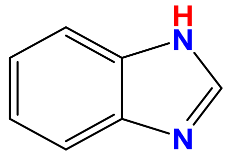
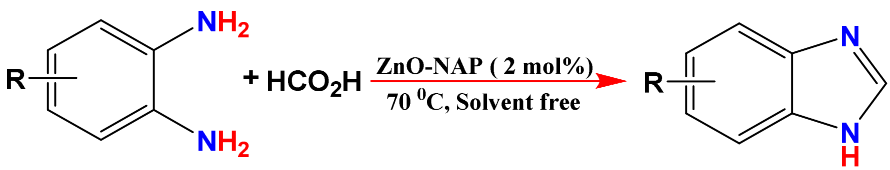


Figure 1. Benzimidazole moiety.

Several methods of synthesizing benzimidazole and its derivatives have been studied in the literature [4,14,15], due to its huge range of pharmacological and biological activities [16-21], industrial and synthetic applications. Benzimidazole is often synthesized by condensation of o-phenylenediamine (2-aminoaniline) with acid derivatives or 2-aminoanilinewith carbonyl compounds (especially aldehydes) in the presence of a suitable oxidant [22-25]. Traditional procedures, on the other hand, suffer from the use of strong inorganic acid, high amount of unwanted waste, difficult recycling process, as well as low atomic economy. Although there are many published procedures that are well effective, some of these published procedures have one or more problems such as the amount of product is low, the reaction conditions used are high such as temperature or pressure or the used time to complete the reaction is very long, also, the occurrence of side reactions; it reduces the purity of the product, as well as the use of toxic solvents and very expensive chemicals. Due to the high surface area resulting from the small size of its particles, which is mainly responsible for its catalytic activity, transition-metal nanoparticles have been exploited as good catalysts in numerous synthetic organic conversions in recent years [25]. Metal oxide-based nanoparticles (MONPs) can have a variety of structural geometries, making them versatile and potentially useful in a variety of fields such as electronics, optics, and life science in general, due to their insulator and semiconductor properties. Furthermore, when compared to bulk materials counterparts, nanoparticle metals have unique physicochemical properties because to their “limited” surface of high density and size [26,27]. For some reason this article aims to show structures of some medicinally and physiologically vital benzimidazole derivatives. It is a research study that includes both traditional and novel approaches using metal oxide nanoparticles as catalyst for synthesizing pharmacologically active benzimidazole derivatives, as well as various methods for constructing nucleus of the benzimidazole.

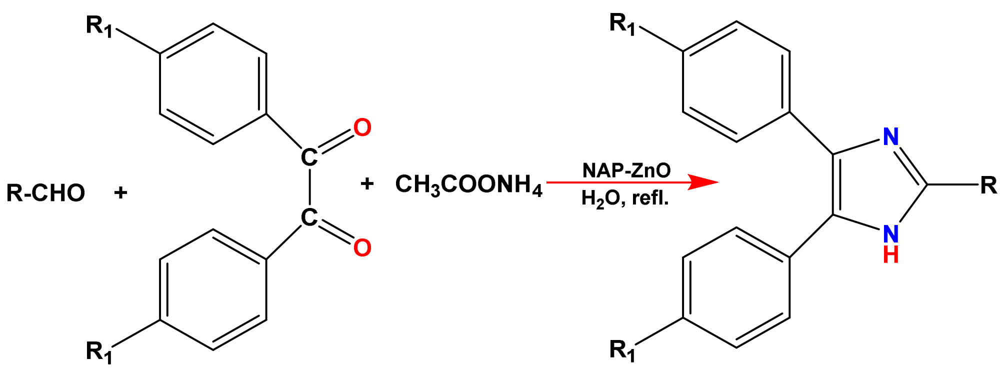
2. Use of Nanotechnology in the Benzimidazoles Synthesis

In practice, all benzimidazole synthesis approaches begin with derivatives of benzene having containing the nitrogen atoms functionalities that are ortho to one another [28,29]. Among the different MNPS utilized as the catalyst, ZnO nanoparticles have been employed the alcohol and phenol in the ortho-acylation processes [30] and the fabrication of ketones-esters in p-acetamido, among other chemical transformations [31]. In this article, the necessary mechanochemical processes that can be used in the presence of NAP-ZnO are explained to convert the formic acid (HCOOH) into a benzimidazole compound with high activity and selectivity [32,33] (Scheme 1).



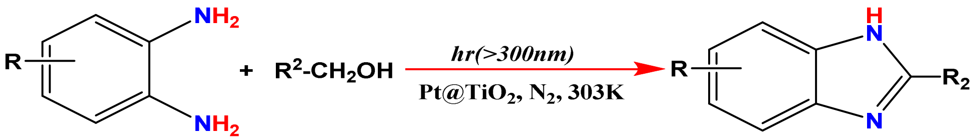
Scheme 1. Benzoimidazoles synthesis using ZnO-NAP as a catalysis.

In 2015, Nikoofar *et al.* [5, 34] were synthesized ZnO nanorod, then utilized this catalyst to produce 2,4,5-triaryl-1H-imidazoles from different aldehydes and benzils presence ammonium acetate in H_2O with reflux under constant temperature (Scheme 2).



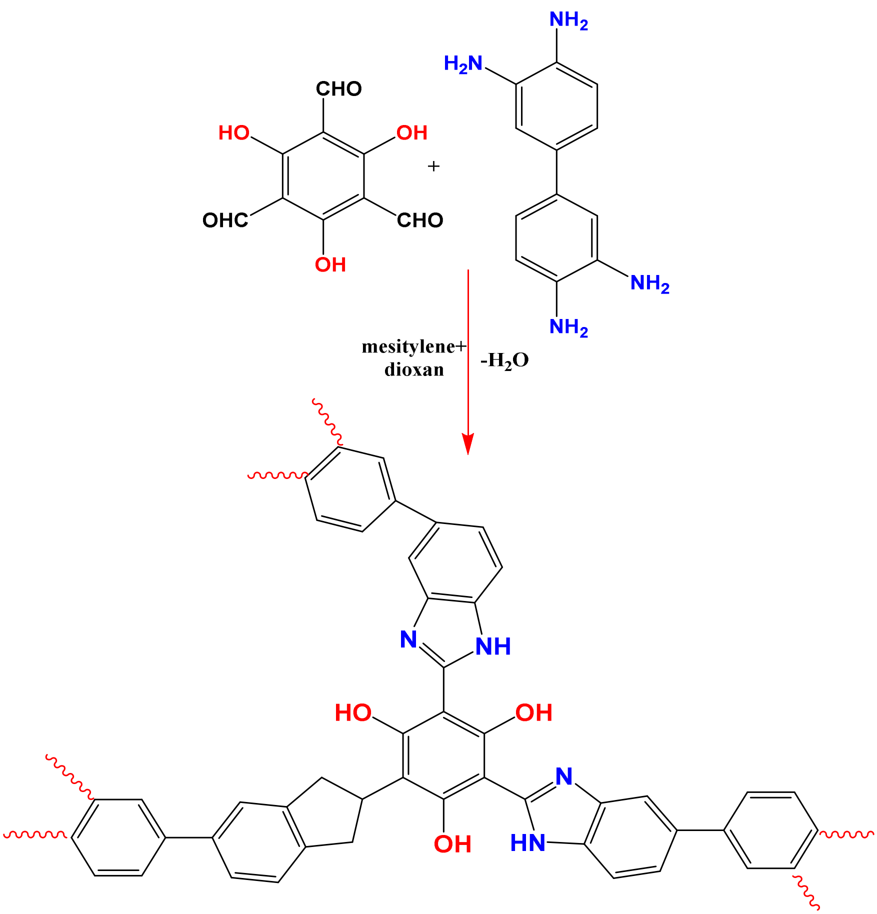
Scheme 2. 2,4,5-triaryl-1H-imidazoles synthesis using ZnO-NAP as a catalysis.

The catalytic activity of NAP-Pt@TiO_2 for the preparation of benzoimidazole derivatives was studied for the mixing of o-phenylene diamine with EtOH under photoirradiation ($\lambda > 300$ nm) in a nitrogen atmosphere [35], (Scheme 3).



Scheme 3. Synthesis of benzimidazoles catalyzed by NAP-Pt@TiO_2.

In Scheme 4, a series of 1,2-benzimidazole derivatives with NAP-ZrO_2-supported with beta-cyclodextrin nanostructures as a catalysis was achieved by a not difficult co-precipitation in one-pot method utilizing ZrOCl2.H2O and ammonium hydroxide. The synthesis of covalent organic frame and its nanocomposite was done via reacting of 1,3,5-triformyl phloroglucinol and 3,3`-diaminobenidine in a mixture of 1,3,5-trimethylbenzene (mesitylene), dioxin and nickel nitride nanoparticles [36].

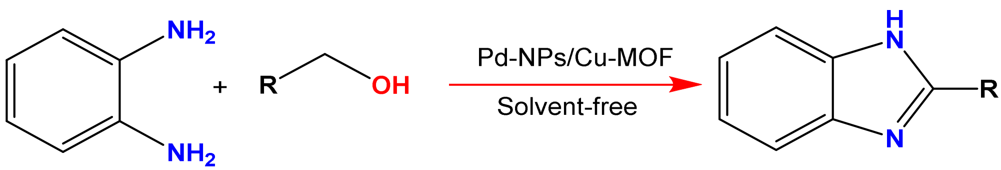


Scheme 4. Synthesis of benzimidazoles catalyzed by NAP-nickel nitride.

Mobinikhaledi *et al.* introduced a new, separable and reusable heterogeneous catalyst, poly(melamine-terephthalate) which contains copper ions (MNPs @Cu-PMT), this catalyst is a porous nanocomposite that exhibits remarkable magnetic properties, which was found to be very stable and have a high activity for the synthesis of benzimidazole [37,38], Scheme 5.

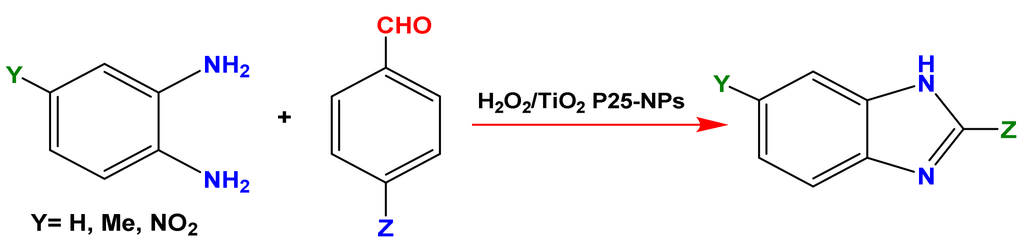
Scheme 5. Benzimidazoles Synthesis using MNPs@Cu-PMTas a catalysis.

Mokhtari and Bozcheloei prepared a new efficient and heterogeneous catalyst, Pd/Cu2(BDC)2(DABCO)-MOF, to produce a wide range of benzimidazoles derivatives by coupling the dehydrogenation of the compound 1,2-phenylenediamine with the alcohol compound (benzyl alcohol). alcohol) with solvent-free natural conditions. This prepared catalyst has a high recyclability (it can be reused four times without loss of efficiency) [39], Scheme 6.



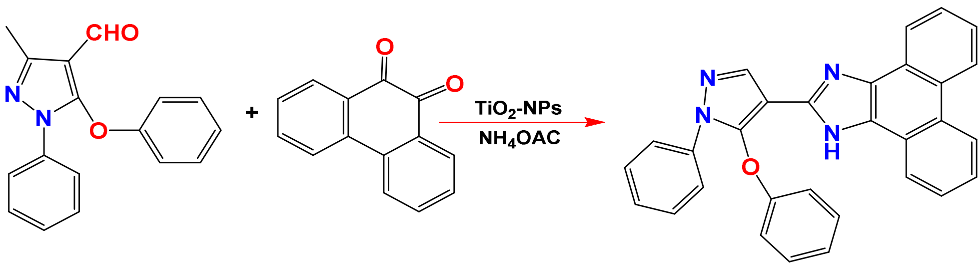
Scheme 6. Synthesis of benzimidazoles catalyzed by $Pd/Cu_2(BDC)_2(DABCO)$-MOF.

Another effective synthetic approach was reported by Kiumars Bahrami et al. When they studied and used the H_2O_2/TiO_2 P25-NPs system to synthesize a large group of benzimidazole derivatives of 1,2-phenylenediamine from the process of aromatic oxidative coupling with different aldehydes group that can carry different types of substitutes [40], Scheme 7.



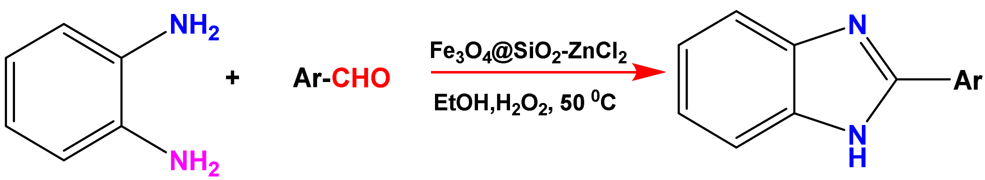
Scheme 7. Synthesis of benzimidazoles catalyzed by H_2O_2/TiO_2 P25-NPs.

It is easy to prepare titanium dioxide nanoparticles easily by the green method using sunflower leaves. These prepared nanoparticles (NPs-TiO_2) are used to synthesize the phenenthro (9,10-d imidazole) derivatives with a good yield through the reaction of phenanthrenequinone with 3-methyl-5-phenoxy-1-phenyl-1H-pyrazole-4-carbaldehyde and NH4OAC [40,41], Scheme 8.



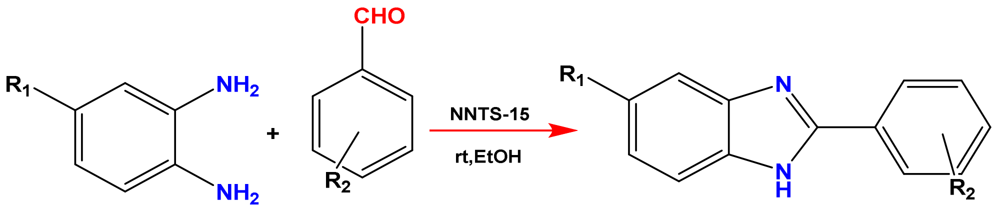
Scheme 8. Synthesis of phenenthro [9,10-dimidazole] derivatives catalyzed by NPs-TiO_2.

Rahimi and Soleimani utilized a magnetic nanocatalyst of $Fe_3O_4@SiO_2$-$ZnCl_2$ in enhances the synthesis of benzimidazole derivatives, Scheme 9. To begin, in the presence of a magnetic nanocatalyst, 2-substituted benzimidazoles were produced in proper to high yields from 1,2 phenylenediamine with a wide variety of aromatic aldehydes [42,43].



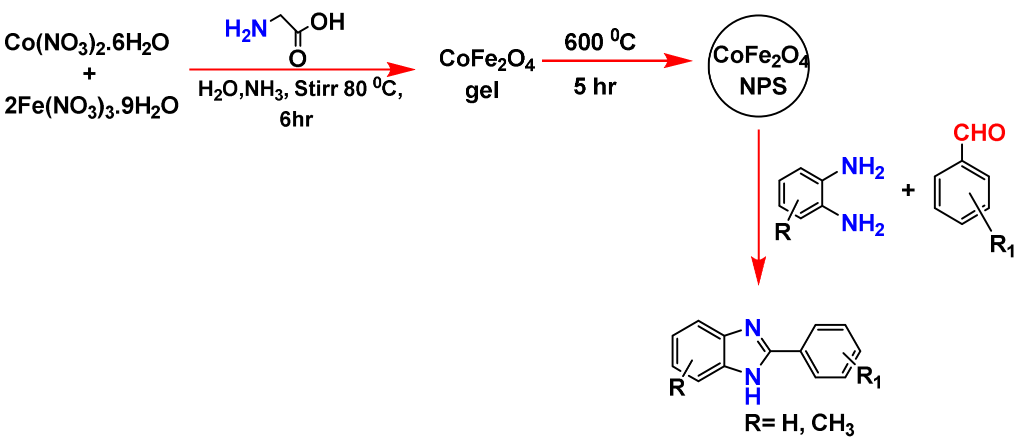
Scheme 9. Synthesis of benzimidazoles catalyzed by $Fe_3O_4@SiO_2$-$ZnCl_2$.

On the other hand, a very efficient and stable decorated nanocomposite was synthesized with SBA-15 [Ni/TCH @SBA-15] by creating modifications on the surface of the silica nanoparticles with 3-chloropropyltriethoxysilane and then followed by a simple modification by coordinating the metal ligand with the nickel ion(II). This new prepared nanocomplex was evaluated for its effectiveness as a catalyst for the production of benzimidazole derivatives, Scheme 10. The main benefits of these used protocols are to shorten the time required to complete the reaction, as well as to give a product with high yield, as well as the simplicity of the techniques used and non-toxicity of the prepared catalyst, and the reaction conditions are simple and easy procedure to complete this work [44].



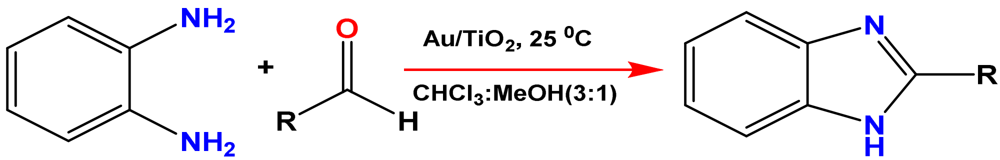
Scheme 10. Synthesis of benzimidazoles catalyzed by Ni/TCH@SBA-15.

Borade *et al.* presented an environmentally friendly method for the synthesis of cobalt ferrite nanocatalyst by spontaneous combustion of the gel, then the researchers worked on developing an efficient and reactive chemical-mechanical protocol for the synthesis of benzimidazole (2-arylbenzimidazole) derivatives using the prepared cobalt ferrite nanoparticles as a heterogeneous type catalyst that is easily magnetically separable, Scheme 11. Also, the method of grinding a mixture of different aldehydes with orthophenylene diamine in an agate motar-pestle with a quantity of CoFe2O4 nanocatalyst to produce benzimidazole derivatives was effective and reliable with good yield [45].



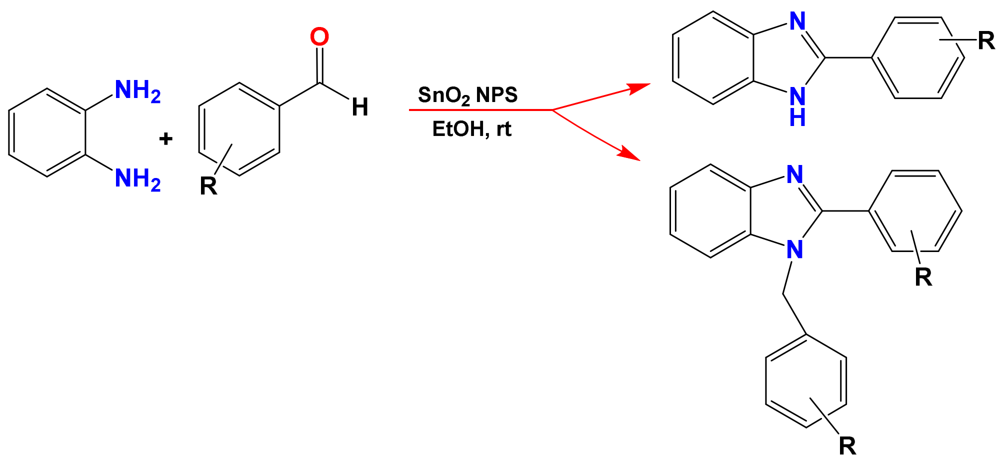
Scheme 11. Synthesis of benzimidazoles catalyzed by $CoFe_2O_4$ gel.

Several methods were utilized to produce benzimidazoles by gold-NPs [46-57]. The efficacy of supported gold NPs (AuNPs) in catalyzing the selective reaction between aldehydes and o-phenylenediamine to form benzimidazole derivatives was examined, as shown in the Scheme 12. The catalytic synthesis methodology is applicable to a wide range of substrates and is an effective method for forming a C-N bond under mild reaction conditions [10].



Scheme 12. Synthesis of benzimidazoles catalyzed by Au NPs.

In Scheme 13, SnO_2 NPs was studied to catalyze efficiently a cyclo-condensation of 1,2-phenylenediamine different aldehydes in EtOH as a solvent at r.t to produce the mono and di-substituted benzimidazole derivatives in excellent yields and short time of the reaction [58].



Scheme 13. Synthesis of benzimidazoles catalyzed by SnO_2 NPs.

3. Conclusion

Benzimidazoles are a type of heterocyclic molecule that is extremely important. This could be because they look a lot like nucleotides that are formed. The importance of elaborate work on the employment of nanotechnology to synthesis benzimidazoles as a drug to anticancer medicines with their different biological characteristics is highlighted in this article. This method entails generating highly active biological molecules that are antifungal and antibacterial agents as well as cancer cells. Several recent approaches of synthesizing benzimidazole derivatives were highlighted. Furthermore, their pharmacological potencies with various derivatives were monitored.

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