

A novel application of $\text{Co}_3\text{O}_4@\text{SiO}_2$ nanocomposite as an efficient and robust catalyst for the preparation of some imidazolone derivatives

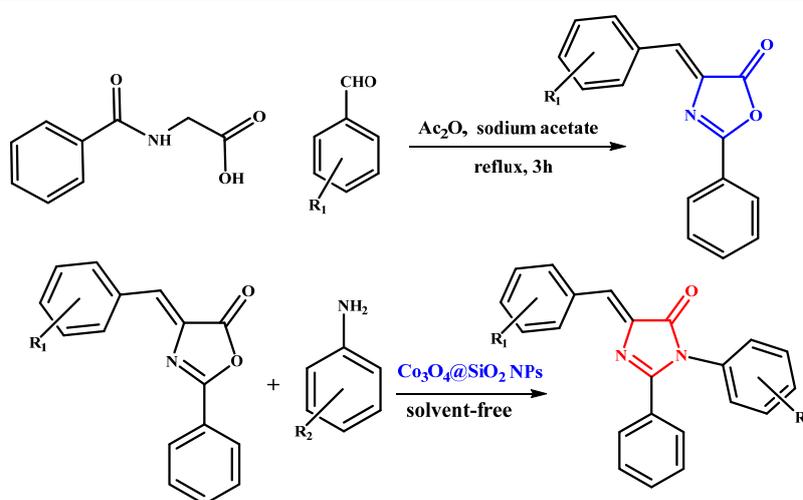
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HIGHLIGHTS

- An efficient synthesis of imidazolone by $\text{Co}_3\text{O}_4@\text{SiO}_2$
- Characterization of the catalyst by FT-IR, FE-SEM, EDX, VSM and XRD analysis
- The main advantages were high yields, short reaction times, and reusability of the catalyst.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present work, a simple, green and efficient procedure for the synthesis of imidazolone derivatives is described via the reaction of oxazolones and different arylamines in the presence of $\text{Co}_3\text{O}_4@\text{SiO}_2$ nanocomposite as a catalyst under solvent-free conditions at 90°C . The catalyst has been fully analyzed by FT-IR, FE-SEM, EDX, and XRD analysis. The present method offers several advantages such as high yields, short reaction times, mild reaction conditions and recoverability of the catalyst. In addition, the obtained heterocyclic compounds were analyzed by FT-IR and ^1H NMR spectroscopy analysis.

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1. Introduction

Imidazolones are one of the most extensively studied classes of heterocyclic compounds and have received much attention from synthetic organic as well as medicinal chemists, because of the diverse range of their biological activities.

Various approaches have been reported for the preparation of imidazolone derivatives which include: three-component reaction of thiohydantoines, arylaldehydes, and halogenoalkanes [1], multi-component condensation of sodium arylsulfonates, trichloroacetonitrile, benzylamines and acetylene dicarboxylates [2], dehydration/base cyclisation of bisamides [3], via the use of azidoacetic acid amides [4], and palladium-mediated arylation of acetone and cyclohexanone-derived 4-chloroimidazolones [5].

The basic imidazolone nucleus, present in oxazolone moiety, is of great importance in generating penicillin type drug intermediates and synthetic hormonal compounds [6]. The oxazolones are starting materials and intermediates for the synthesis of several types of compounds including α -amino acids, peptides, dye, fluorescent protein chromophore and also show a wide range of pharmaceutical properties such as, antimicrobial, anticancer, and antifungal activities [7-11]. The different substituted oxazol-5-one were treated with aryl amines in the presence of glacial acetic acid to get analogs unsaturated imidazol-5-one. Imidazolone derivatives have been reported to exhibit different kinds of antibacterial, antifungal, antimicrobial activities, fungicidal, herbicidal and vasodilator activities [12-16].

Recently, metal oxides nanocomposites have attracted broad consideration in different catalytic procedures due to their unique properties such as mild experimental conditions, easy setup and workup, rapid reaction rates, selectivity and easy removal/recycling. This high reactivity is due to high surface areas combined with unusually reactive morphologies [17].

The cobalt oxide nanoparticle (Co_3O_4 NPs) is a kind of metal oxide nanoparticle which exhibits interesting properties and applications including: oxidation reaction [18], supercapacitor application [19], immunohistochemical Assay [20], catalytic and photocatalytic applications [21-24].

Here, we report a simple and novel procedure for the synthesis of some new imidazolone derivatives in the presence of $\text{Co}_3\text{O}_4@SiO_2$ core-shell nanocomposite as

heterogeneous Lewis acid under solvent-free conditions. This approach offers several advantages such as high yields, short reaction times, mild reaction conditions and recoverability of the catalyst.

2. Experimental

2.1. Materials and techniques

Chemicals were purchased from Sigma-Aldrich and Merck companies in high purity. All of the materials were of commercial reagent grade and were used without further purification. All melting points were determined in a capillary tube on a Boetius melting point microscope. ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker 400 MHz spectrometer with DMSO-d_6 as solvent using TMS as an internal standard. FT-IR spectrum was recorded on a Magna-IR, spectrometer 550. The elemental analyses (C,H,N) were obtained from a Carlo ERBA Model EA 1108 analyzer. Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer of X'pert Company with mono chromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Microscopic morphology of products was visualized by SEM (LEO 1455VP). The mass spectra were recorded on a Joel D-30 instrument at an ionization potential of 70 eV. Magnetic properties were obtained on a BHV-55 vibrating sample magnetometer (VSM) made by MDK-Iran. The compositional analysis was done by energy dispersive analysis of X-ray (EDX, Kevex, Delta Class I).

2.2. Preparation of $\text{Co}_3\text{O}_4@SiO_2$ core-shell nanocomposites (I)

The $\text{Co}_3\text{O}_4@SiO_2$ nanocomposites were prepared in two steps according to the procedures described by Ghasemzadeh *et al.* with some modifications [25].

First step, formation of cobalt (II,III) oxide (Co_3O_4) NPs: A warm (50°C) solution containing cobalt(II)nitrate hexa-hydrate (0.029 mol, 8.60 g) in ethanol (100 mL) was prepared by vigorous stirring and kept for 30 minutes. Then, oxalic acid (0.024 mol, 2.14 g) was added quickly to the solution and stirred at 50°C for 2 hr. The formed precipitates of cobalt (II) oxalate were collected by centrifuge, washed with ethanol, dried at room temperature and finally calcined for 2 hr at 400°C to produce the dark cobalt (II,III) oxide nanoparticles.

Second step, formation of $\text{Co}_3\text{O}_4@\text{SiO}_2$ core-shell nanocomposites: To a mixture containing Co_3O_4 nanoparticles (0.5 g), ethanol (350 mL) and cetyltrimethylammonium bromide (2.2 g), was added dropwise into a concentrated ammonia aqueous solution (40 mL, 28 wt%) under sonication for 20 minutes. Then, tetraethylorthosilicate (0.4 mL) in ethanol (10 mL) was added to the above mixture under ultrasound irradiation and the reaction mixture stirred at room temperature for 20 hr. The Co_3O_4 /porous-silica core-shell nanocomposites were collected by centrifugation and washed three times with deionized water and finally calcined at 600°C for 6 hours.

2.3. Preparation of hippuric acid (2)

The amino acid glycine (5 g) was dissolved in a solution of sodium hydroxide 10 % (50 mL) in a 100 mL two-necked flask equipped with a condenser, addition funnel and a magnetic stirrer. Then, benzoyl chloride (9 mL) was added dropwise to the solution and the reaction mixture heated under reflux with constant stirring at 80°C for about 3 hr. The progress of the reaction was carefully observed by TLC paper. The reaction is complete when all of the benzoyl chloride has disappeared (no oily droplets) and the smell of it is no longer present. After completion, a clear solution was obtained, transferred into a large beaker, cooled (eventually on a crushed ice-water bath) and acidified with concentrated chloride acid gradually and continuously stirred (checked with pH paper). The resulting precipitate was filtered by gentle suction, washed with a large amount of cold water and recrystallized from hot ethanol to afford the pure product.

2.4. General procedure for the synthesis of 5-oxazolone derivatives (3a-b)

A round-bottom flask (25 mL) containing hippuric acid (1mmol), appropriate arylaldehydes (1mmol), acetic anhydride (3 mmol), and anhydrous sodium acetate (1 mmol) was refluxed at 110°C for about 3-4 hr. After completion of the reaction, indicated by TLC, the mixture was cooled and ethanol (5 mL) was added to the mixture. A yellow solid was separated by filtration, washed first with ice-cold ethanol and finally with boiling water. After drying, the solid was recrystallized from ethanol to afford the pure product.

2.5. General procedure for the synthesis of 4-imidazolone derivatives (4a-d)

In a flask (25 mL), the mixture of arylamine (1 mmol), substituted oxazolone derivatives (1 mmol) and $\text{Co}_3\text{O}_4@\text{SiO}_2$ nanocomposite (3 mg) were heated with stirring under solvent-free conditions at 90°C for 1-2 hr. When the TLC analysis showed the completion of the reaction, the resultant mixture was cooled and poured into ice cold water. Afterwards the catalyst was separated by an external magnet. The precipitate was filtered and washed with cold water. The product was further purified by crystallization from hot ethanol. The filtered catalyst was repeatedly washed with dichloromethane, used for reusability tests and kept for more reactions. Spectral data of the new products are available in Supporting Information (Fig. S6-S13).

2.6. Catalyst recovery

Upon completion of the reaction the catalyst was separated by an external magnet, washed with dichloromethane, and finally the recycled catalyst was saved for more reaction. We observed that the $\text{Co}_3\text{O}_4@\text{SiO}_2$ nanocomposite catalyst can be easily recovered from the reaction systems and efficiently reused for up to six successive runs without loss of significantly catalytic activity, as shown in Fig. 1.

3. Results and discussion

3.1. Preparation of imidazolone derivatives

The synthetic approaches of the prepared compounds are shown in Schemes 1-3. The acylation of glycine in an

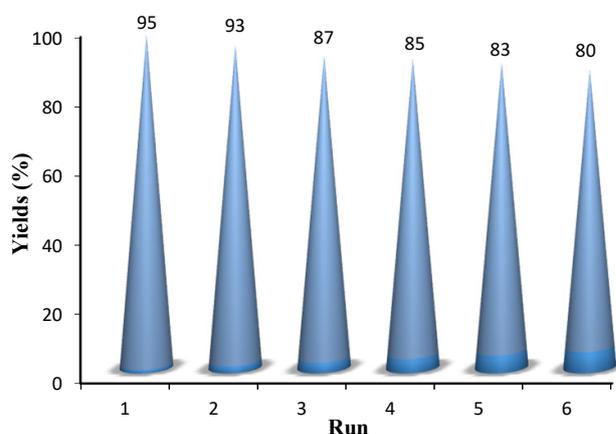


Fig. 1. Reusability of the $\text{Co}_3\text{O}_4@\text{SiO}_2$ NPs.

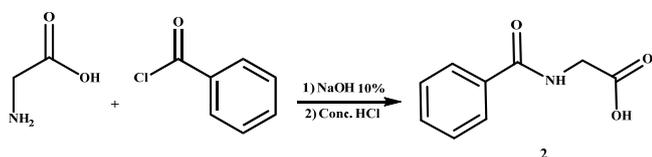
aqueous basic solution led to formation of amide bond from benzoyl chloride and finally afforded hippuric acid (2) (Scheme 1). Preparation of oxazolones (3) via condensation between arylaldehydes and hippuric acid (2) in the presence of acetic anhydride catalyzed by anhydrous sodium acetate (Scheme 2).

The oxazolone derivatives were reacted with arylanilines in the presence of $\text{Co}_3\text{O}_4@\text{SiO}_2$ nanocomposite to produce imidazolones (4) under solvent-free conditions (Scheme 3).

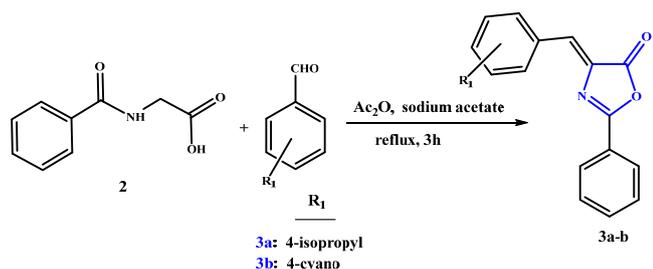
3.2. Optimization of the reaction conditions

In order to obtain the best reaction conditions for the synthesis of imidazolone derivatives, we examined different reaction conditions including: reaction temperature, time, amount of the catalyst and the effect of various nano-catalysts in the absence or presence of solvents. In this research, the reaction of p-tolylaniline and oxazolone (3b) was selected as a model study in order to synthesis imidazolone (4b) (Scheme 3). Comparison of the optimization of the model reaction by various catalysts, solvents and temperatures are shown in Table 1.

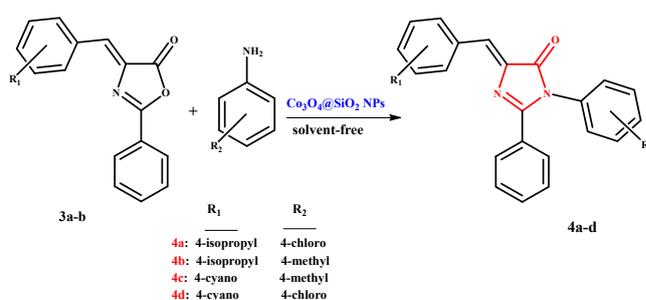
According to Table 1, no product was isolated from the model reaction in the presence of the catalyst at room temperature or without any catalyst at 90°C (Entries 1 and 2). Therefore, the catalyst and heating play crucial roles in the success of the reaction and product yield. The oxazolone (3a) as model substrate reacted with 4-methyl-aniline in the presence of different amounts of $\text{Co}_3\text{O}_4@\text{SiO}_2$ NPs catalyst from 3 to 20 mg (See Table 1, Entries 3-8). Also, the results of Table 1 show that the



Scheme 1. Acylation of glycine.



Scheme 2. Preparation of oxazolones.



Scheme 3. Preparation of imidazolones under solvent-free conditions.

optimum amount of the catalyst was 3 mg of $\text{Co}_3\text{O}_4@\text{SiO}_2$ NPs and amounts higher than 15 mg did not react favorably and led to change yield and time reaction. In addition, we examined the effect of solvents in the model reaction using $\text{Co}_3\text{O}_4@\text{SiO}_2$ NPs (See Table 1, Entries 9-12). The summarized results in Table 1 show that the best yield was obtained when the reaction was carried out at 90°C catalyzed by $\text{Co}_3\text{O}_4@\text{SiO}_2$ NPs under solvent-free conditions. In order to show the merit of the present research, we have investigated the activity of the different nanocatalysts such as Co_3O_4 , Fe_3O_4 , ZnO , MgO , TiO_2 and CuI under solvent-free conditions. As a result, the most effective nano-catalyst was $\text{Co}_3\text{O}_4@\text{SiO}_2$ in comparison to the other nano-catalysts (See Table 1, Entries 13-18).

In this research, practical applications for $\text{Co}_3\text{O}_4@\text{SiO}_2$ nanocomposite as catalyst in the preparation of imidazolone derivatives were observed because of significant results such as high catalytic activity, simple work-up, easy recovery and reusability. Heterogeneous nanocatalysts have performed better in comparison with other commercially available catalysts [26]. The improvement in reaction rate, excellent yield, high catalytic activity, easier work-up and milder reaction conditions are the some advantages of $\text{Co}_3\text{O}_4@\text{SiO}_2$ NPs as a nanocatalyst.

Next, the generality of our research was investigated when we applied different types of aromatic anilines, including those bearing electron-withdrawing groups (such as chloro), and electron-donating groups (such as methyl). The reactions gave the corresponding products good to excellent yields (Table 2).

According to Table 2, the arylanilines with electron-donating groups, such as methyl, in 4-position reacted with oxazolone derivatives (3a-b) very smoothly, while the reactants with electron-withdrawing groups, such as chloro in 4-position, proceeded with a shorter reaction time and the higher product yields.

Table 1. Comparison of the optimized reaction conditions by catalyst, solvent, and temperature^a.

Entry	Catalyst	Amount of catalyst (mg)	Solvent	Temperature (°C)	Time (min)	Yield ^b (%)
1	None	0	Solvent-free	90	420	-
2	Co ₃ O ₄ @SiO ₂ NPs	30	Solvent-free	r.t	420	-
3	Co ₃ O ₄ @SiO ₂ NPs	30	Solvent-free	90	120	89
4	Co ₃ O ₄ @SiO ₂ NPs	15	Solvent-free	90	90	95
5	Co ₃ O ₄ @SiO ₂ NPs	10	Solvent-free	90	90	95
6	Co ₃ O ₄ @SiO ₂ NPs	5	Solvent-free	90	90	95
7	Co ₃ O ₄ @SiO ₂ NPs	3	Solvent-free	90	90	95
8	Co ₃ O ₄ @SiO ₂ NPs	1	Solvent-free	90	140	82
9	Co ₃ O ₄ @SiO ₂ NPs	3	EtOH	reflux	240	60
10	Co ₃ O ₄ @SiO ₂ NPs	3	CH ₂ Cl ₂	reflux	720	45
11	Co ₃ O ₄ @SiO ₂ NPs	3	C ₃ H ₅ N	reflux	180	88
12	Co ₃ O ₄ @SiO ₂ NPs	3	DMF	reflux	240	65
13	Co ₃ O ₄ NPs	3	Solvent-free	90	150	75
14	Fe ₃ O ₄ NPs	3	Solvent-free	90	180	45
15	ZnO NPs	3	Solvent-free	90	160	85
16	MgO NPs	3	Solvent-free	90	360	67
17	TiO ₂ NPs	3	Solvent-free	90	150	88
18	CuI NPs	3	Solvent-free	90	240	55

^a Reaction conditions: 4-(4-isopropylbenzylidene)-2-phenyl-oxazol-5(4H)-one (3a) and 4-methyl-aniline (1:1 mmol). ^b Yields refer to pure isolated products.

Table 2. Synthesis of imidazolone derivatives (4a-d) catalyzed by Co₃O₄@SiO₂ NPs.

Product	Oxazolone derivative	Arylanilines	Molecular formula	MW (g/mol)	Mp (°C)	Time (min)	Yield (%)
4a	3a	4-Chloro	C ₂₅ H ₂₁ ClN ₂ O	400.91	209	115	91
4b	3a	4-Methyl	C ₂₆ H ₂₄ N ₂ O	380.49	211	90	95
4c	3b	4-Methyl	C ₂₄ H ₁₇ N ₃ O	363.24	157	110	93
4d	3b	4-Chloro	C ₂₃ H ₁₄ ClN ₃ O	383.08	241	120	90

3.3. General reaction mechanism for the synthesis of imidazolone derivatives by Co₃O₄@SiO₂ NPs

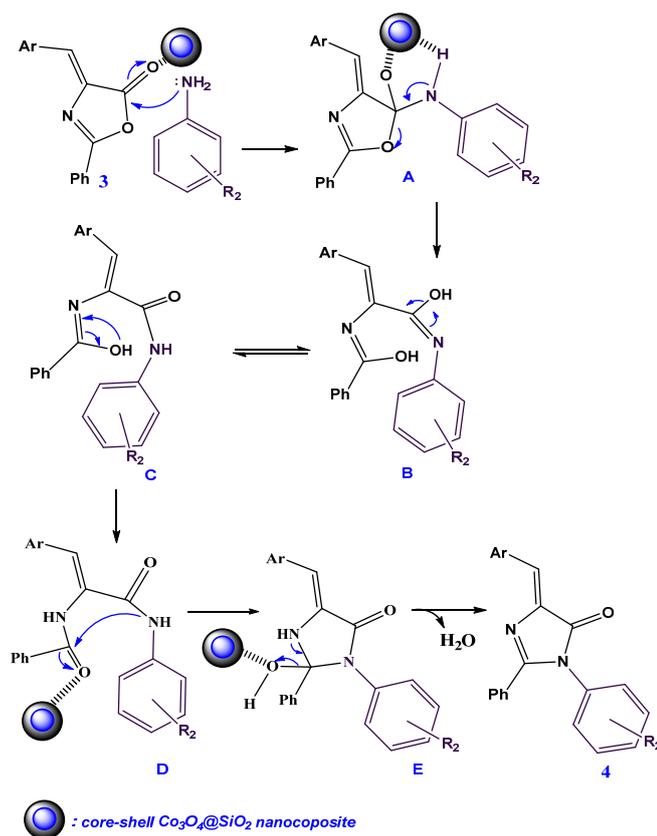
The reaction mechanism of the synthesized imidazolone derivatives using Co₃O₄@SiO₂ nanocomposites is shown in Scheme 4. Co₃O₄ is a member of the spinel group which has the standard formula A(B)₂O₄. In the case of magnetite, Co₃O₄, the A metal is Co₂ and the B metal is Co⁺³; two different metal ions in two specific sites. This arrangement causes a transfer of electrons between the different irons in a structured path or vector. This electric vector generates a magnetic field. In addition, Co⁺² and Co⁺³ have unoccupied d orbitals and cause the Lewis acid properties of Co₃O₄ [27, 28]. Therefore, Co₃O₄@SiO₂ accepts electron pairs to enhance the electrophilicity properties of the carbonyl

groups containing of oxazolone (3) and intermediates and ultimately lead to a decrease in reaction times. Firstly, the nucleophilic attack from thenitrogen site of arylamine to the carbonyl group of oxazolone leads to the formation of intermediate A, and then intermediate B was afforded with a ring opening of oxazolone.

Afterwards, a tautomization occurs between intermediates B and C in order to form intermediate D, followed by the intramolecular cyclization to obtain intermediate E catalyzed by the Co₃O₄@SiO₂ core-shell nanocomposites. Finally, the dehydration of intermediate E leads to formation of the final product 4.

4. Conclusions

In summary, a novel and efficient method has been reported for the synthesis of imidazolones which are as



Scheme 4. Mechanism of the synthesis of imidazolone derivatives using $\text{Co}_3\text{O}_4@\text{SiO}_2$ nanocomposite.

nucleus in the synthesis of several biologically important organic molecules. In this procedure the silica-coated cobalt oxide nanoparticles has been successfully applied as a catalyst for the reaction of oxazolones and various arylamine derivatives under solvent-free conditions. The present method offers several advantages such as high yields, short reaction times, mild reaction conditions and recoverability of the catalyst.

Associated Content

Additional results on characterization and catalytic performance tests of $\text{Co}_3\text{O}_4@\text{SiO}_2$ nanocomposite and also FT-IR and ^1H NMR spectra of the new compounds are provided here (See the Supporting Information for a detailed description).

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