

Recent Progress in Fe₃O₄ Nanoparticles and Their Green Applications in Organic Transformations

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Received 14 July 2023; received in revised form 15 September 2023; accepted 26 September 2023 (DOI: 10.30495/IJC.2023.1991397.2024)

ABSTRACT

It's fascinating to see how much research has been done on ferrite nanoparticles over the past few years. These small magnetic particles have unique properties that allow them to be manipulated at a very small scale. This review article is focused on the preparation of ferrite magnetic nanoparticles and silica-coated ferrite nanoparticles using various functionalized compounds. Recently, it has been found that these nanoparticles can be used as nanocatalysts in a variety of reactions, including coupling and multicomponent reactions. They provide excellent and environmentally friendly yields, which is a great benefit. It's exciting to see how these tiny particles can have such a big impact on the world of science.

Keywords: Biodegradable, Iron oxide, Recyclability, Synthetic methods, Synthesis

1. Introduction

In modern material science, nanocatalysts play a crucial role in organic reactions by providing a sustainable route that connects the environment's vitality and reaction [1-3]. The use of green catalysis is becoming increasingly important for achieving commercial targets and supporting the global economy [4-7]. The scientists aim to create sustainable and environmentally friendly reactions that don't require solvents [8-11]. Toxic solvents and catalysts harm the environment in organic transformations. Green and sustainable alternatives are used to reduce pollution [12-14]. The goal is to convert reactants to products with less waste, energy, and safer chemicals [15, 72, 74, 76]. Based on the principles of green chemistry, the catalyst used is less toxic, inexpensive, easily prepared, recyclable, and can be easily separated from the reaction [16-19].

Iron oxide (Fe₃O₄) nanoparticles are highly regarded for their unique features that make them beneficial in a range of sectors, including magnetic data storage, pigment manufacturing, separation technologies, and MRI [83]. The materials with soft magnetic properties

can be magnetized and demagnetized easily, and have a coercive field strength of 40 A/m. These materials possess distinct qualities that render them valuable in various devices such as generators, transformers, motors, and others. Iron oxide nanoparticles have been extensively researched and synthesized through sol-gel, co-precipitation, micro-emulsion, and hydrothermal methods. Magnetic nanoparticles find applications in electronics, biotechnology, biomedicine, metal ion extraction, optical imaging, catalysts, and magneto-resistance [77-82].

The interest of researchers in synthesizing and developing nanomaterials has increased due to current research on magnetic nanoparticles. Organic reactions using these catalysts are less toxic, do not require solvents or aqueous conditions, and are environmentally friendly. Additionally, the nanocatalyst yields excellent results and is recyclable [20-25]. Various synthetic methods were utilized to successfully prepare the nanoparticles, with the assistance of diverse metals, metal oxides, and acid-functionalized compounds [71, 73]. The nanoparticle catalysts supported by metal

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various plant extracts' effect on insect pests, and chemical analysis of protein, lipids, carbohydrates, and fat from certain animals.

oxides, including ruthenium, cobalt, and nickel, are successfully prepared and characterized using various techniques [26-29]. Nanoparticles have several advantages including easy preparation, lower toxicity levels, and the ability to be recycled [30]. The ferrite nanoparticles are easily synthesized using the Co-precipitation method. Fe (II) and Fe (III) ions are dissolved in water in the presence of alkaline bases to obtain ferrite nanoparticles [31]. We can make a positive impact on the environment by exploring eco-friendly options for chemical reactions. [84, 85] By utilizing catalysts, reagents, and synthetic methods that are safer for the planet, we can help reduce the number of toxic substances released into the environment. Let's work towards a healthier and cleaner world [32-34].

Ferrite nanoparticles used for C-C bond formation or coupling reaction

The latest research on C-C bond formation or coupling reaction is an important part of organic synthesis [35-38]. The coupling reaction was first reported by Suzuki scientists in 1979. He developed an organometallic Pd (0) complex in the presence of catecholborane helpful for the preparation of an arylation reaction. The synthesis of different drugs, molecules, and intermediates in the medical field is under the Suzuki coupling reaction [39-42]. Ali Reza Sardarian, Habib Firouzabadi, and Mohsen Esmaeilpour [43] reported the synthesis of magnetite nanoparticles (Fe_3O_4) with previous literature. The nanoparticles were easily prepared from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (4.8 mmol), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (4.5 mmol), and polyvinyl alcohol (1 g) in surfactant mixture was dissolved in 30 mL of water with vigorous stirring at 80°C for 30 min. Then, dropwise hexamethylenetetramine (HMTA) (1.0 mol/L) with constant stirring within 15 min to maintain a pH is 10, and the mixture was stirred for about 2 h at 60°C to obtain. Finally, Fe_3O_4 was collected using an external magnet, washed with water and ethanol many times, and dried well at 80°C for 10 h.

In the Second Step, the silica-coated ($\text{Fe}_3\text{O}_4 @ \text{SiO}_2$) nanoparticle is prepared in the presence of tetraethyl orthosilicate (TEOS) coating on the Fe_3O_4 nanoparticles by using the Stober method. The synthesized above Fe_3O_4 nanoparticles (0.5 g) dispersed in 50 mL ethanol 5 mL de-ionized water and (0.2 mL) tetraethyl orthosilicate (TEOS) with the stirring at room temperature then the sodium hydroxide solution (10 wt. %) (5 mL) dropwise to maintain the pH and solution was stirring about 30 min at room temperature. Finally, the nanoparticles using a magnet with ethanol, and then dried at 80°C under a vacuum. Briefly, the author synthesis $\text{Fe}_3\text{O}_4 @ \text{SiO}_2 @ \text{NH}_2$ NPs using the mixture of (3-aminopropyl) triethoxysilane (1 mmol) dissolved in ethanol (10 mL) then added $\text{Fe}_3\text{O}_4 @ \text{SiO}_2$ nanoparticle (1.0 g), and the mixture was heated at 90°C for 12 h. Alter the $\text{Fe}_3\text{O}_4 @ \text{SiO}_2$ nanoparticle ($\text{Fe}_3\text{O}_4 @ \text{SiO}_2 @ \text{NH}_2$) was collected by magnetic decantation process washed with aqueous ethanol several times and dried in a vacuum at 80°C for 6 h. In the next step, $\text{Fe}_3\text{O}_4 @ \text{SiO}_2 @ \text{NH}_2$ (1.0 g) was dispersed in the prepared solution of cyanuric chloride (1.0 mmol) and di-isopropyl ethylamine (DIPEA) (1 mmol) in THF solvent (10 mL). The solution was stirred at room temperature for 16 h. The resultant nanoparticle $\text{Fe}_3\text{O}_4 @ \text{SiO}_2 @ \text{TCT}$ was collected using a magnet and washed with ethanol to dry it well. The mixture of bis (3-aminopropyl) amine (2 mmol) and DIPEA (2 mmol) dissolved in solvent DMF (5 mL) and $\text{Fe}_3\text{O}_4 @ \text{SiO}_2 @ \text{TCT}$ (1.0 g) was dispersed, the mixture was reflux at 80°C for 12 h. The nanoparticle

($\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TCT}@\text{NH}_2$) was separated using an external magnet and washed with ethanol for a long time, then dried at 70°C for 4 h. A solution of theophylline (1 mmol), 1, 3-dibromopropane (2 mmol), and K_2CO_3 (2 mmol), dissolved in DMF (5 mL) with stirring at room temperature for 24 h. Then water (20 mL) to obtain the product it was filtrated. Then, the product of N-(3-bromopropyl)-theophylline (1.0 mmol), and ethyl iodide (1.5 mmol) in CH_3CN (5.0 mL) reflux with vigorous stirring for 5 h in an oil bath. The reaction progress was analyzed by TLC. After completion of the reaction, the solution was extracted with ethyl acetate to obtain the product. Finally prepared $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{NHC}@\text{Pd}$ (II) MNPs using (1 g) of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TCT}@\text{NH}_2$ nanoparticles were dispersed in solvent DMF (5 mL). Then, a mixture of theophylline derivative (3 mmol) and DIPEA (3 mmol) was added to the above mixture was refluxed at 80°C for 12 h. The theophylline $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs ($\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Theophylline}$) was then collected by using an external magnet and then dried at 60°C for 3 h. Last step, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{NHC}@\text{Pd}$ (II) MNPs were prepared by using (1 g) of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Theophylline}$ MNPs were added in (10 mL) of THF using ultrasound irradiation, and then (0.18 g) of palladium acetate (0.8 mmol) to above mixture and mixture again stirred at 50°C for 8h. The catalyst was collected by an external magnet washed with ethanol, and then dried under vacuum at 60°C for 5 h. (**Scheme 1**)

The synthesized catalyst is used in the coupling reaction Suzuki as well as Sonogashira coupling reaction. The reaction between $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{NHC}@\text{Pd}$ (II) (0.37 mol %), phenylboronic acid (1.1 mmol), aryl halide (1.0 mmol), and mild base K_2CO_3 (2 mmol) in H_2O (3 mL) was stirred at 60°C for the specific time. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was collected by an external magnetic and washed with de-ionized water (5 mL) and ethyl acetate (10 mL). The ethyl acetate layer was separated and evaporated to obtain crude. The obtained crude was purified by using column chromatography using n-hexane and ethyl acetate as eluent (**Scheme 2**).

In the Sonogashira coupling reaction, the mixture of aryl halide (1 mmol), alkyne (1.1 mmol), Piperidine (2 mmol) and the $\text{Fe}_3\text{O}_4@\text{SiO}_2-\text{NHC}-\text{Pd}$ (II) catalyst (0.43 mol %) was vigorous stirring at 90°C , monitored reaction by TLC. After completion of the reaction, the reaction mixture was extracted with ethyl acetate (10 mL), and the catalyst was collected with an external magnet. The ethyl acetate layer was evaporated under vacuum and the product was purified by column (**Scheme 3**).

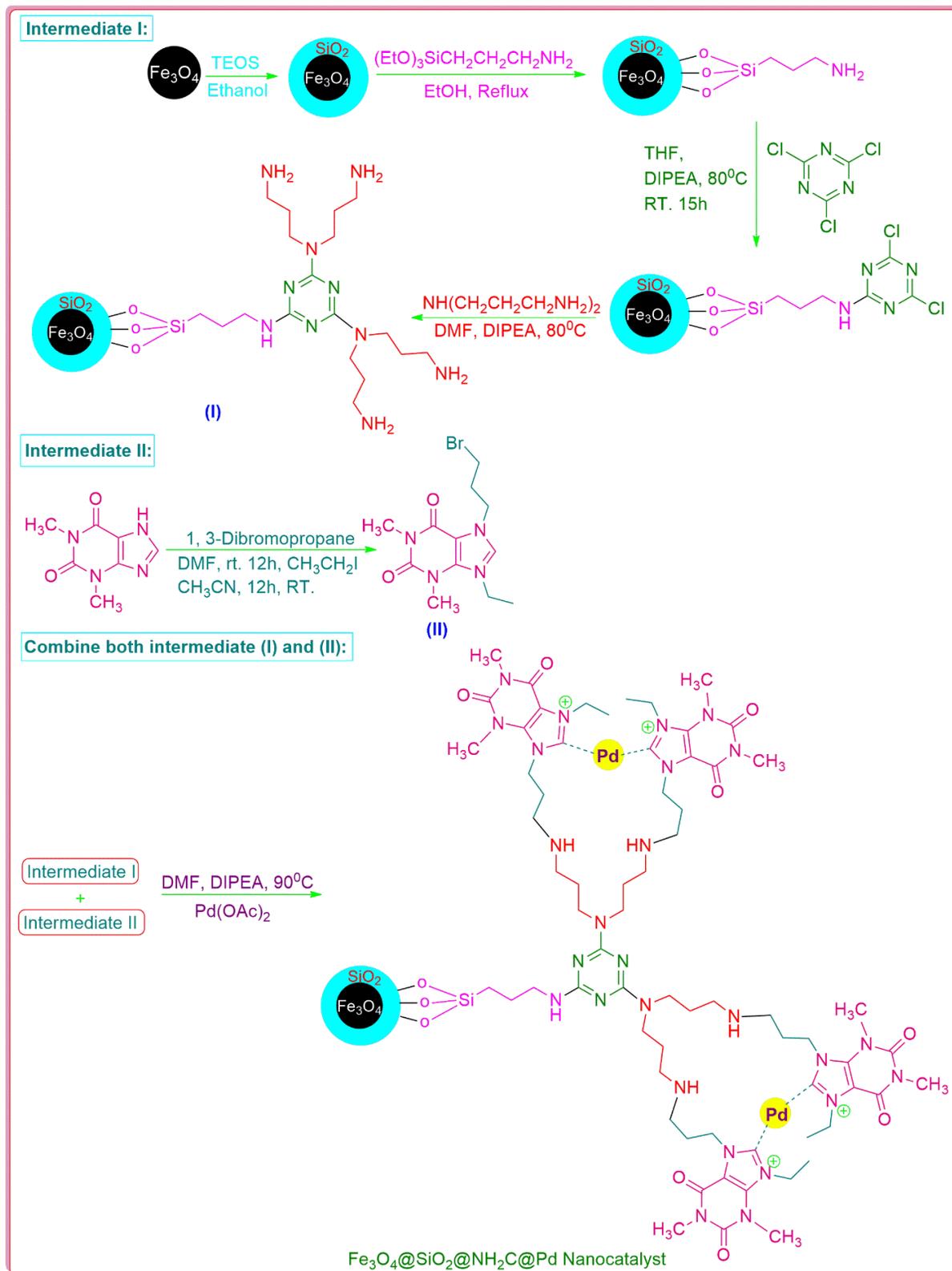
Ali Maleki et al. [44] are reported to have developed the palladium-decorated ortho phenylenediamine functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ MNPs used in the Suzuki-Miyaura coupling reaction. This method uses a simple convenient route for the synthesis of nanocatalysts and applicable in Suzuki-Miyaura coupling reactions with different aromatic halides with phenylboronic acids are synthesis. Applications of this method have an excellent yield of about 98% and have been obtained within 10 min. $\text{Fe}_3\text{O}_4/\text{SiO}_2$ MNPs (0.4 g) were well added in tetrahydrofuran (8.0 mL) with sonicated by ultra-sonication for 10 min. Then NaH (0.2 g, 8.33 mmol) was in the solution, then CPTES (3.0 mL) was added drop by drop at room temperature, and the mixture was stirred for 12 h at 60°C . Collected the nanoparticle with an external magnet, washed it with ethanol, deionized water much time, with dried at 60°C , we got the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{CPTES}$ MNPs. In the second step (0.3 g) $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{CPTES}$ MNPs were dispersed in ethanol (10 mL) with ultra-sonication for 10 min. Then ortho phenylene diamine (o-PDA) (0.03 g, 0.277 mmol) in the mixture was vigorously stirred for 1 h at room temperature. Then this solution was stirred continuously under reflux conditions for 12 h. To prepare $\text{Fe}_3\text{O}_4/\text{o-PDA}$ MNPs it was again collected magnetically, washed with ethanol and deionized water, and then dried under a vacuum oven for 24 h. Finally, $\text{Fe}_3\text{O}_4/\text{o-PDA}$ MNPs (0.2 g) were well dispersed in pure acetone (20 mL) and palladium acetate (0.23 g, 1.28 mmol) by stirring for 12 h at room temperature. The $\text{Fe}_3\text{O}_4/\text{o-PDA}$ MNPs magnetic nanocatalyst was then magnetically separated from the reaction mixture, washed with acetone and deionized water for much time, and dried under vacuum at 50°C (**Scheme 4**).

The reaction between aryl halides (1 mmol), phenylboronic acid (1.2 mmol), NaBH_4 (0.1 mmol), with mild basic condition K_2CO_3 (1.5 mmol), and triphenylphosphine (0.1 mmol) the mixture was stirring for 10 min at room temperature. After completion of the reaction, the magnetic nanocatalyst was separated by using an external magnet, washed with ethanol-water many times, and again reused in the next reaction. This catalyst was recycled a minimum of ten times without any significant loss of catalytic properties (**Scheme 5**).

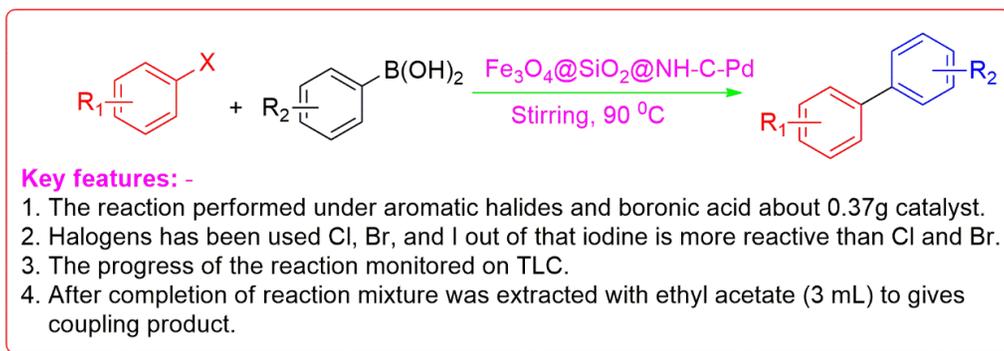
Dariush Khalili et al. [45] reported that the synthesis of heterocyclic catalyst CuFe_2O_4 supporting mesoporous graphite carbon nitride was developed and characterized by analytic technique. This catalyst used in the Ullmann reaction is used for O-arylation. Mesoporous graphitic carbon nitride (mpg- C_3N_4) was synthesis using Melamine (0.5 g) and cyanuric acid (0.51 g) was dissolved in solvent DMSO (10 mL) with sonication for

5 min at room temperature to obtain a white solid precipitate. Then, it was separated from the solution by simple filtration and washed with ethanol many times.

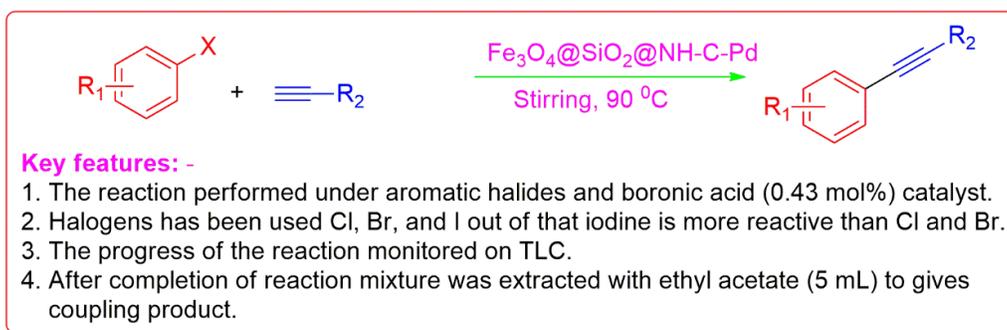
The resulting powder was dried at 60 °C and washed with water then it powder was calcined for 5h at 500 °C under a nitrogen atmosphere (**Scheme 6**).



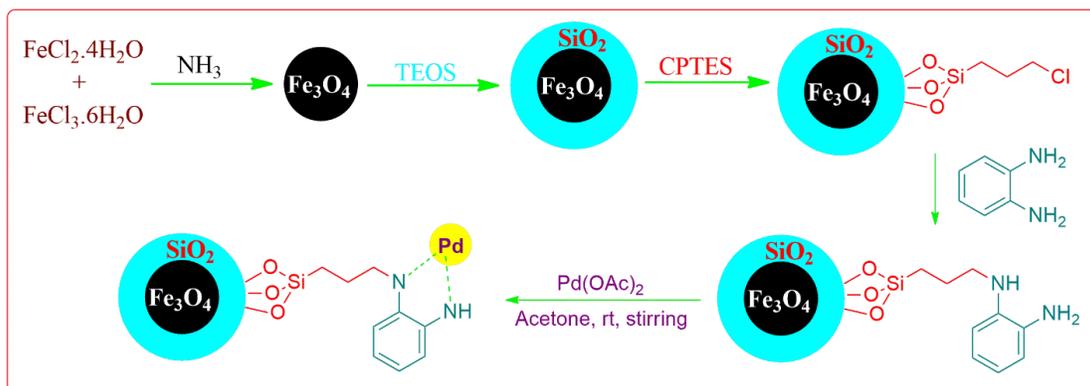
Scheme 1. Synthetic process of *N*-Heterocyclic carbene-Pd (II) complex based on theophylline Supported on Fe₃O₄@SiO₂ NPs (Fe₃O₄@SiO₂@NH₂C@Pd (II) MNPs)



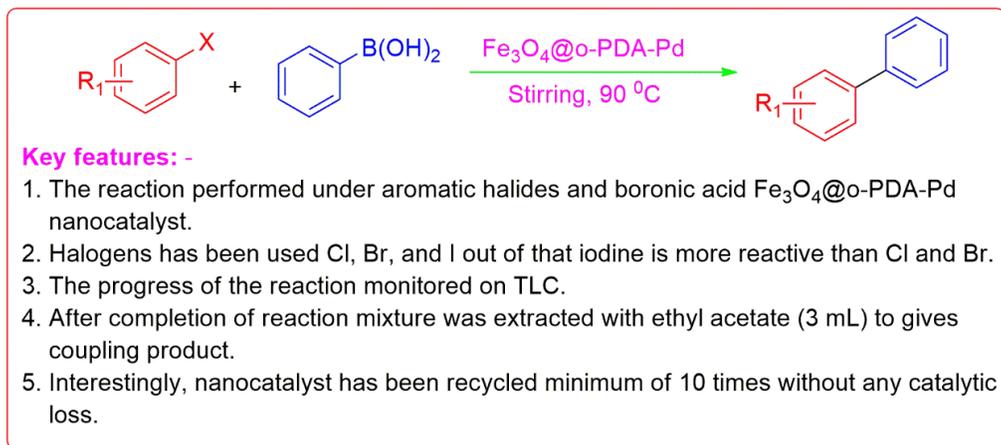
Scheme 2. Suzuki coupling reaction catalyzed under $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NHC-Pd (II)}$



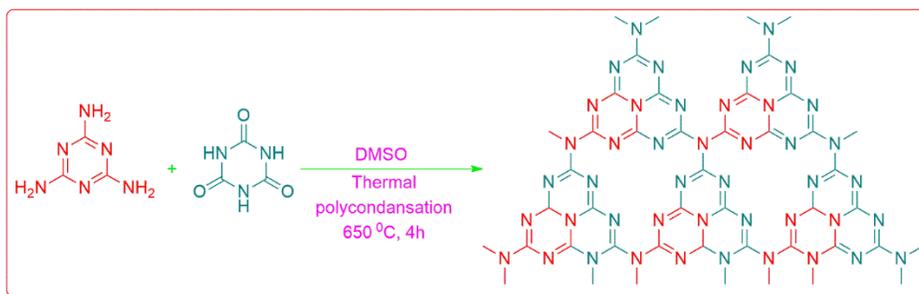
Scheme 3. Sonogashira coupling reaction catalyzed under $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NHC-Pd (II)}$



Scheme 4. Preparation route of $\text{Fe}_3\text{O}_4/\text{o-PDA-Pd}$ nanocatalyst



Scheme 5. $\text{Fe}_3\text{O}_4/\text{o-PDA-Pd}$ catalyst by Suzuki Coupling reaction

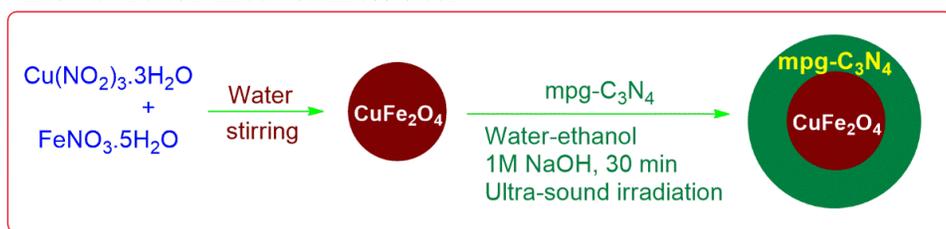


Scheme 6. Schematic representation of synthesis of mpg-C₃N₄

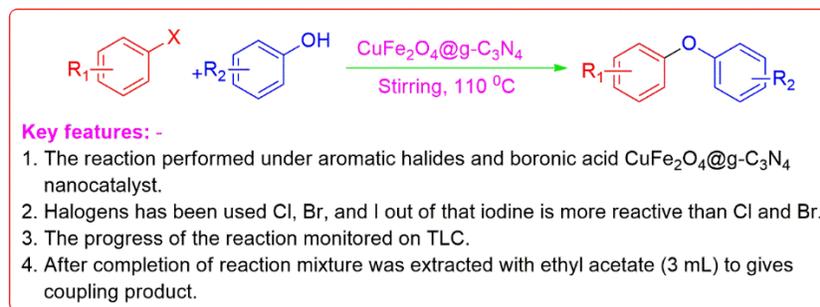
In the second step, CuFe₂O₄ NPs were synthesized by the simple co-precipitation method. The solution of Cu (NO₃)₂·3H₂O (0.5 g), and Fe (NO₃)₃·9H₂O (1.67 g) dissolved in 35 mL of distilled water, then added NaOH 4M (10 mL) at room temperature with stirring for 15 min. The solution became turn reddish-black precipitate. The resulting mixture was refluxed to 90 °C in an oil bath with stirring about 2 h.

After completion of the reaction mixture was cooled at room temperature, and the obtained magnetic nanoparticles were separated by an external magnet, washed with water and ethanol, and dried at 80 °C overnight. Finally, the magnetic catalyst was dry and heated in a furnace at 700 °C. The preparation of CuFe₂O₄/g-C₃N₄ nanocatalyst, using the 0.5 g of mpg-C₃N₄ was dissolved in water-ethanol (1:1) solution with ultra-sonication. Then prepare a solution 1 Equiv. of Cu (NO₃)₂·3H₂O and 2 Equiv. of Fe (NO₃)₃·9H₂O were dissolved in distilled water and added into the above solution dropwise. Then 1M NaOH (20 mL) solution to maintain the pH and the reaction mixture was continuously stirred for 30 min. Finally, the solution was transferred into a Teflon-lined stainless-steel

autoclave and again reacted at 140 °C for 12 h. After completion of the reaction mixture was cooled at room temperature to obtain a black precipitate. The nanoparticle was collected by using a magnet, it will be washed with deionized water and then dried overnight in an oven at 60 °C (**Scheme 7**). Synthesized nanocatalyst is used in the Ullmann reaction, in this reaction a mixture of aromatic halides (1.0 mmol), aromatic phenols (1.0 mmol), Nanocatalyst CuFe₂O₄/g-C₃N₄ (15 mg), K₂CO₃ (2.0 mmol) and dissolved in DMF (5 mL) at 110 °C reflux condition under vigorous stirring for 5 h. Monitored the reaction using TLC by ethyl acetate and n-hexane. After completion, the reaction mixture was cooled to room temperature, and the nanocatalyst was separated by an external magnet from the reaction mixture. The catalyst was recycled then washed with acetone, dried at 70 °C for 4 h, and then catalyst directly used for the next reaction without any purification. The organic layer is extracted with ethyl acetate. The organic layer evaporated under reduced pressure to give a pure o-arylated coupling product, the compound was purified by column chromatography with n-hexane/diethyl ether (**Scheme 8**).



Scheme 7. Synthesis of CuFe₂O₄/g-C₃N₄ mesoporous nanocatalyst



Scheme 8. Ullmann cross-coupling reaction of aryl-halide with phenols under nanocatalyst

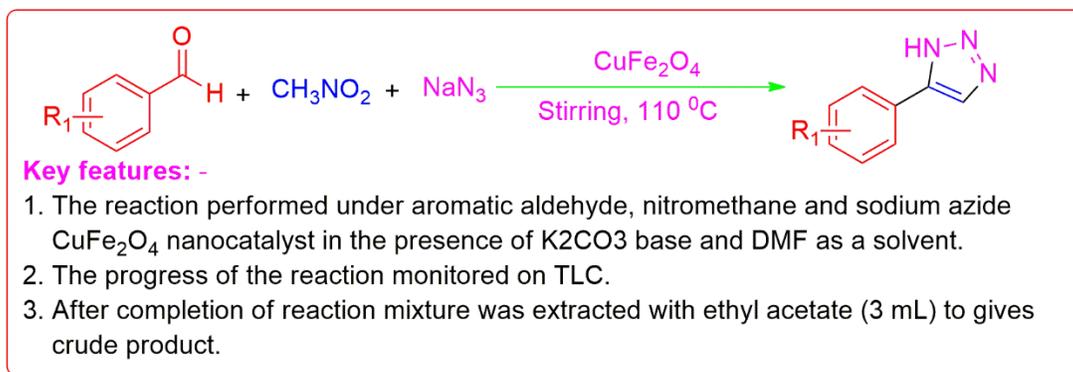
Ferrite nanoparticle catalyst used multicomponent reaction

Lakshinath Saikia et al. [46] reported the synthesis of 4-aryl, 1H-1, 2, 3- triazole in the presence of magnetically recyclable copper ferrite nanoparticles under microwave irradiation. The author is a synthesis of triazole derivative in the presence of aromatic aldehyde (1 mmol), NaN_3 (1.2 mmol), CH_3NO_2 (1.5 mmol), and nanocatalyst CuFe_2O_4 (5 mol %) in a DMSO (3 mL) round-bottomed flask cork with a refluxing condenser under the microwave irradiation (700 W) using a monomode microwave synthesizer by Raga's Scientific Microwave Synthesis System for the appropriate time. Monitored the reaction using, then completion of reaction nanoparticle (CuFe_2O_4) was separated by using a magnet. The reaction mixture was extracted with ethyl acetate and evaporated to give the pure product. The nanocatalyst washes with ethanol and dries well. The product was purified by using column chromatography in the presence of silica gel (100-200 mesh) and adsorbent and ethyl acetate-hexane as eluent (**Scheme 9**).

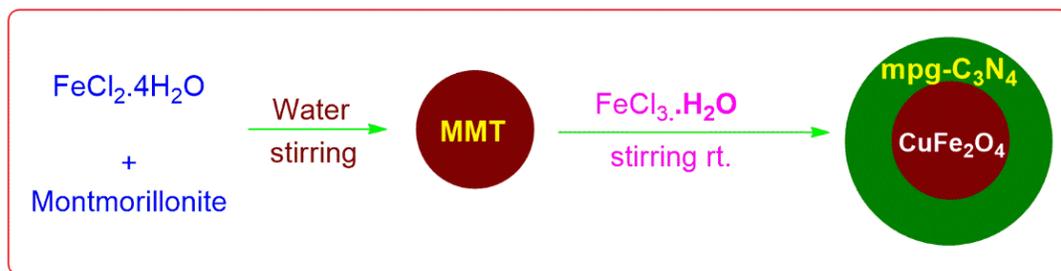
Javad Safari and co-workers [47] reported that the synthesis of Fe_3O_4 magnetic nanoparticles in the layers

of Montmorillonite (K_{10}) heterogeneous nanocatalyst was developed and characterized by successfully using analytical techniques. The $\text{MMT@Fe}_3\text{O}_4$ Nano clay was synthesized by the simple chemical co-precipitation method. The nano clay was prepared using $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (1.05 g) and was dissolved in 100 mL of deionized water, Montmorillonite (1.00 g) was added to the solution and the mixture was stirred for 30 min. Then, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.52 g) was to the above solution, and vigorous stirring to obtain a black color precipitate. After completion of this reaction, the nanoparticle was collected by using a magnetic field. Then nanocatalyst was dried under a vacuum for 12 h (**Scheme 10**).

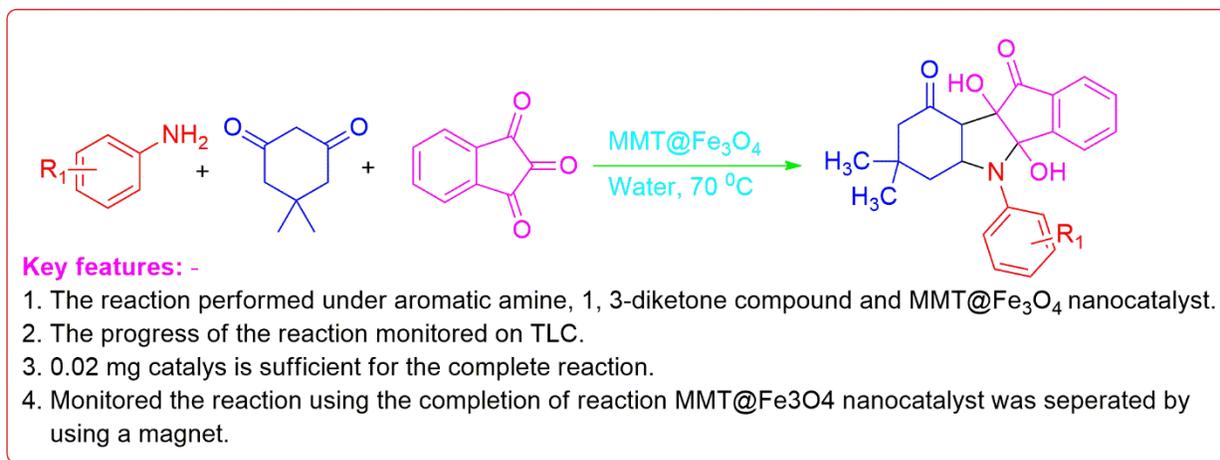
The synthesized $\text{MMT@Fe}_3\text{O}_4$ nano clay is used to prepare indeno[1, 2]indole-9,10-diones derivatives using a mixture of aromatic amine (1.0 mmol), 1,3-diketone compound (1.0 mmol), and $\text{MMT@Fe}_3\text{O}_4$ nano clay (0.02 g) mixture was stirred in 5 mL of water reflux at 70°C for 5 min. Then, ninhydrin (1.0 mmol) was added slowly, and the solution again refluxed. Monitored the reaction on TLC and after completion of the reaction mixture to cooled at room temperature and the magnetic nano clay catalyst was removed by an external magnet. The mixture was extracted with diethyl ether with evaporate will get the crude product (**Scheme 11**).



Scheme 9. CuFe_2O_4 catalyzed cascade synthesis of 4-aryl-1H-1, 2, 3-triazoles derivatives



Scheme 10. Synthesis of $\text{MMT@Fe}_3\text{O}_4$ Nano clay by Co-precipitation method



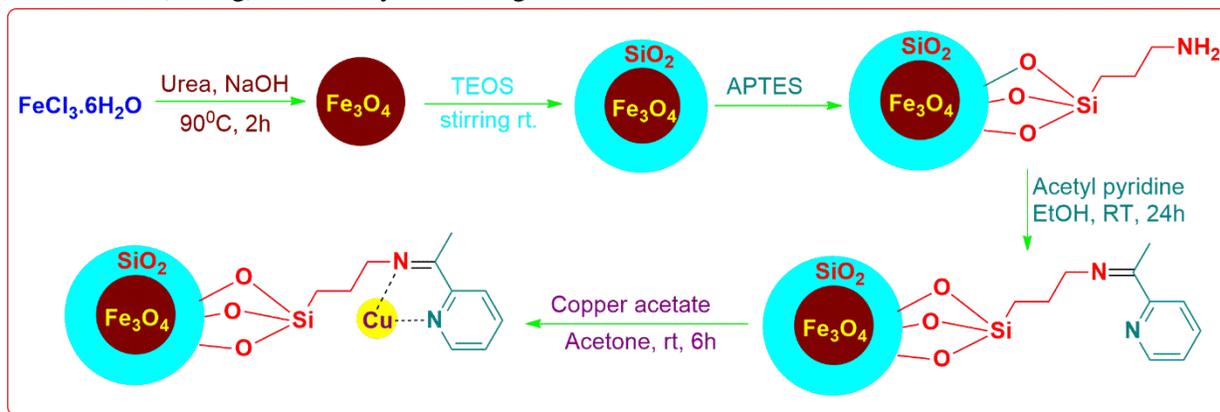
Scheme 11. Synthesis of indeno [1, 2] indole-9, 10-diones derivatives using MMT@Fe₃O₄

D. M. Pore et al. [48] reported that the synthesis of magnetically separable catalyst Cu-ACP-Am-Fe₃O₄@SiO₂ is used in Huisgen 1, 3-dipolar cycloaddition under triazole synthesis. The author develops novel magnetically separable silica-supported copper a heterogeneous catalyst that is successfully developed. The silica-coated nanoparticle was prepared using the Co-precipitation method. The Fe₃O₄@SiO₂ (1g) nanoparticles dispersed in ethanol (200 mL) with stirring at room temperature for 24h. Finally, ACP-Am, copper acetate, and Fe₃O₄@SiO₂ (1 g) solution were again stirred for 6 h at room temperature. The resulting nanoparticle was removed by using magnet wash with acetone and dried in an oven to generate Cu-ACP-Am-Fe₃O₄@SiO₂ nanocatalyst (**Scheme 12**).

The reaction between the aromatic halide (1 mmol), sodium azide (1.2 mmol), alkyne (1 mmol), and sodium ascorbate dissolved in ethanol with adding Cu-ACP-Am-Fe₃O₄@SiO₂ (40 mg) nanocatalyst with vigorous

stirring at 80 °C for 20 min. The reaction was monitored on TLC. After completion of the reaction, the catalyst was separated using an external magnet, and the mixture was extracted with ethyl acetate. The organic layer was evaporated under a vacuum to obtain crude product. In this work, various aryl halides and alkynes are used for the preparation of triazole derivatives containing electron-donating as well as electron-withdrawing substituents (**Scheme 13**).

After completion of the reaction, the catalyst was separated from the reaction mixture by using an external magnet, washed with water and ethanol for much time, dried in the air, and reused for the next cycle. It was observed that the catalyst was recycled a minimum of six times without any loss in yield. After the sixth cycle catalyst was analyzed by using SEM and TEM techniques, and it was observed that no change occurred in the particle size of the nanoparticle.



Scheme 12. Synthesis of silica-coated ferrite-supported organic-inorganic hybrid copper catalyst (Cu-ACP-Am-Fe₃O₄@SiO₂)

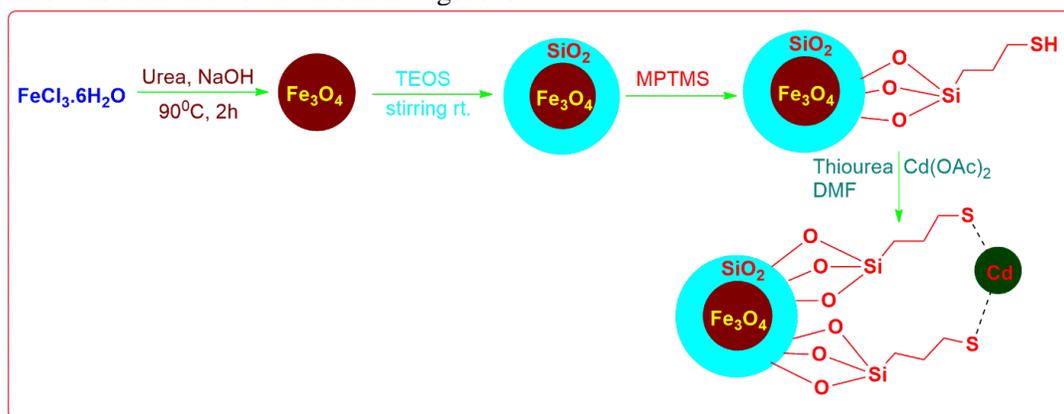


Scheme 13. Synthesis of 1, 2, 3-triazoles by click approach

P. Eskandari and F. Kazemi [49] are reported to prepare and characterization of Fe₃O₄@SiO₂@CdS nanocomposite which is a photocatalyst used for the reduction of the nitro compound using visible LED irradiation. The synthesis of Fe₃O₄ nanoparticles in the presence of FeCl₂·4H₂O (5.4 g) and FeCl₃·6H₂O (2 g) in 2 M hydrochloric acid (25 mL) solution, and then ammonia solution was added dropwise for about 30 minutes with vigorous stirring. Presence of the reaction, argon gas flowed in the flask. The magnetic nanoparticles were separated using a magnet and washed with deionized water, the catalyst will be dried at 60 °C for 12 h in a vacuum oven. In the second step, to prepare silica-coated magnetic Fe₃O₄/SiO₂ nanoparticles by mixing (2 g) of Fe₃O₄ nanoparticles were dispersed in a solution of ethanol (50 mL) and deionized water (10 mL) sonicated for 15 min. Then tetraethyl orthosilicate (TEOS) was added dropwise and the mixture was continuously sonicated for 10 min. Finally, add ammonia solution (1 mL) dropwise for 10 min. The hydrolysis of the reaction mixture with TEOS under alkaline conditions was carried out in ultrasound irradiation for 3 h. The silica-coated particles were separated using an external magnetic field, washed three times with ethanol, and dried in a vacuum oven at 60 °C for 12h. The synthesized silica-coated nanoparticle (2 g) dispersed in toluene (40 mL) then added dropwise (2 mL) of 3-(mercaptopropyl) trimethoxysilane (MPTMS) and the mixture was refluxed for 24 h under vigorous

stirring. The product was obtained [Fe₃O₄-SiO₂PrSH (TMNP)] It will be separated by an external magnet, washed with EtOH for a long time, and dried in a vacuum oven at 45 °C for 12 h. The synthesis of bare CdS using DMF (25 mL) solution containing cadmium acetate (2 mmol), and thiourea (3.75 mmol) was heated at 135 °C for 15 min. The resulting yellow solids product was filtered and washed with EtOH three times and dried in an oven at 45 °C for 12 h. And finally, The obtained thiopropyl-coated Nanomagnets (TMNP) with supporting CdS. TMNP (200 mg) was added in 25 mL of DMF solution, containing a different proportion of cadmium acetate and thiourea (Amount of cadmium acetate: thiourea were 1:1.82, 2:3.75, 4:7.5 mmol). Then the reaction mixture was placed in ultrasound for 15 min followed by heating at 135 °C for 15 min. After completion of the reaction resulting brownish solid nanoparticles were separated using a magnet washed with ethanol three times, and dried in an oven at 45 °C for 12 h (**Scheme 14**).

The photocatalytic activities of synthesized Fe₃O₄@SiO₂@CdS nanocatalysts are used as a reduction of nitro compounds under blue lead irradiation. The author studied the impact of solvents such as ethanol and isopropyl alcohol and verities of substituted aromatic amine conversion and selectivity of product (**Scheme 15**).



Scheme 14. Preparation of Fe₃O₄/SiO₂/CdS Nanocomposite

**Key features: -**

1. The reduction of the substituted nitrobenzene catalyzed by $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{CdS}$ in isopropyl alcohol and blue lead.
2. In this work, electron-withdrawing and electron-donating substituent also studied.
2. The progress of the reaction monitored on TLC.
3. The 0.5 mg catalysis is sufficient for the complete reaction.
4. Monitored the reaction using the completion of reaction nanocatalyst was separated by using a magnet.

Scheme 15. Photocatalytic reduction of nitrobenzene

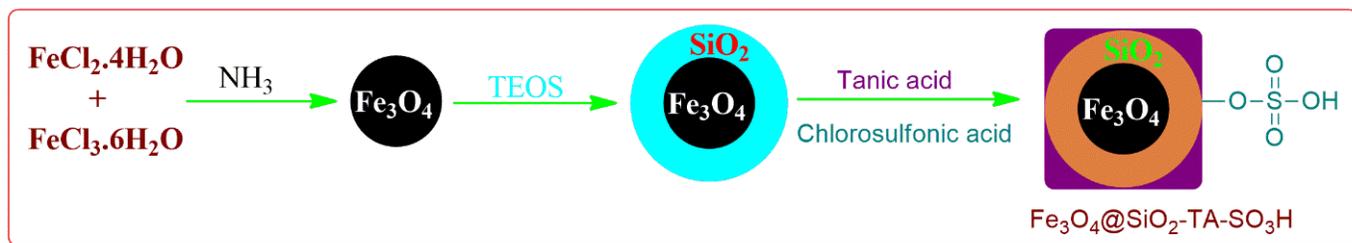
A. Fakhir, A. Naghipour, and Z. H. Ghasemi [50] are reported to develop tannic acid- SO_3H supported on $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles used for the synthesis of 2, 3-dihydroquinazolin-4 (1H)-one derivative. The preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -TA nanoparticle using $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (1 g) was dispersed in deionized water (50 mL) with stirring for 30 min then added a prepared solution of tannic acid (0.5 g/20 mL deionized water) and 2 mL triethylamine to the mixture and stirred at room temperature for 24h. The obtained $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -TA nanoparticles were separated by magnetic decantation, washed many times with deionized water, and dried at 40 °C. $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -TA nanoparticles were sulfonated using chlorosulfonic acid. The $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TA}$ nanoparticles (1 g) were dispersed in dry CH_2Cl_2 by ultrasonic bath for 20 min and slowly dropwise added chlorosulfonic acid (0.5 mL) about 30 min at room temperature to occur $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -TA- SO_3H nanoparticle (**Scheme 16**).

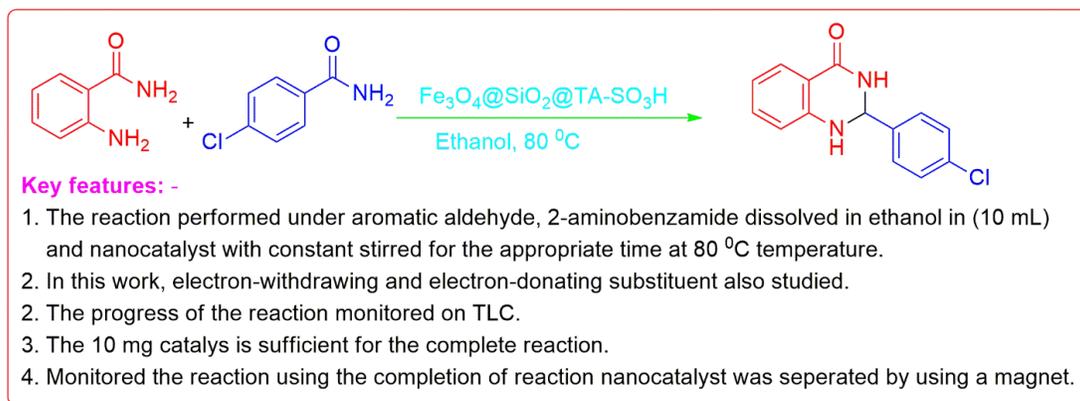
The author used synthesized catalyst in the preparation of 2, 3-dihydroquinazolin derivatives using a mixture of aromatic aldehyde (1 mmol), 2-aminobenzamide (1 mmol) dissolved in ethanol (10 mL), and added (10 mg) of the Nanocatalyst with constant stirred for the appropriate time at 80 °C. After completion of the reaction as monitored by TLC, the reaction was cooled to room temperature, and extracted with CH_2Cl_2 was added to the mixture. The catalyst was separated by an external magnet and reused directly as a catalyst for the next cycle. The filtrate was evaporated to remove the

solvent under a vacuum. The obtaining solid was then washed with cooled ethanol to give pure 2, 3-dihydroquinazolin-4(1H)-one derivative (**Scheme 17**).

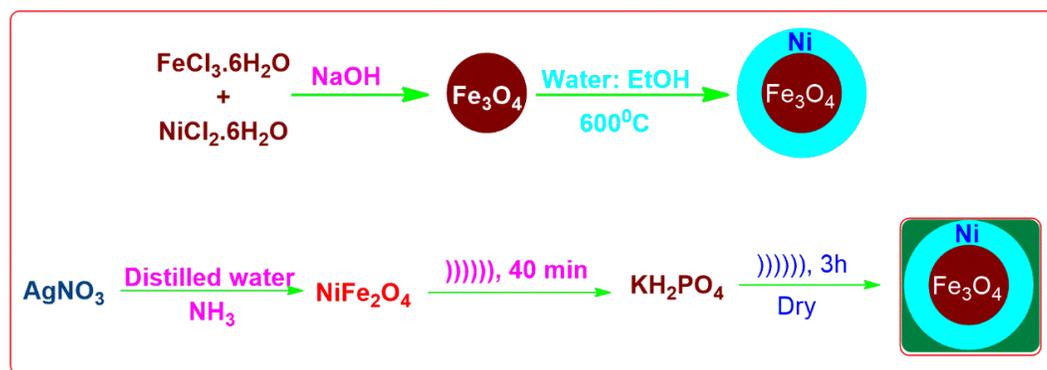
N. Hosseini Nasab and J. Safari [51] reported the synthesis of spiroindenoquininoxaline derivatives using newly prepared $\text{NiFe}_2\text{O}_4/\text{Ag}_3\text{PO}_4$ nanoparticles which is the heterogeneous catalyst. The author prepared NiFe_2O_4 MNPs from the reported work, using 3M sodium hydroxide solution was added to the solutions of ferric chloride (0.4 M) and nickel chloride (0.2 M) with the addition of the sodium hydroxide solution, to maintain a pH is 12 of the solution. Then 3 drops of oleic acid acting as a surfactant were added to the above solution and the solution was again stirred at 80 °C for 40 min. The resulting nanoparticle was separated by using an external magnet and washed many times with distilled water, it will dry under 600 °C for 24 h.

The synthesis of $\text{NiFe}_2\text{O}_4/\text{Ag}_3\text{PO}_4$ nanocomposite using (0.510 g) of AgNO_3 was dissolved in 20 mL distilled water with (1.0 M) NH_3 solution added dropwise addition to the above solution to obtain a clear solution. Then, (0.015 g) NiFe_2O_4 was dispersed into the solution and sonicated for 10 min. Finally added (10 mL) of KH_2PO_4 (0.10 M) was added dropwise to the above dispersion during sonication, and the resulting mixture was again sonicated for about 20 min. The resulting nanoparticle was separated by using an external magnet, washed many times with distilled water, and dried at 60 °C for 3 hours (**Scheme 18**).

**Scheme 16.** Schematic representation of Preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -TA- SO_3H nanoparticle



Scheme 17. Synthesis of 2-(4-chlorophenyl)-2, 3-dihydroquinazolin-4(1H)-one



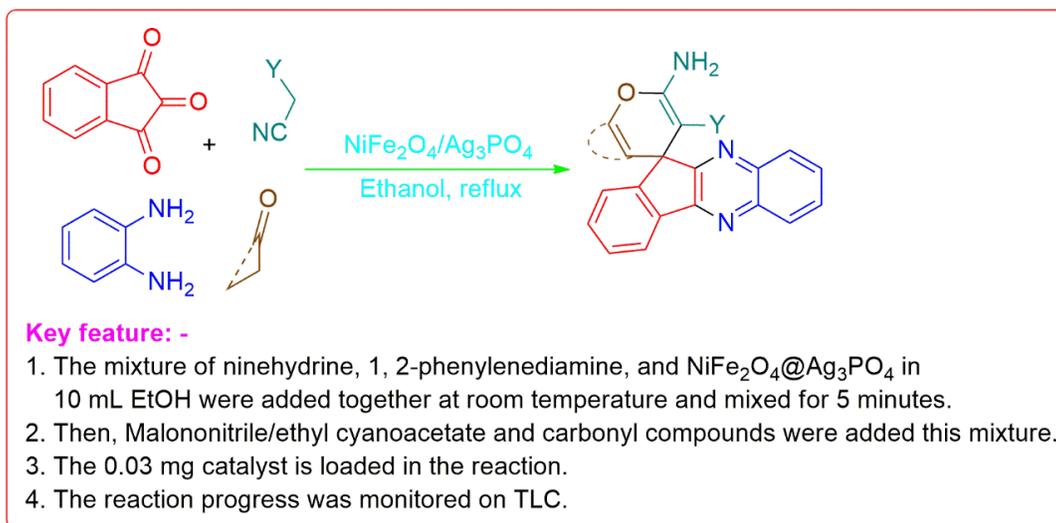
Scheme 18. General procedure for preparation of NiFe₂O₄/Ag₃PO₄

The mixture of ninhydrin (1 mmol), 1, 2-phenylenediamine (1 mmol), and NiFe₂O₄/Ag₃PO₄ (0.03 g) in 10 mL EtOH were added together at room temperature and mixed for 5 min. Then, Malononitrile/ethyl cyanoacetate (1 mmol) and a-methylene carbonyl compounds (1 mmol) were added to this mixture. The mixture was placed in reflux condition for an appropriate time. After the completion of the reaction as indicated by TLC (n-hexane/AcOEt 1:3), the catalyst was separated by an external magnet and then, the reaction mixture was cooled at room temperature for 1 h, and the generated solid product was filtered. To gain the net product, the product was washed with ethanol and 20 mL diethyl ether two times and dried (**Scheme 19**).

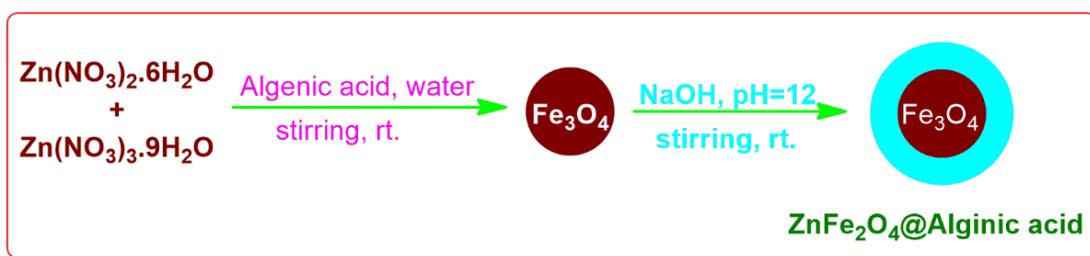
A. Maleki et al. [52] reported that the preparation and characterization of an eco-friendly ZnFe₂O₄@alginic acid nanocomposite is used for the synthesis of 2-amino-3-cyano-4H-pyran derivatives. Alginic acid is a linear polysaccharide derivative from natural resources used as a green catalyst. The ZnFe₂O₄@alginic acid nanocomposite was prepared in a simple Co-precipitation method. Precipitation of Fe(NO₃)₃·9H₂O (4 mmol) and Zn(NO₃)₂·6H₂O (2 mmol) was dissolved in 20 mL of deionized water. Then 0.5 g Alginic acid

solution was added dropwise with vigorous stirring in metal solution, and finally, this reaction mixture was dispersed under ultrasonic for 40 min at 80 °C. Addition (15 mL) of 5 M NaOH solution drop by drop to the above reaction mixture with continuous stirring at room temperature for 10 min. The mixture was again sonicated at 80 °C for 2h and then it was cooled down at room temperature. The final product was separated by an external magnet. The nanocomposite was washed several times with distilled water and ethanol and dried in an oven at 60 °C for 3 h to recycle ZnFe₂O₄@alginic acid nanocomposite (**Scheme 20**).

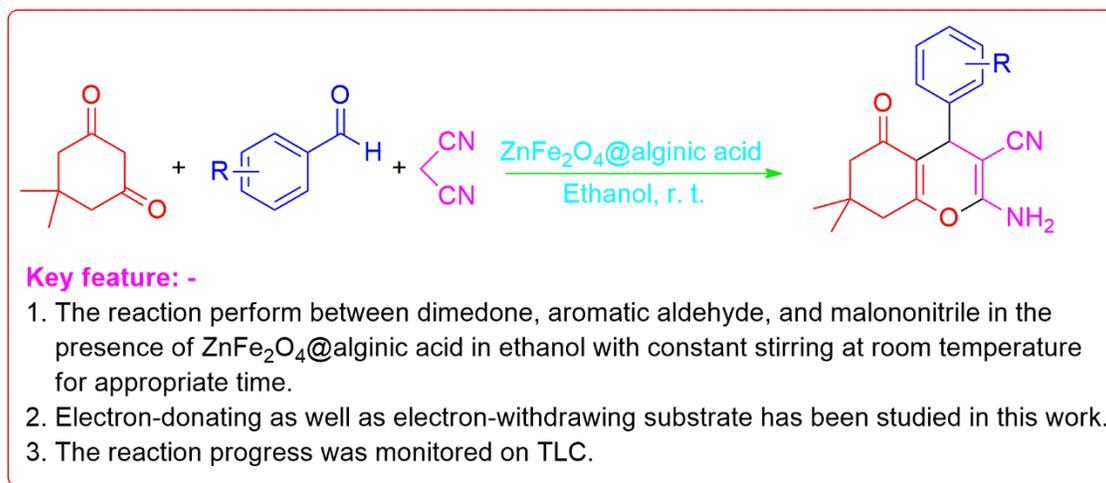
A reaction between dimedone (1 mmol), aromatic aldehyde (1 mmol), and malononitrile (1 mmol) in the presence of a nano catalytic ZnFe₂O₄@alginic acid (5 mg) in (2 mL) ethanol was stirring at room temperature for the appropriate time. Progress of the reaction is monitored on TLC, after the completion of the reaction the nanocatalyst separated from the reaction mixture using a magnet. The resulting mixture was extracted with ether and filter, the organic layer was evaporated under a vacuum to give the pure product. A separated nanoparticle is washed with water and ethanol for a long time, dried at 60 °C in the oven, and reused in the next reaction (**Scheme 21**).



Scheme 19. Synthesis of spiro indeno [1, 2-b] Quinoxaline derivatives



Scheme 20. Synthesis of $\text{ZnFe}_2\text{O}_4@alginate$ nanocomposite



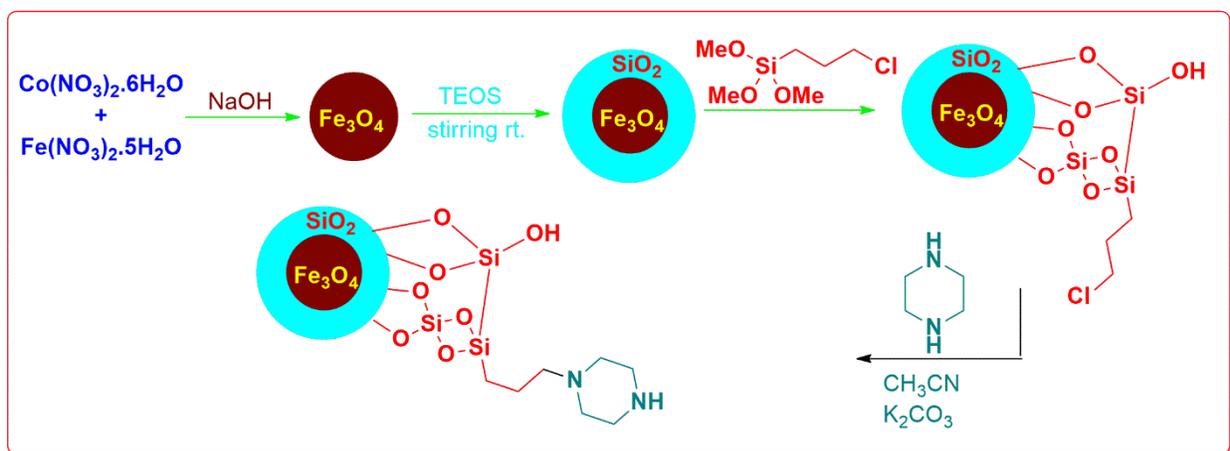
Scheme 21. Synthesis of 2-amino-3-cyano-4H-pyran catalyzed under $\text{ZnFe}_2\text{O}_4@alginate$ acid

A. Safari et al. [53] reported that the synthesis and characterization of $\text{CoFe}_2\text{O}_4\text{SiO}_2@NH-NH_2\text{-PCuW}$ as an acidic nanocatalyst is applicable for the synthesis of 1, 4-benzodiazepine derivatives. Cobalt ferrite MNPs were prepared by a simple chemical co-precipitation method. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.01 mol) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.005 mol) were dissolved in deionized water with constant stirring. The 3M solution of NaOH (25 mL) was added drop by drop to the above

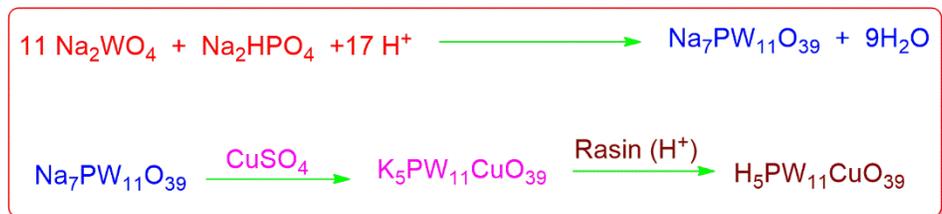
solution under stirring to maintain a pH basic of about 11-12. Then, (1 g) of Polyvinyl Pyrrolidone (PVP) as a surfactant was slowly added and heated at 90 °C for 2 hours. The MNPs were separated by using an external magnet and were washed many times with distilled water and ethanol and dried overnight at 80 °C in the oven. In the second step, the author's synthesis of Silica-coated CoFe_2O_4 MNPs was prepared through the reported Stobber method. Synthesized CoFe_2O_4 (1 g)

nanoparticle was dispersed in aqueous ethanol and an added ammonia solution (1 mL) mixture was placed under ultra-sonication for 30 min. Then dropwise added (0.4 mL) of tetra ethyl orthosilicate (TEOS) with continuously stirred at room temperature for 24 h. The silica-coated MNPs were magnetically separated and washed with deionized water and ethanol and dried at 80 °C for 12 h. In the third step, prepared $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ (0.7 g) was added to the solution of 3-chloropropyltrimethoxysilane (1 mL) in solvent-dry toluene (100 mL) and the mixture was refluxed for 48 h. After completion of the reaction, $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-Cl}$ MNPs were separated by the magnetic field, washed well using double-distilled water and ethanol (10 mL), and dried at 80 °C for 12h to give the $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-Cl}$ (Scheme 22).

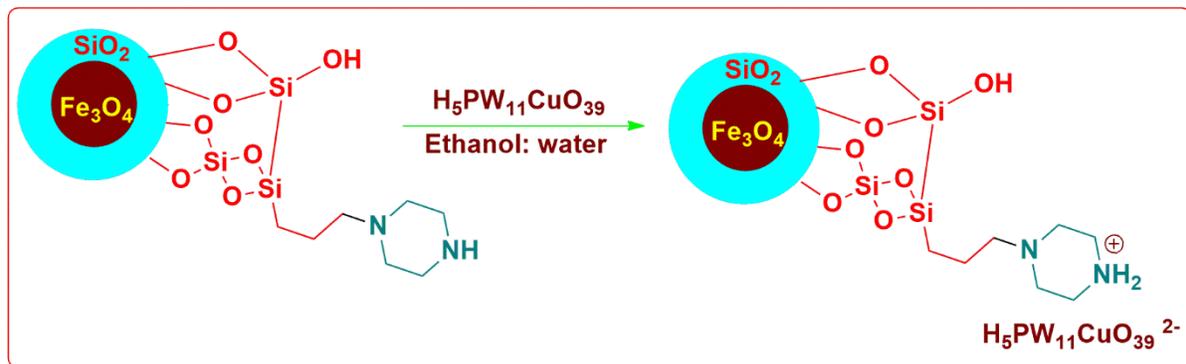
In the last step, the $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-Cl}$ nanoparticle (0.7 g) was dispersed in 70 mL of CH_3CN and ultra-sonicated for 20 min. Then, base K_2CO_3 (7 mmol), KI (7 mmol), and piperazine (10 mmol) were added and refluxed for 24h. The solid was collected using a permanent magnet washed with aqueous ethanol and dried at 80 °C for 12 h. Finally, the preparation of diamine-modified silica-coated magnetite polyoxometalate nanoparticles, $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{NH-NH}_2\text{-PCuW}$ (1 g) and $\text{H}_5\text{PW}_{11}\text{CuO}_{39}$ (1 g) (Scheme 23), nanoparticle dispersed in (50 mL) aqueous ethanol and again stirred for 6h. After completion of the reaction, $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{NH-NH}_2\text{-PCuW}$ was removed from the reaction mixture using a magnetic field, and washed several times with water, and dried at 80 °C in the oven for 4h (Scheme 24).



Scheme 22. Preparation of $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{N-NH}$



Scheme 23. Preparation of $\text{H}_5\text{PW}_{11}\text{CuO}_{39}$



Scheme 24. Preparation of $\text{CoFe}_2\text{O}_4@\text{SiO}_2@\text{NH-NH}_2\text{-PCuW}$

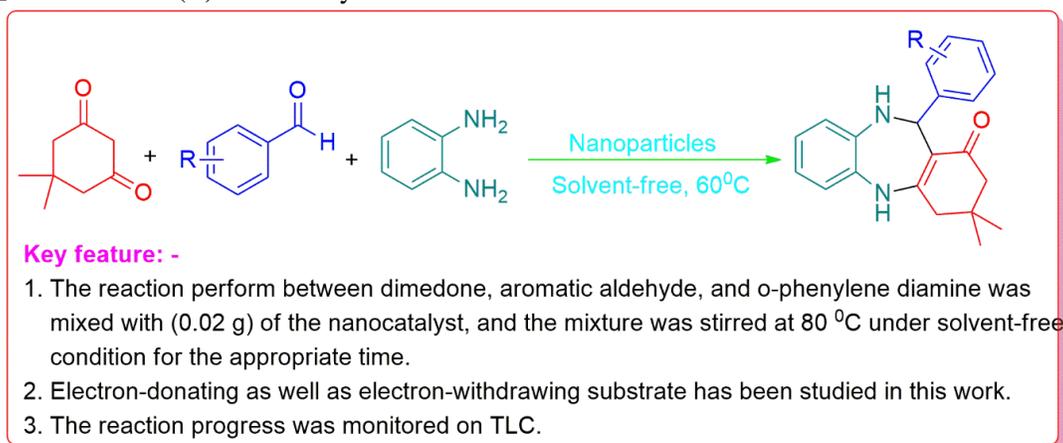
Synthesis of benzodiazepine using aromatic aldehyde (1 mmol), dimedone (1 mmol), and *o*-phenylene diamine (1 mmol) was mixed with (0.02 g) of the nanocatalyst, and the mixture was stirred at 80 °C under solvent-free conditions for the appropriate time. The progress of the reaction is monitored on TLC (EtOAc/n-hexane), after the completion of the reaction mixture was extracted with (5 mL) CH₃CN, and the catalyst was separated from the mixture using an external magnet. The organic layer was then evaporated under reduced pressure to obtain the pure product. The remaining nanocatalyst was washed with ethanol and dry it well at 60 °C then again re-used for the next reaction (**Scheme 25**).

A. Safari *et al.* [54] reported to development of CoFe₂O₄@SiO₂ magnetically recyclable heterogeneous catalyst for the synthesis of Spiro-oxindole derivatives in aqueous reaction conditions. CoFe₂O₄ was prepared using Fe(NO₃)₃·9H₂O and Co(NO₃)₂·6H₂O we get CoFe₂O₄@SiO₂ nanoparticles, and the synthesized nanoparticle is dispersed in EtOH/H₂O and then, added dropwise tetra ethyl orthosilicate to the above reaction. The mixture was stirred at room temperature for 24h, After completion of the reaction nanoparticle was collected using an external magnet to give a corresponding heterogeneous CoFe₂O₄@SiO₂ catalyst (**Scheme 26**).

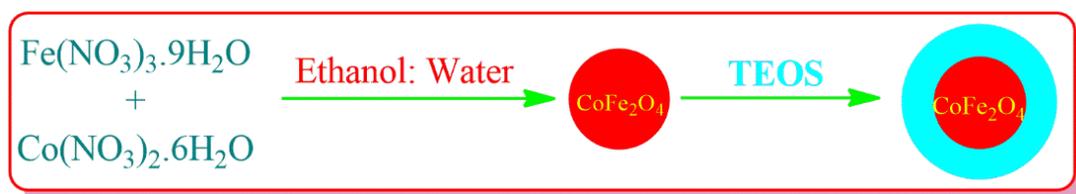
S. Lotfi *et al.* [55] reported the synthesis of Fe₃O₄@SiO₂/isoniazid/Cu (II) nanocatalyst is used to

preparation of Quinoline derivatives. The author was a synthesis nanoparticle using (3 g) of FeCl₃·6H₂O and (1 g) of FeCl₂·4H₂O dispersed in the water (120 mL) with vigorous stirring. Then concentrated NH₃ (28%) solution was to maintain a solution pH of 11. The solution stirred under atmosphere N₂ at 60 °C was stirred vigorously for one hour. The black precipitate was separated by a magnet, washed with distilled water several times, and dried at 50 °C in an oven for 24h. In the second step synthesis of Fe₃O₄@SiO₂ nanoparticles, using Fe₃O₄ (1 g) nanoparticles were dispersed in isopropyl alcohol/water under ultrasound irradiation for 15 min, then added (1.0 mL) tetraethyl orthosilicate (TEOS) and (4.80 mL) NH₃ (28%) were added to the solution at room temperature under constant stirring. The nanoparticle was collected using a magnet and washed several times with distilled H₂O/EtOH. The product was dried at 50 °C under the oven (**Scheme 27**).

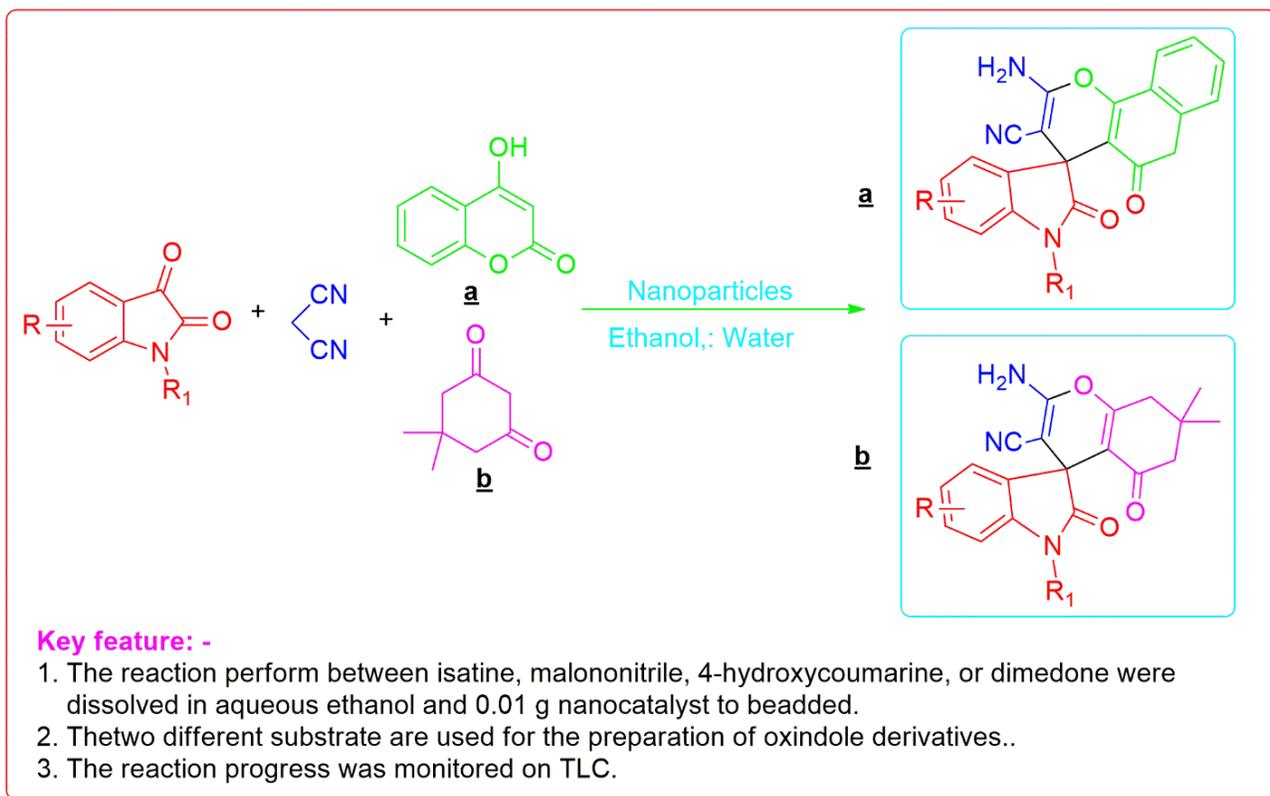
The Fe₃O₄@SiO₂ (0.5 g) nanoparticles were dispersed in toluene under an ultrasonic bath for 5 min, then 3-chloropropyltriethoxysilane (CPTES) (0.6 mL) was added to the mixture and solution again stirred at 100 °C for 48h. The precipitate (Fe₃O₄@SiO₂-pr-Cl) was separated by a magnet that was washed many times with EtOH and dried at 60 °C in an oven for 48h. In the next step, Fe₃O₄@SiO₂-pr-Cl nanoparticle (0.5 g) was dispersed by an ultrasonic bath in toluene solvent, and isoniazid ligand (2 mmol) was added to the above solut-



Scheme 25. Synthesis of benzodiazepine derivatives using CoFe₂O₄@SiO₂@NH-NH₂-PCuW



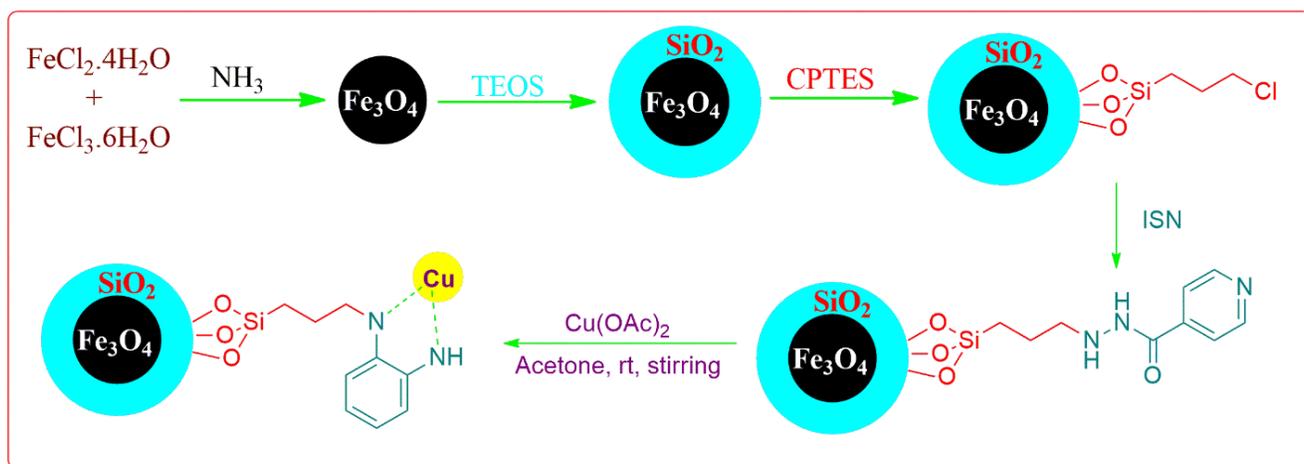
Scheme 26. Preparation of CoFe₂O₄@SiO₂ nanocatalyst using TEOS



Scheme 27. Synthesis of oxindole derivatives catalyzed by $\text{CoFe}_2\text{O}_4@\text{SiO}_2$

-ion. The mixture was continuously stirred under a nitrogen atmosphere at $80\text{ }^\circ\text{C}$ for 24h. The nanoparticle was collected by an external magnet, and washed several times with ethanol/water, dried at $40\text{ }^\circ\text{C}$ for 48h. In the third step, the preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{isoniazid}$ (0.5 g) is dispersed in acetonitrile under ultrasonic irradiation. Then, added $\text{Cu}(\text{OAc})_2$ (50 mg) to the above reaction mixture, and

stirring was applied vigorously at $50\text{ }^\circ\text{C}$ for 10h. The product $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{isoniazid}/\text{Cu}$ (II) MNPs was separated by using an external magnet that was washed many times with distilled H_2O and EtOH to remove impurities the product was dried at $50\text{ }^\circ\text{C}$ for 24h (**Scheme 28**).



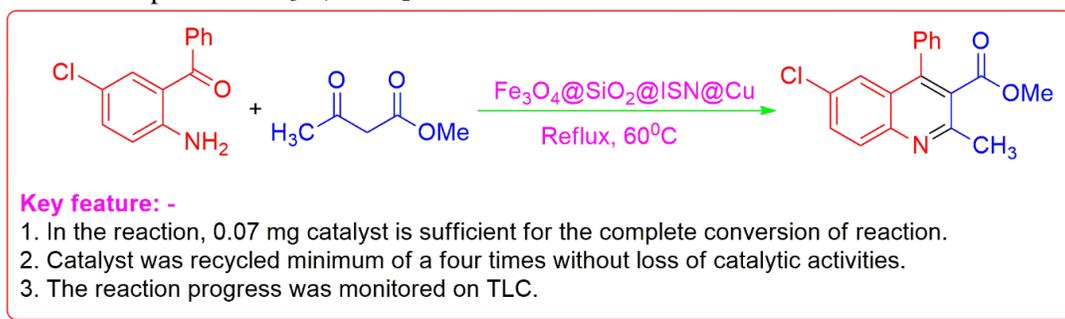
Scheme 28. Preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{isoniazid}/\text{Cu}$ (II)

The reaction between α -CH-acid (1.2 mmol), 2-aminoaryl ketone (1.0 mmol), and nanocatalyst (0.07 g) was dissolved in ethanol solvent and heated vigorously stirred until the end of the reaction. Confirm the reaction was completed, via TLC technique, the nanocatalyst was separated from the reaction mixture by a magnet, which was then washed with EtOH (about 5 mL). The final product was recrystallized by ethanol (**Scheme 29**).

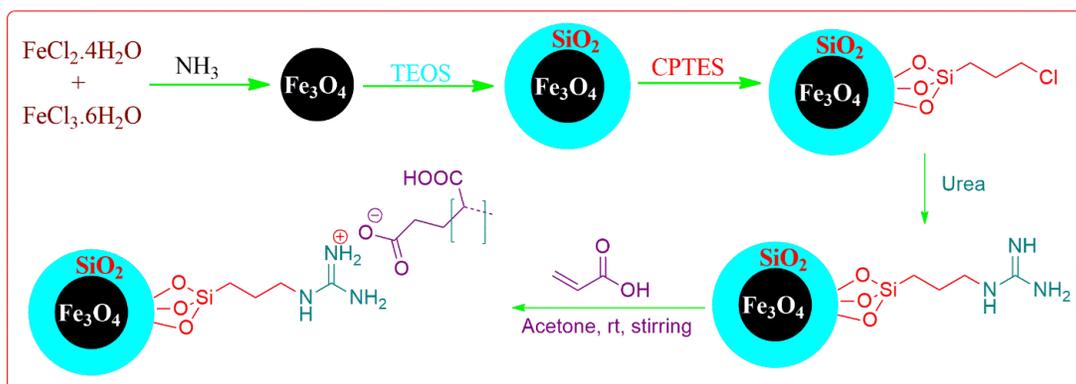
Mohammadi and Sheibani [56] studied and developed $\text{Fe}_3\text{O}_4@SiO_2$ guanidine-poly acrylic acid nanocatalyst used for the preparation of 4H-benzo-pyrans and dihydropyran chromenes derivatives and reaction carried out in aqueous medium. The Fe_3O_4 MNPs (1 g) were dispersed in (200 mL) of ethanol and (5 mL) of 28% wt. concentrated ammonia aqueous solution, and then added (2 mL) of tetraethyl orthosilicate (TEOS) was added to this mixture. This mixture was stirred for 20h at room temperature, the resultant suspension was washed and separated using a magnet and dried at room temperature. The $\text{Fe}_3\text{O}_4@SiO_2$ (1 g) in the form of powder was poured into the mixture of (3-chloropropyl) triethoxysilane (5 mmol) and toluene (50 mL) and the mixture again stirring for 12h at reflux and cooled down to ambient temperature. Then, the product was separated through an external magnetic field washed with ethanol/water solution to remove possible impurities, and dried at ambient temperature. $\text{Fe}_3\text{O}_4@SiO_2\text{-Cl}$ core-

shell particles (1 g) were dispersed in ethanol (50 mL) ethanol under ultra-sound irradiation for 30 min. Then, add (5 mmol) guanidine into the above mixture under stirring for 20h. The isolation of product was separated from the solution through filtrating using a magnetic field, washed with ethanol, and lastly dried at ambient temperature. The $\text{Fe}_3\text{O}_4@SiO_2\text{-guanidine}$ (500 mg) powder was dispersed in (50 mL) of deionized water. Then, slowly added (1 mL) of acrylic acid was poured into the mixture. In the next step, (0.25 g) of the ammonium persulfate (APS) as a radical initiator was added to the reaction mixture. The solution was stirred for 5h with heated in a water bath with a temperature of 70°C under an N_2 atmosphere. The resultant product was washed much time with de-ionized water and dried at room temperature (**Scheme 30**).

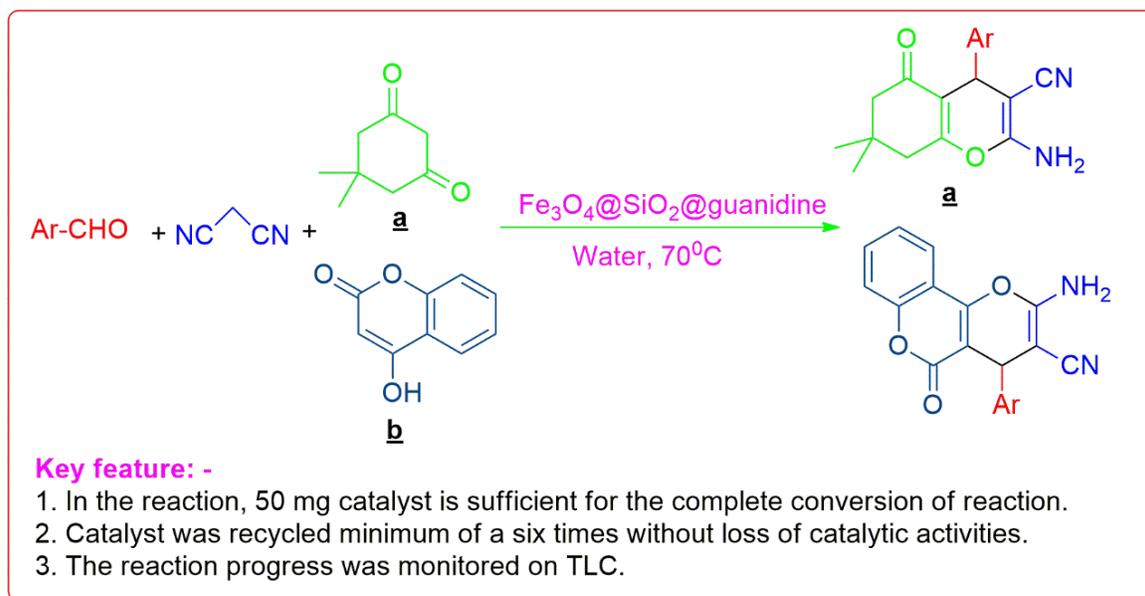
A reaction between aromatic aldehyde (1 mmol), malononitrile (1.2 mmol), the magnetic nano catalytic system ($\text{Fe}_3\text{O}_4@SiO_2\text{-guanidine-PAA}$), and water (5 mL) was dissolved and reflux at a temperature of 70°C for half an hour. Then 4-hydroxycoumarin or dimedone (1 mmol) was poured into the mentioned mixture and the reaction was monitored by using TLC. After completion of the reaction of the nanoparticle using an external magnet, the mixture was extracted with ethyl acetate. In this work, nanoparticles are recycled a minimum of 6 times (**Scheme 31**).



Scheme 29. Synthesis of Quinoline derivatives using $\text{Fe}_3\text{O}_4@SiO_2$ /isoniazid/Cu (II)



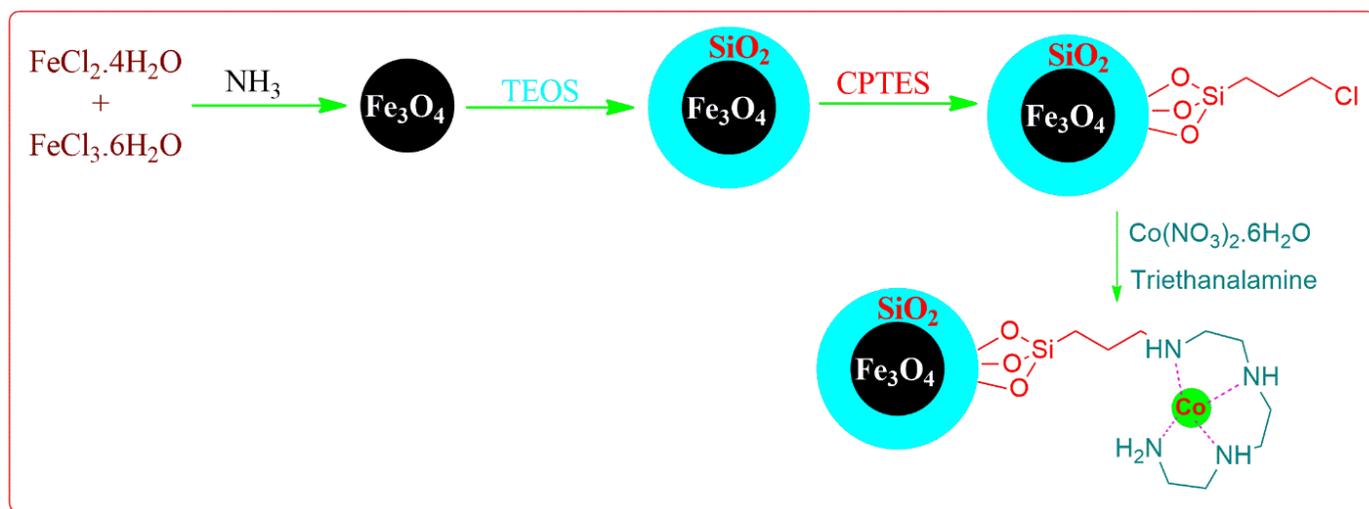
Scheme 30. Preparation of $\text{Fe}_3\text{O}_4@SiO_2$ with poly acrylic acid



Scheme 31. Synthesis of dihydropyran-chromene and 4H-benzo-pyran derivatives

A. Allahresani, *et al.* [57] is a synthesis of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-NH}_2\text{-Co (II)}$ Nanoparticle is used in the Biginelli reaction. The author was a synthesis of $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ nanoparticles from previous literature. A reaction of triethylenetetramine (1 mmol) and triethanolamine (2 mmol) was dissolved in (30 mL) EtOH and 3-chloropropyltriethoxysilane (APTMS) was dissolved in 20 mL EtOH. Afterward, for 24h under reflux conditions, a solution of 3-chloropropyltriethoxysilane (APTMS) was dropped by drop added to this above solution. Afterward, remove the solvent by a rotary evaporator and precipitate the product obtained yellow powder. In the second step, take (40 mL) of dry toluene and added (0.7 mL) of $\text{NH}_2\text{-Pr}$

were dissolved, then (0.2 g) of $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ was mixed, and the resulting mixture was stirred for 48h at 105°C under Argon gas. The precipitate was washed with toluene and ethanol and at 105°C , $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-NH}_2$ was dried for 12h. In the next step, the nanoparticle $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-NH}_2$ (1 g) dispersed in (20 mL) EtOH then added a solution of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (4.2 mmol, 0.8 g in 20 mL EtOH) was slowly added. The mixture is stirred under reflux conditions for 25h. Afterward reaction was completed nanoparticle was separated using an external magnet, and the resulting nanoparticle of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-NH}_2\text{-Co (II)}$ NPs product was collected and washed repeatedly with EtOH. Then, dried under vacuum for 12h at 80°C (**Scheme 32**).



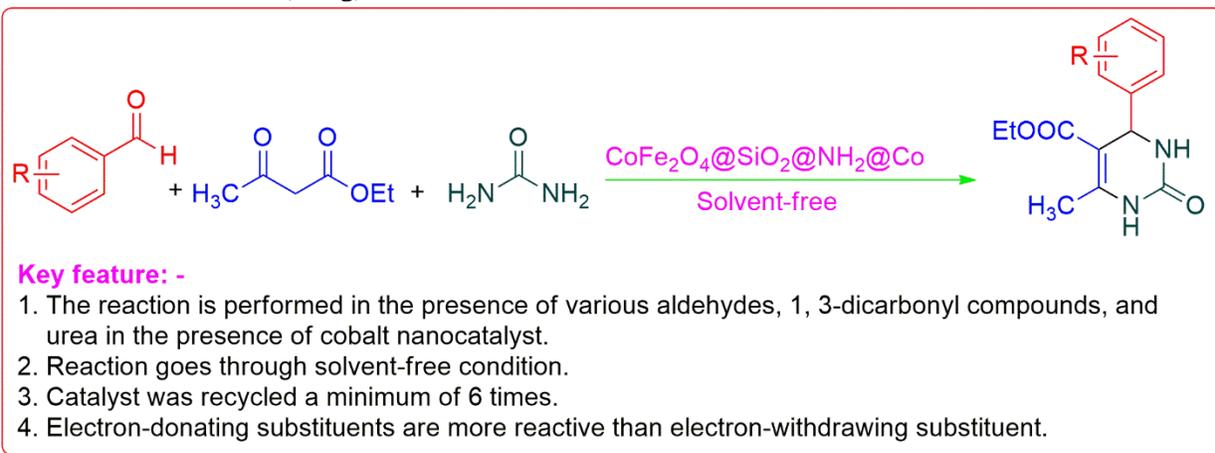
Scheme 32. Preparation of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-NH}_2\text{-Co (II)}$ NPs

A mixture of benzaldehyde (1 mmol), urea or thiourea (1 mmol), ethyl acetoacetate (1 mmol), and $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-NH}_2\text{-Co}$ (II) NPs (0.01 g) as a nanocatalyst was stirred with refluxing for 15 min, the progress of reaction monitored the reaction on TLC. Then the reaction mixture and extracted with ethyl acetate, which gave the pure product, and the nanocatalyst was recycled washed with acetone, and dried well (**Scheme 33**).

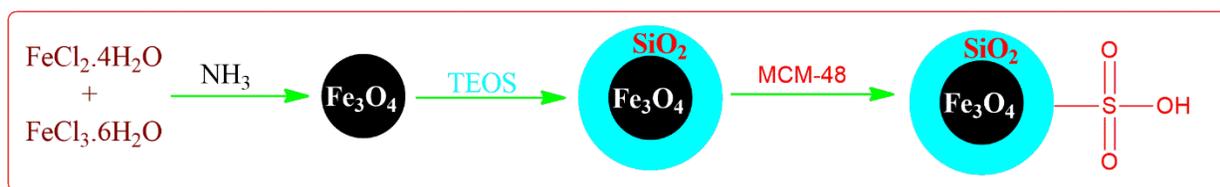
H. Kefayati et al. [58] reported the synthesis of $\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$ magnetic nanoparticle catalyzed under preparation of benzochromeno-2, 3-pyrimidinone derivatives under solvent-free conditions. The $\text{Fe}_3\text{O}_4@\text{SiO}_2$ MNPs were prepared using reported previous literature. $\text{Fe}_3\text{O}_4@\text{SiO}_2$ supported with functionalized with SO_3H groups by adding $\text{Fe}_3\text{O}_4@\text{SiO}_2$ MNPs (2.0 g) dispersed into the aqueous solution of $\text{NaHSO}_4\cdot\text{H}_2\text{O}$ (20 mL, 5 mmol) and solution under ultra-sound irradiation at 25°C for 1 min. Finally, the nanoparticle was separated using an external magnet, and the powder was dried in an oven at 90°C for 2 h, will obtain solid sulfonic acid-functionalized silica MNPs ($\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$). $\text{Fe}_3\text{O}_4@\text{MCM-48}$ was prepared using mixing Fe_3O_4 MNPs (1.5 g) and ammonia solution (5 mL) added in distilled water (50 mL) and ultrasonic wave for 2 min at 40°C . Then, TEOS (10 mL), NaOH (0.9 g), and NaF (0.19 g) mixture were stirred at ambient temperature for 2h. Cetyltrimmonium bromide (7.0 g) was added to the

mixture and continuously stirred at 40°C for 2 h. The magnetic nanoparticle was then hydrothermally treated at 120°C for 48h in an autoclave. Afterward 2 days, the resultant solid was filtered, washed with de-ionized water, and dried at 60°C . Finally, the nanoparticle was separated by calcination of the synthesized particles for 3h at 300°C . $\text{Fe}_3\text{O}_4@\text{MCM-48}$ was functionalized with SO_3H groups by adding the prepared mesoporous using $\text{Fe}_3\text{O}_4@\text{MCM-48}$ nanoparticles (1.5 g) dispersed in an aqueous solution of $\text{NaHSO}_4\cdot\text{H}_2\text{O}$ (20 mL, 5 mmol) and ultra-sound at 25°C for 1 min. The mixture was stirred for 30 min to adsorb the NaHSO_4 on the mesoporous MNPs. Lastly, the water was removed and the powder was dried in an oven at 90°C for 2h. A brown solid is obtained, i.e., sulfonic acid-functionalized MCM-48 mesoporous MNPs ($\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$), was obtained (**Scheme 34**).

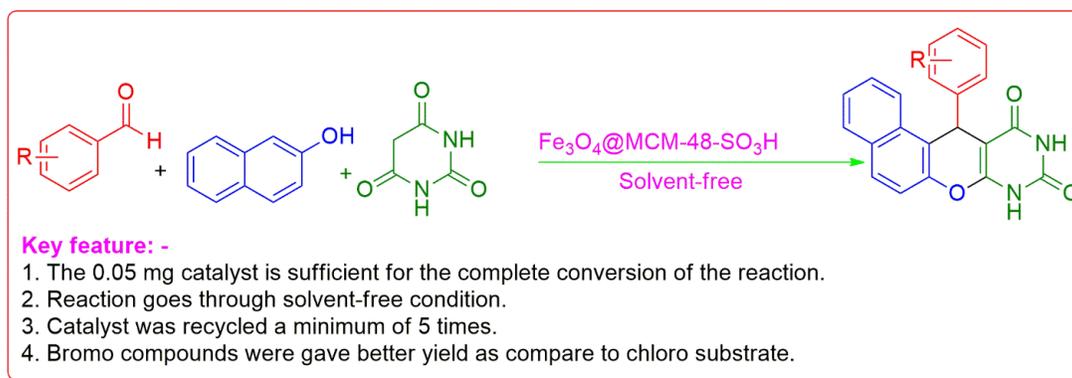
The reaction takes place in between a mixture of an aryl aldehyde (1 mmol), β -naphthol (1 mmol), barbituric acid (1.2 mmol), and $\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$ nanocatalyst was stirred at room temperature under solvent-free conditions. Progress reactions were monitored on thin-layer chromatography (TLC). After completion of the reaction, the mixture was dissolved in ethanol. The magnetic nanocomposite was then separated in the presence of a magnetic field and dried well. Evaporate the alcohol to give a pure recrystallized product (**Scheme 35**).



Scheme 33. Biginelli reaction catalyzed by $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-NH}_2\text{-Co}$



Scheme 34. Schematic representation of $\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$

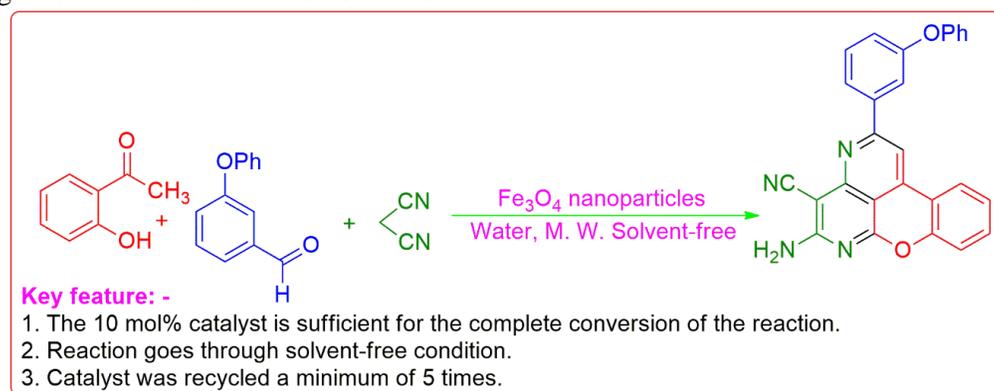


Scheme 35. Benzo-chromeno [2, 3] pyrimidine's catalyzed under $\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$

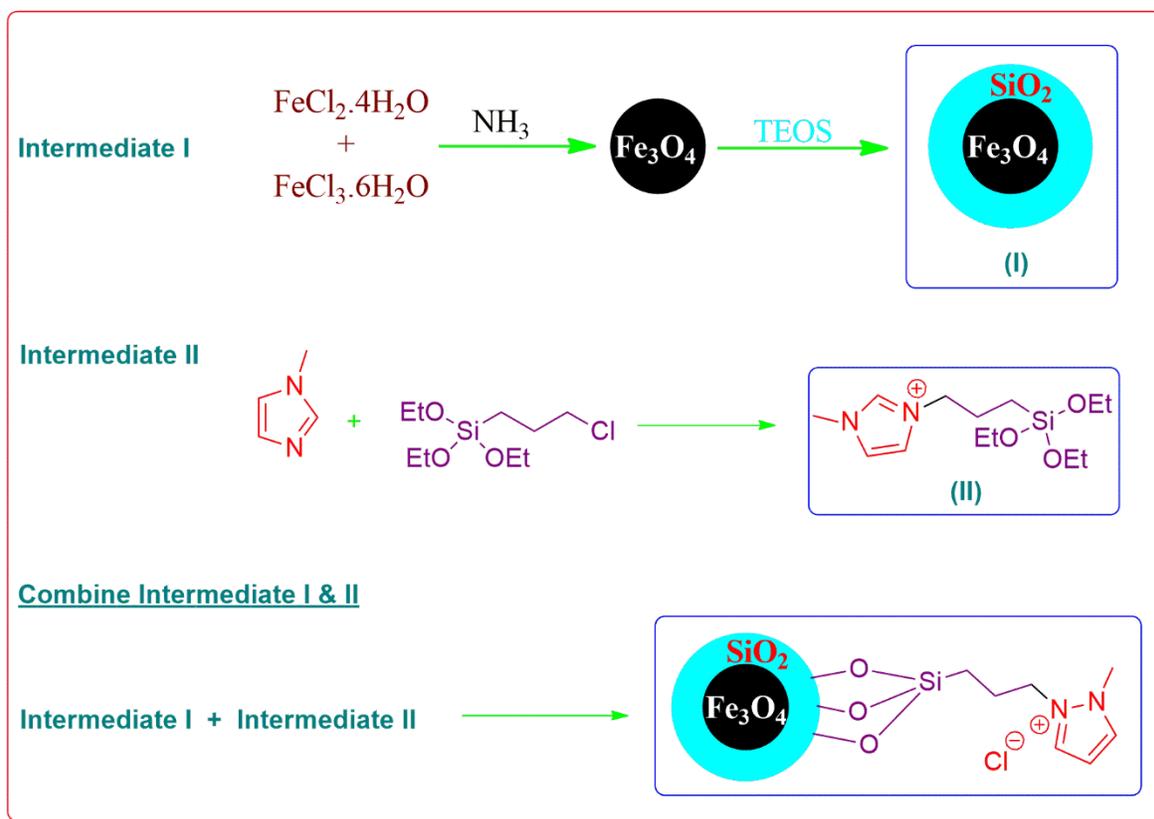
A. Dandia et al. [59] are reported as microwave-assisted Fe_3O_4 nanoparticle catalyzed under the synthesis of chromeno [1,6] naphthyridine in aqueous reaction conditions. The Fe_3O_4 nanoparticle was synthesized using a simple Co-precipitation method. The synthesis of chromeno [1,6] naphthyridine derivatives using aromatic aldehyde (1 mmol), malononitrile (2 mmol), 2-hydroxy acetophenone (1 mmol), and 5 mol% of Fe_3O_4 NPs in water (10 mL). The reaction mixture was placed in the microwave cavity under irradiation for a specific time at 70°C using a power of 400W. After the completion of the reaction, Fe_3O_4 NPs were separated by using an external magnet, and form crude product was purified by recrystallization using ethanol (**Scheme 36**).

N. Azgomi and M. Mokhtary *et al.* [60] reported the synthesis of nano- $\text{Fe}_3\text{O}_4@\text{SiO}_2$ supported ionic liquid as an efficient catalyst used for the preparation of 1, 3-thiazolidine-4-ones under solvent-free reaction conditions. The synthesis of Fe_3O_4 MNPs using $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ (0.01 mol) and $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (0.03 mol) was dissolved into 200 mL de-ionized water under constant stirring, then added dropwise NaOH solution to maintain the pH value about in the range 12. Then, different amounts of hydrazine hydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, 80% concentration) were added to the above solution. The reaction was again stirred for about 24 hours at ambient

temperature. The black precipitate of Fe_3O_4 MNPs was wash with distilled water for much time and dried at 60°C under a vacuum. In the second step, $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles synthesized in the presence of Fe_3O_4 MNPs (0.02 mol) were dispersed in a mixture of aqueous ethanol (80:20) and then 28 wt. % concentrated ammonia (2.0 mL) aqueous solution, also the addition of tetraethyl orthosilicate (TEOS) (0.20 mL) with constant stirring for 24h, the final product was washed, filtered several times and dried at 60°C in the air. The preparation of ionic liquid using 1-Methylimidazole (13.6 mL) and (3-chloro-propyl) trimethoxysilane (31 mL) were refluxed at 80°C for three days in the absence of any catalyst and solvent under Argon atmosphere. The unreacted materials were washed with diethyl ether ($3\times 8\text{ mL}$). The diethyl ether was removed under vacuum to give a yellowish viscous liquid. The yield of the product was obtained at 98%. The synthesis of MNPs@ SiO_2 -IL $\text{Fe}_3\text{O}_4@\text{SiO}_2$ MNPs (2 mmol) and 20 mL THF were mixed in a beaker, and then (20 mmol) of NaH was dispersed into the mixture under ultra-sound irradiation. Then 1-methyl-3-(3-trimethoxysilylpropyl)-1H-imidazole-3-ium chloride (22 mmol) was added drop by drop at room temperature and stirred for 16h at 60°C . The resultant products were collected and washed with ethanol and deionized water in sequence and then dried under vacuum at 60°C for 2h (**Scheme 37**).



Scheme 36. Fe_3O_4 nanoparticle catalyzed under the synthesis of chromeno [1, 6] naphthyridine



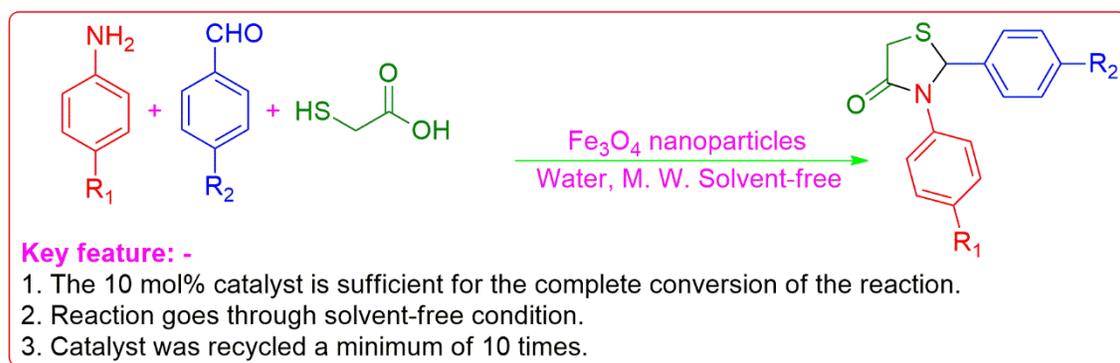
Scheme 37. Schematic representation of $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-IL}$ MNPs

The synthesis of 1, 3-thiazolidine-4-ones using a mixture of aromatic aldehyde (1 mmol), anilines (1 mmol), thioglycolic acid (1 mmol), and $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-IL}$ MNPs (0.0007 g) was stirring at 70°C for the appropriate time. After completion of the reaction check on TLC. The reaction mixture was cooled to ambient temperature, and the crude solid residue was extracted with ether, the nanoparticle was separated by the magnet, and the organic layer was evaporated to the obtained pure product of 1, 3-thiazolidine-4-ones in about 86-95% yields (**Scheme 38**).

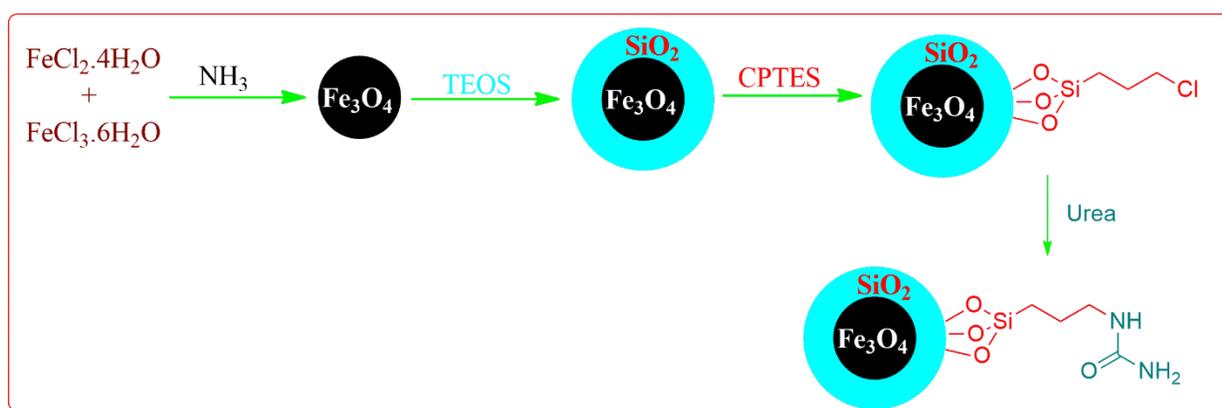
A. Maleki et al. [61] are reported as a designing, preparation, and characterization of urea-functionalized silica-coated ferrite nanoparticles which is used in multicomponent synthesis of substituted imidazole derivatives. The synthesis of Fe_3O_4 MNPs in the presence of iron (III) chloride hexahydrate (4.6 g) and iron (II) chloride tetrahydrate (2.2 g) was dissolved in 100 mL water and sonicated well to dissolve completely. Then, 10 mL of 25% aqueous ammonia dropwise into the reaction mixture under the N_2 atmosphere. The precipitates were collected using an external magnet and washed with distilled water. Silica-coated nanoparticle synthesis using the stober method under MNPs (1 g) was dispersed in 50 mL of de-ionized water by ultrasonic irradiation for 20 min. Then, the

solution dispersion was centrifuged for 30 min and adjusted to 2.0 wt. %. (2 mL) of the Ferrofluid was first added with water (40 mL), the consequence suspension and (5 mL) of $\text{NH}_3\cdot\text{H}_2\text{O}$ were poured in (140 mL) of ethanol with stirring at 40°C . Then added (1 mL) of TEOS diluted in ethanol (20 mL) was dropwise added to this dispersion. The preparation of $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-Cl}$ (1 g) and KI (1.66 g) was added to a solution of urea (0.6 g) and K_2CO_3 (1.38 g) in acetonitrile (50 mL) in a round bottom flask and the mixture was stirred under reflux condition for 8h. The obtained nanoparticle was then separated by using a magnet collected from the solution and washed with aqueous ethanol followed by drying at 80°C for 12 h (**Scheme 39**).

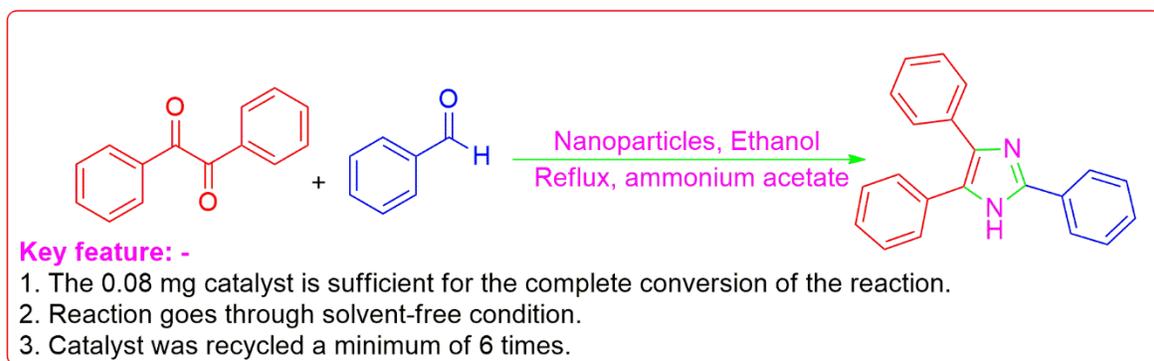
$\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-urea}$ MNPs (0.088 g) were added to a mixture of Benzil or benzoin (1.0 mmol), various substituted aromatic aldehydes (1.0 mmol), and NH_4OAc (4.0 mmol) dissolved in ethanol and stirring for appropriate times. The progress was monitored by TLC. After completion of the reaction, the catalyst was separated by an external magnet and the product was separated by using a simple filtration method. To obtain pure products purified using re-crystallization by EtOH (**Scheme 40**).



Scheme 38. Synthesis of 1, 3-thiazolidine-4-ones using $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-IL}$ MNPs



Scheme 39. Urea-functionalized silica-coated ferrite nanoparticle



Scheme 40 Synthesis of imidazole catalyzed under $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{urea}$

M. Sheykhani et al. [62] reported the synthesis of a novel co-operative Lewis acid or Brønsted base catalyst successfully synthesized and characterized by using XRD, SEM, and TEM techniques. Author this catalyst is used in the synthesis of 3, 4-dihydro-pyrimidine-2-(1H)-thione derivatives under solvent-free conditions. The Fe_3O_4 MNPs were synthesized using Ferric chloride (5.0 mmol) and ferrous chloride (2.5 mmol) was dissolved in double-distilled water (20 mL) with added slowly aqueous ammonia (25%, 40 mL) under constant stirring to maintain the pH-12. Then the addition of tetraethyl orthosilicate (TEOS) at 90 °C with vigorous stirring was continued overnight. The resulting silica-supported magnetite nanoparticle was separated with an

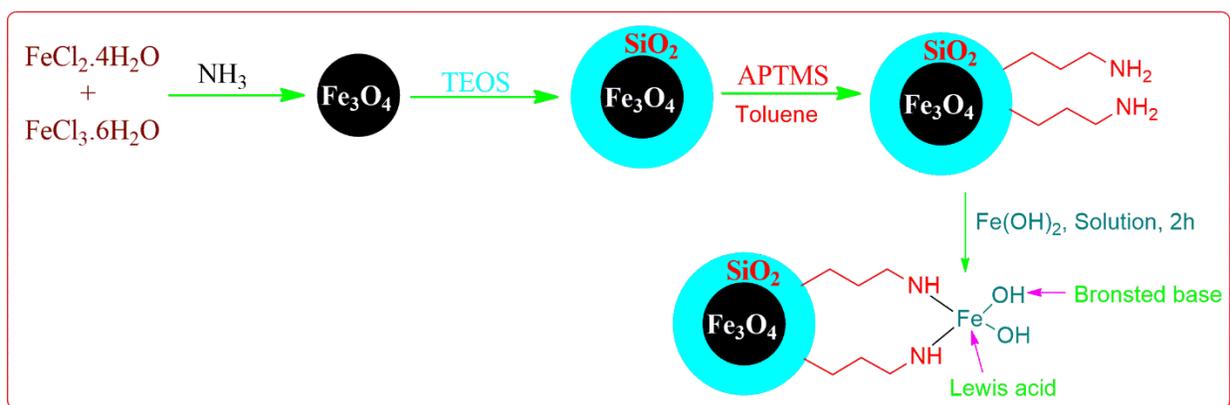
external magnet and washed with water and EtOH. Then, the final dark-brown powder was dried at 200 °C. After that, 3-Aminopropyltrimethoxysilane (4.5 mL) was added to a suspension of silica-supported magnetite (1 g) dispersed in anhydrite toluene and refluxed to 110 °C for 10 h. Afterward, the nanoparticle was collected by the magnetic field, washed with water and DCM many times, and dried at 60 °C overnight. The resulting nanoparticle was $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTMS}$ formed purely. In the next step, synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTMS-Fe}(\text{OH})_2$ sing in the presence of Ferric chloride (0.5 mmol) and potassium carbonate (2 equiv.) was dissolved in water led to the generation of $\text{Fe}(\text{OH})_2$ which was added to prepared $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTMS}$

MNPs (1 g) in water with refluxed overnight. After drying at 100 °C, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTMS-Fe(OH)}_2$ was obtained in about 89% yield (**Scheme 41**).

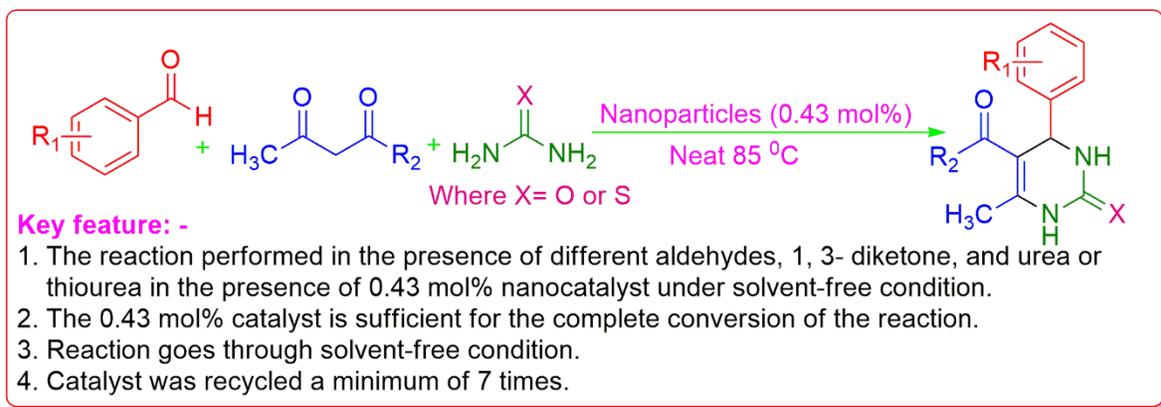
The synthesis of 3, 4-dihydro-pyrimidine-2-(1H)-one/thione derivatives (10 mg) of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTMS-Fe(OH)}_2$ catalyzed by a mixture of ethyl acetoacetate (1 mmol), an aryl aldehyde (1 Equiv.), and urea/thiourea (1.2 Equiv.) under the solvent-free reaction condition. Progress of reaction monitored on TLC by Ethyl acetate/pet ether (9:1) solvent. After completion of the reaction, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTMS-Fe(OH)}_2$ was magnetically recycled after the addition of cold EtOH. The product was purified by using simple re-crystallization from EtOH (**Scheme 42**).

J. Javidi et al. [63] reported that the synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMAN}$ magnetic porous nanosphere as a recoverable nanocatalyst for the green synthesis of Quinoxaline derivatives at room temperature will get an excellent yield of the product. In this work, the author developed new biologically active compounds those compounds show antifungal activities. The core-shell $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanocatalyst is synthesized using previous literature by the Stober method. The mixture was prepared by using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (4.8 mmol) dissolved in water (15 mL) was added to the solution of polyvinyl alcohol (PVA15000), as a surfactant, and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (4.5 mmol) in water (15 mL), which is prepared and then completely dissolving PVA in water followed by addition of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$. The resultant solution was stirred for 30 min at 80 °C. Then, hexamethylenetetramine (HMTA) (1.0 mol/l) was added drop by drop with constant stirring to produce a black solid product when the pH was 10. The resultant mixture was heated in a water bath for 2 h at 60 °C and the black magnetite solid product was filtered and washed with ethanol three times and was then dried at

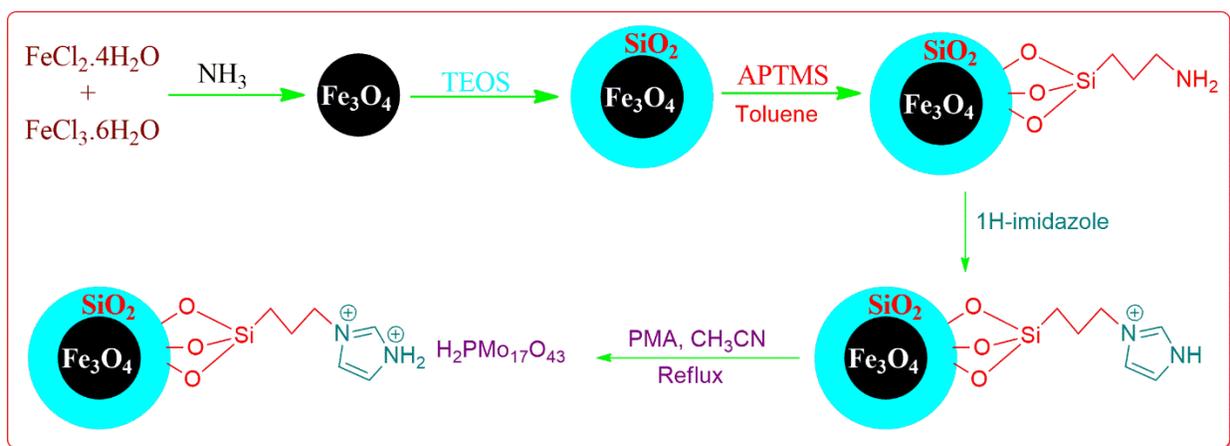
80 °C for 10h. Then Fe_3O_4 nanoparticle (2.1 mmol) was dispersed in the mixture of ethanol (50 mL), deionized water (5 mL), and drop by drop addition of tetraethoxysilane (TEOS) (0.20 mL) with vigorous stirring at room temperature than the addition of (5 mL) of NaOH (10 wt.%) with a continuous solution was stirred for 30 min at room temperature. Then the product, $\text{Fe}_3\text{O}_4@\text{SiO}_2$, was separated by an external magnet, and washed with deionized water and ethanol three times, and dried at 80 °C for 10h. In the second step, synthesis of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ nanoparticles using (5 mmol) of bulk $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (PMAb) was dispersed in (50 mL) n-Octane, and the resulting dispersion was stirred continuously for 30 min at ambient temperature to form a homogeneous dispersion. This dispersion was transferred into a Teflon-lined stainless autoclave filling 80% of the total volume. The autoclave was sealed under constant temperature at 150 °C for 12h. The autoclave was then cooled to room temperature. Finally, the resulting powder was filtered and washed many times by Octane, and dried in a vacuum at 80 °C for 12h. Finally, the synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (1 g) nanoparticles was dispersed into the solution of 3-chlorotriethoxypropylsilane (1 mmol), and imidazole (1 mmol) in p-xylene (20 mL), and the resultant mixture was under reflux for 24h under nitrogen atmosphere. After refluxing for about 24h, the mixture was cooled to room temperature, the nanoparticle was recovered by an external magnet, and the product was washed with xylene to remove unreacted material and dried at 70 °C for 6h. $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid}$ (1.0 g) was dispersed into an acetonitrile solution of PMAb (1.0 mmol) and the mixture was refluxed for 24h under a nitrogen atmosphere. After 24 h complete the reaction, then the mixture was filtered by an external magnet, washed with acetonitrile and dichloromethane, and dried at 70 °C for 6h (**Scheme 43**).



Scheme 41. Schematic representation of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTMS-Fe(OH)}_2$ MNPs



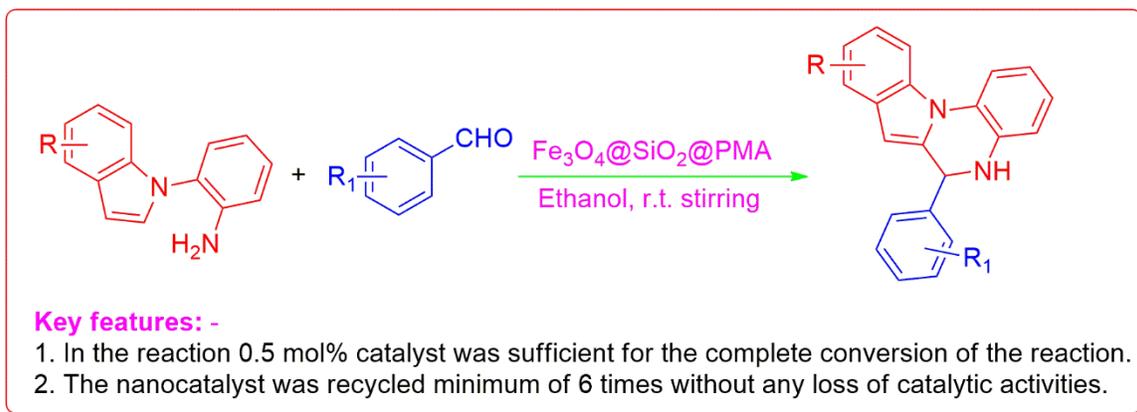
Scheme 42 Synthesis of 3, 4-dihydro-pyrimidine-2-(1H)-one/thione derivatives



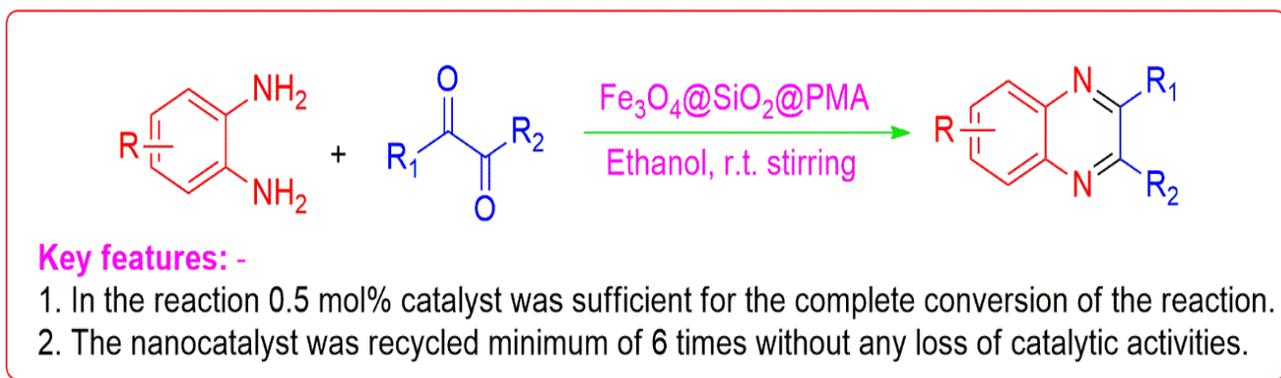
Scheme 43. Preparation of Fe₃O₄@SiO₂-PMA

The synthesis of Quinoxaline derivatives in the presence of aromatic amine (1 mmol) and carbonyl compounds (1 mmol) dissolved in EtOH (5 mL) was added Fe₃O₄@SiO₂-imid-PMA (0.03 g). Progress of the reaction is monitored on thin-layer chromatography

(TLC). After completion of the reaction, the mixture was extracted by ethyl acetate, and the catalyst was separated by a magnetic field. The dissolved organic layer is evaporated to obtain a pure product (**Schemes 44 & 45**).



Scheme 44. Synthesis of Quinoxaline derivative from aldehyde



Scheme 45. Synthesis of Quinoxaline derivative from Benzil

The author developed new biologically active compounds; those compounds show antifungal activities. The Selected compounds were dissolved in acetone as per 60 mg/mL. The mixture was then added to sterilized Petri dishes. All types of fungi were incubated in PDA at 30 °C for about five days will get the mycelium for the antifungal assays, and a mycelia disk in 5 mm diameter cut from the culture medium was removed with a sterilized inoculation needle and inoculated in the center of the PDA Petri dishes. Acetone was added to PDA after that, the sample was prepared by mixing Acetone with PDA, without any compounds (**Fig. 1**). Somayeh Hashemi-Uderjia et al. [64] reported the synthesis of novel Fe₃O₄@FSM-16-SO₃H nanoparticles used for the preparation of pyrano[2,3-c]pyrazoles derivatives under an aqueous alcoholic condition with refluxing reaction mixture within 30 min to give moderate to excellent yield (**Scheme 46**).

The prepared Fe₃O₄@FSM-16-SO₃H nanoparticles have been used for the preparation of pyrano[2,3-c]pyrazole derivatives under the aqueous-alcoholic condition. The reaction performed between aryl aldehyde, malononitrile, 3-methyl-1-phenyl-2-pyrazoline-5-one, and Fe₃O₄@FSM-16-SO₃H (30 mg) was stirred in a mixture of aqueous ethanol at reflux conditions. The reaction progress was monitored on TLC. After the completion of the reaction, the mixture was extracted with ether, and nanoparticles were collected through an external magnetic field (**Scheme 47**).

N Janaki et al [65] reported the synthesis of Fe₃O₄/FDU-12 nanocatalyst for the oxidation of alcohol derivatives. A highly efficient and magnetically separable nanocatalyst applicable for the oxidation of primary,

secondary, and allyl Alcohol derivatives has been studied. The catalyst shows the fastest reaction rates with electron-rich benzylic and allylic alcohols (**Scheme 48**).

N Tandon *et al.* [66] reported the synthesis of a novel Montmorillonite-supported silica-coated ferrite magnetic nanoparticle successfully. Then nanoparticles were analyzed by using FT-IR, PXRD, FE-SEM, and EDX techniques. The silica-coated nanoparticles were dispersed in ethanol and sonicated well for about 15 min. Then add 0.5 g Montmorillonite and the mixture was stirred for about 20h. After that, nanoparticles were collected through an external magnetic field and dried in an oven (**Scheme 49**). The prepared nanoparticles were used for the acylation of alcohols, phenols, amines, and thiol derivatives under solvent-free conditions. In the reaction 20 mol% catalyst is sufficient for complete conversion of the reaction. After completion of the reaction nanoparticles were recycled a minimum of 10 times without loss of catalytic activities (**Scheme 50**). Shripad *et al.* [67] reported the prepared nanocatalyst has been used for the N-Boc protection of amine substrate under solvent-free conditions that give the best results. In work, amine substrates containing electron-donating and electron-withdrawing and aliphatic substrates have been studied. The catalyst was reused ten times in this work without losing its catalytic activity (**Scheme 51**). Shripad *et al.* [75] reported the prepared nanocatalyst has been used for the multicomponent reaction (Betti reaction) under solvent-free conditions that give the best results. In work, amine substrates containing electron-donating and electron-withdrawing and aliphatic substrates have been studied. The catalyst was reused 15 times in this work without losing its catalytic activity (**Scheme 52**).

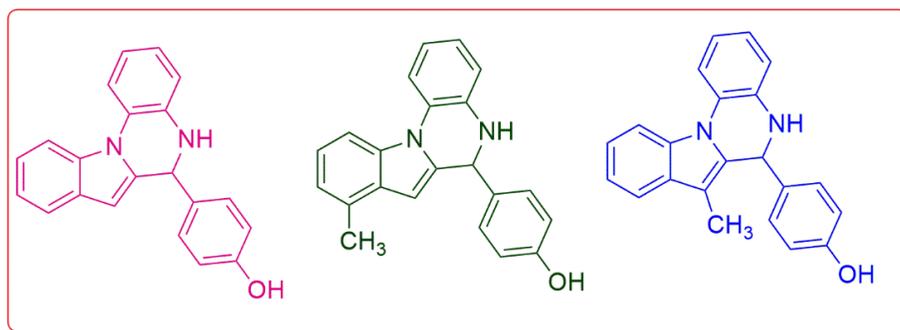
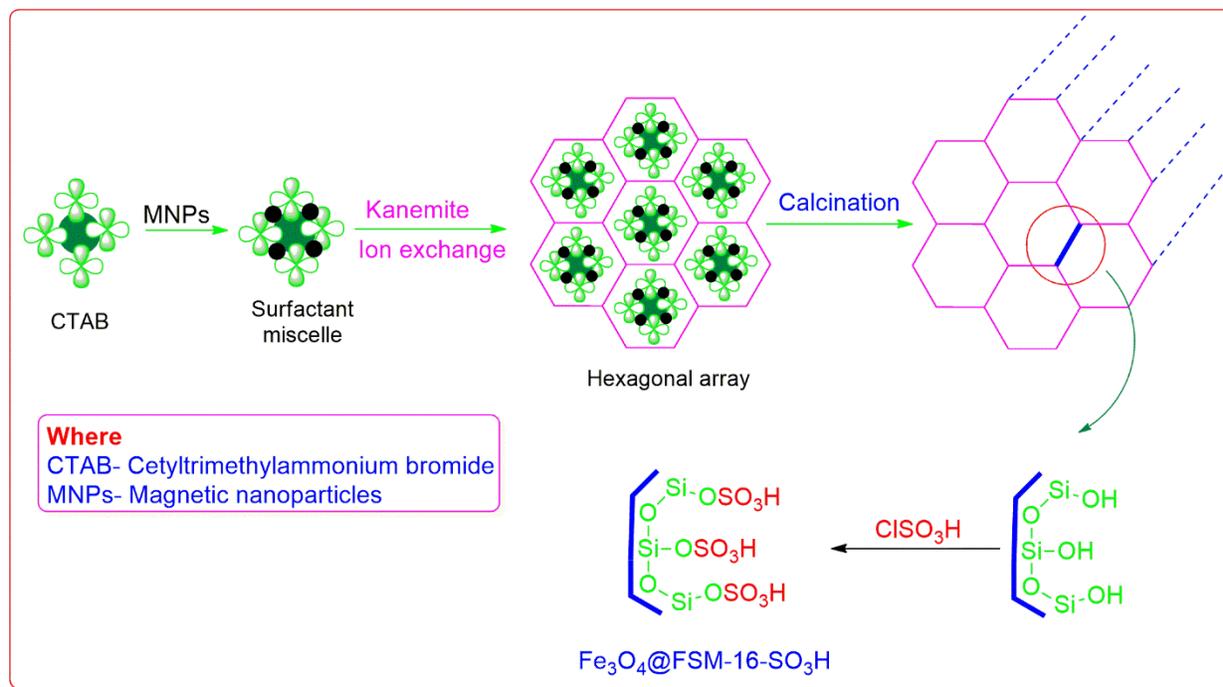
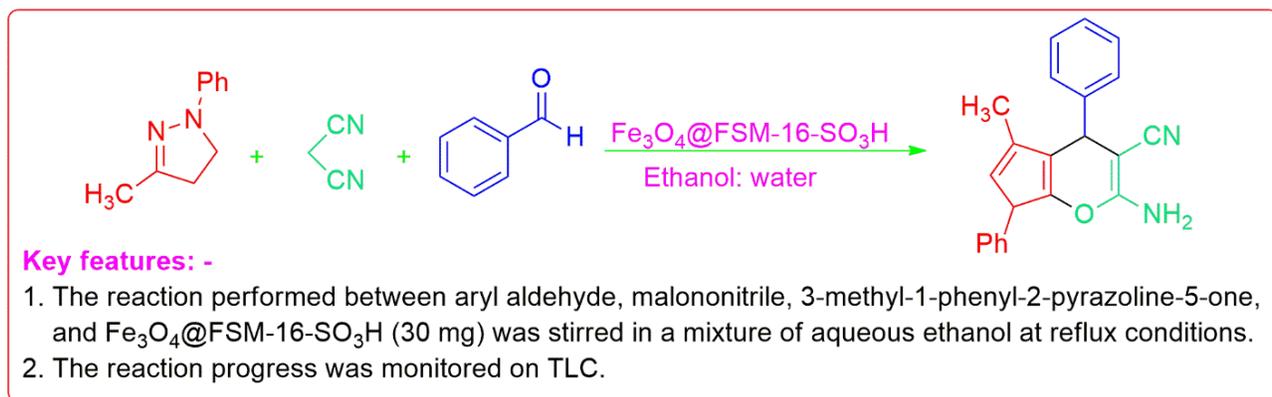


Fig. 1. Compounds show the antifungal activity



Scheme 46 Synthesis of $\text{Fe}_3\text{O}_4@\text{FSM-16-SO}_3\text{H}$ nanoparticle using Co-precipitation method



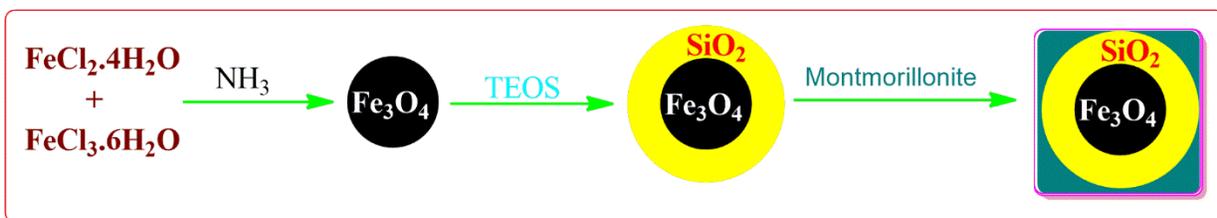
Scheme 47 Synthesis of pyrano[2,3-c]pyrazoles derivatives catalyzed by $\text{Fe}_3\text{O}_4@\text{FSM-16-SO}_3\text{H}$



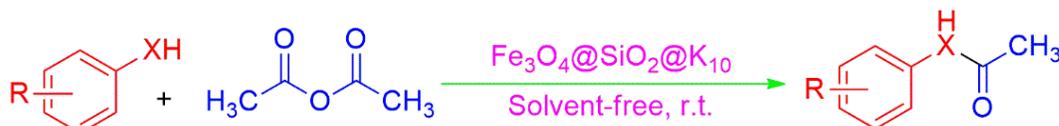
Key features: -

1. A highly efficient and magnetically separable nano-catalyst applicable for the oxidation of primary, secondary, and allyl Alcohol derivatives has been studied.
2. The reaction progress was monitored on TLC.
3. The catalyst shows the fastest reaction rates with electron-rich benzylic and allylic alcohols.

Scheme 48 Oxidation of alcohol derivatives catalyzed under Fe₃O₄/FDU-12 nanocatalyst



Scheme 49. Synthesis of Fe₃O₄@SiO₂@K₁₀ nanoparticle using Co-precipitation method

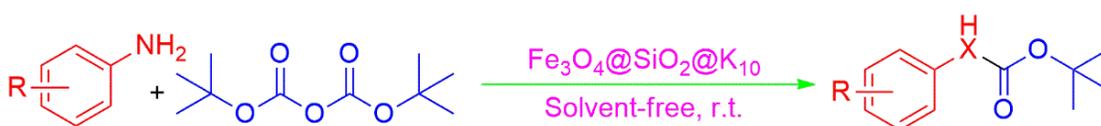


Where
R= alkyl, NO₂, halogens
X= O, N, & S

Key features: -

1. In the reaction, 20 mol % catalyst is sufficient for the complete conversion of reaction.
2. In this work various alcohol, phenol, amine, and thiols substrate are studied.
3. The nancatalysts was recycled a minimum of 10 times.

Scheme 50. Fe₃O₄@SiO₂@K₁₀ nanoparticles catalyzed under acylation of O, N, and S substrate

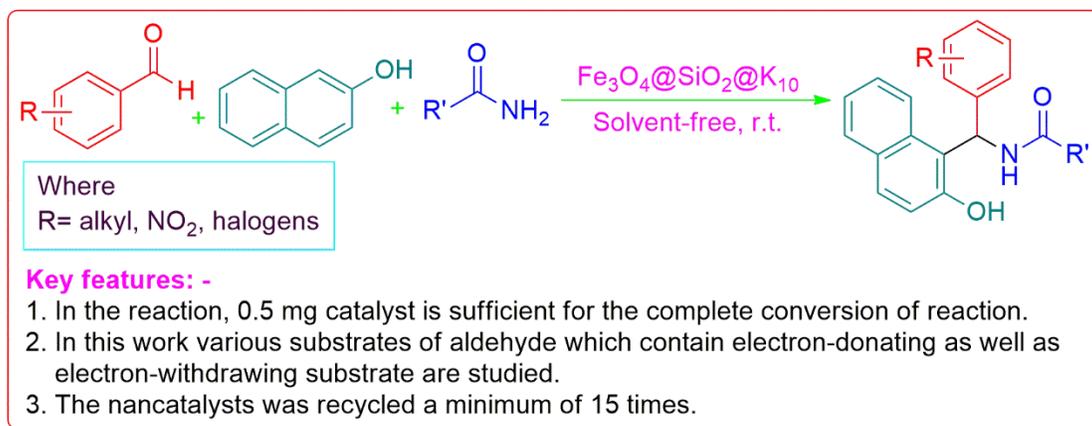


Where
R= alkyl, NO₂, halogens

Key features: -

1. In the reaction, 20 mol % catalyst is sufficient for the complete conversion of reaction.
2. In this work various substrates of amines which contain electron-donating as well as electron-withdrawing substrate are studied.
3. The nancatalysts was recycled a minimum of 10 times.

Scheme 51. Fe₃O₄@SiO₂@K₁₀ nanoparticles catalyzed under N-Boc protection of amine substrates

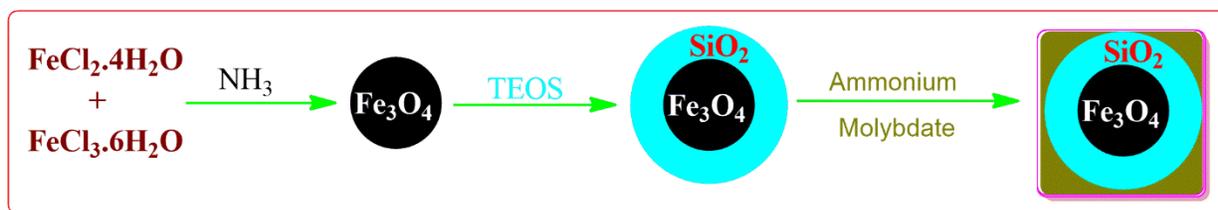


Scheme 52. Fe₃O₄@SiO₂@K₁₀ nanoparticles catalysed by multicomponent reaction (Betti reaction)

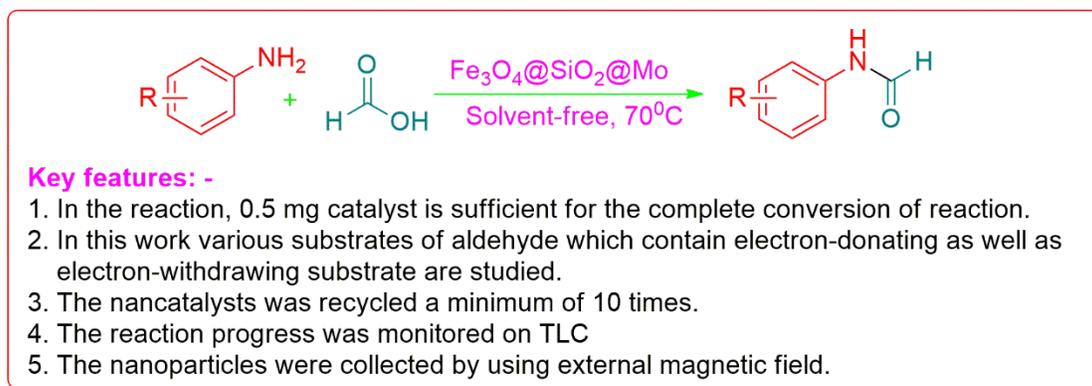
R Tandon *et al.* [68] reported the synthesis of novel Molybdate-supported silica-coated ferrite magnetic nanoparticles and that catalysts were used for N-formylation reaction. Then nanoparticles were characterized by using FT-IR, PXRD, FE-SEM, and EDX techniques. The silica-coated nanoparticles were added to ethanol and stirred well for about 24 hours. Then add (0.6 g) ammonium molybdate and the mixture was stirred for about 12h. After that, nanoparticles were collected through an external magnetic field and dried in the oven (**Scheme 53**).

The prepared nanocatalyst was used in the N-formylation reaction. In this work, various aromatic, aliphatic, cyclic, and heteroaromatic compounds have been studied. Interestingly, the nanoparticles give the best result in the reaction (**Scheme 54**).

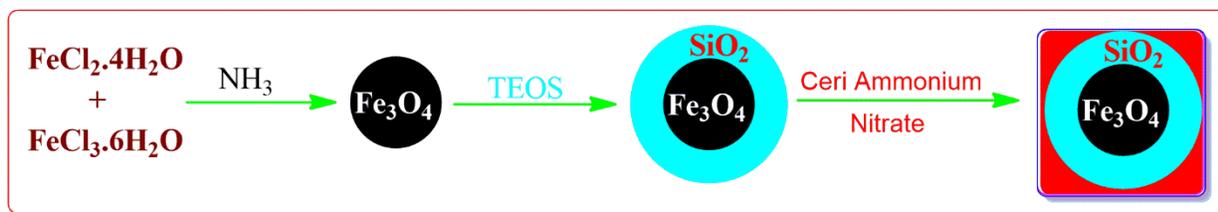
Shripad Patil *et al.* [69] reported the synthesis of novel cerium oxide-supported silica-coated ferrite magnetic nanoparticles and that catalysts were used for the protection of amine and phenols substrate using di-ter-butyl carbonate. Then the prepared nanoparticles were characterized by using FT-IR, PXRD, FE-SEM, EDX, ICP-OES, TGA, and TEM techniques (**Scheme 55**).



Scheme 53. Synthesis of Fe₃O₄@SiO₂@Mo nanoparticle using Co-precipitation method



Scheme 54. Fe₃O₄@SiO₂@Mo nanoparticles catalyzed under N-formylation of amine substrates



Scheme 55. $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Ce}$ nanoparticles catalyzed under *N*-Boc and *O*-Boc protection

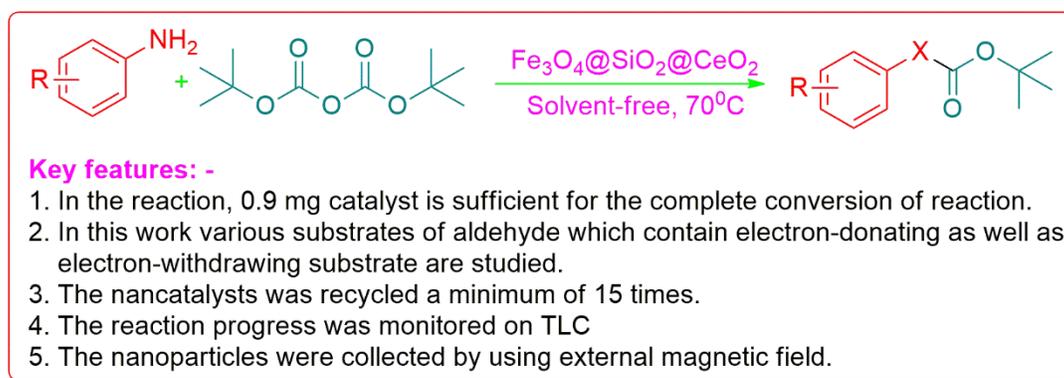
The prepared nanocatalyst was used in the protection of amine and phenol derivatives (*N*, *O*-Boc). In this work, various aromatic, aliphatic, cyclic, and heteroaromatic compounds have been studied. After that, nanoparticles were collected through an external magnetic field and dried in the oven (**Scheme 56**).

Shripad Patil *et al.* [70] reported the synthesis of novel Cobalt-supported silica-coated ferrite magnetic nanoparticles and that catalysts were used for *N*, *O*, and *S*-acylation reactions. Then nanoparticles were characterized by using FT-IR, PXRD, FE-SEM, EDX, TEM, TGA, and ICP-OES techniques. Then add (0.2 g) cobalt chloride and the mixture was stirred for about 48h. After that, nanoparticles were separated through an external magnet and dried in the oven at 60 °C (**Scheme 57**).

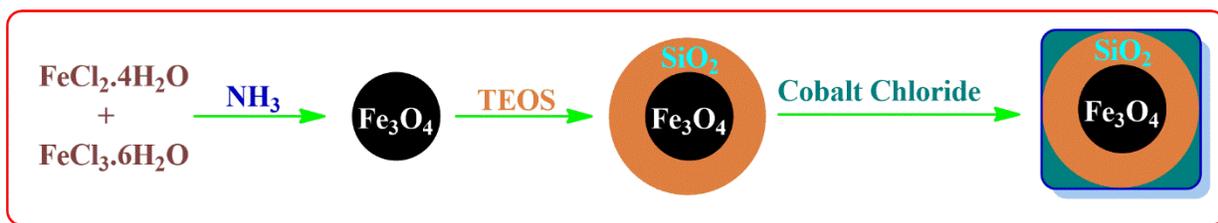
The prepared nanoparticles were used for the acylation of alcohols, phenols, amines, and thiols derivatives under solvent-free conditions. In the reaction, 0.09 mg catalyst is sufficient to complete the reaction. After completion of the reaction nanoparticles were recycled

a minimum of 15 times without loss of catalytic activities. This reaction gives the best result after 10 to 15 cycles (**Scheme 58**).

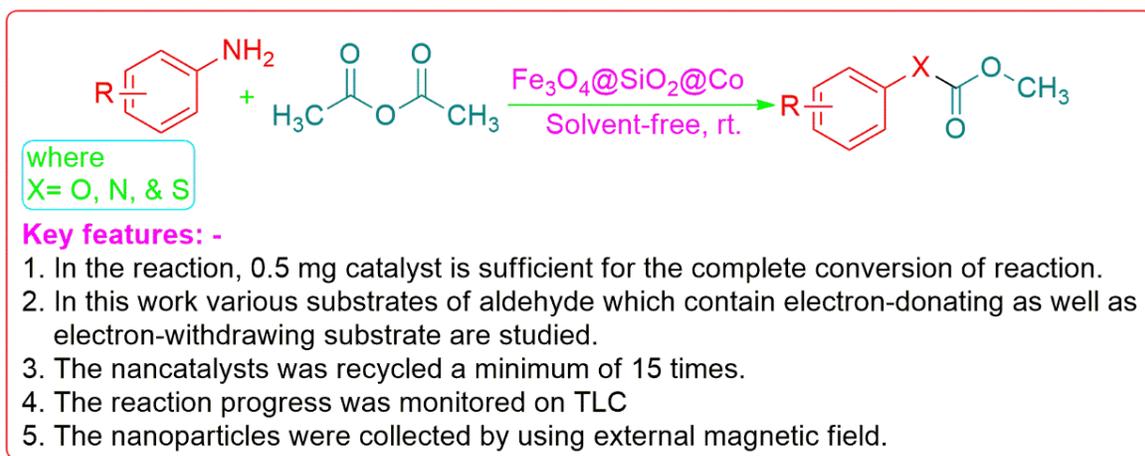
K Nouri and co-workers [86] reported to synthesis of palladium-supported imidazolium organometallic complex on iron oxide nanoparticles and those catalyst has been used Suzuki coupling reaction. Then nanoparticles were characterized by using X-ray diffraction (XRD), Raman, transmission electron microscopy (TEM), thermogravimetric analysis (TGA), energy-dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), inductively coupled plasma (ICP), and vibrating sample magnetometer (VSM), and Fourier transform infrared (FT-IR), techniques. The catalytic effectiveness of this novel nanocatalyst was evaluated in the mild Heck-Mizoroki and Suzuki-Miyaura cross-coupling processes using PEG-400 as an environmentally friendly and recyclable solvent. Additionally, this stable nanocatalyst is easily extracted from the reaction mixture, recovered, and re-used for at least 8 cycles without noticeably losing its catalytic properties (**Scheme 59**).



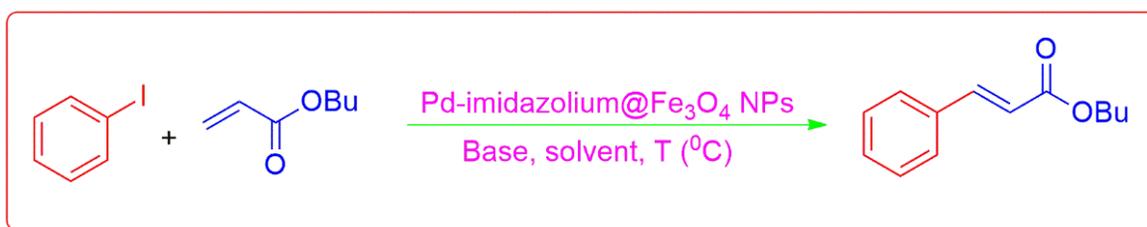
Scheme 56. $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Ce}$ nanoparticles catalyzed under *N*-Boc and *O*-Boc protection



Scheme 57. $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Co}$ nanoparticles catalyzed under *N*, *O*, and *S*-acylation reaction



Scheme 58. $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Co}$ nanoparticles catalyzed under acylation of amine, phenol, alcohol, and thiols derivatives

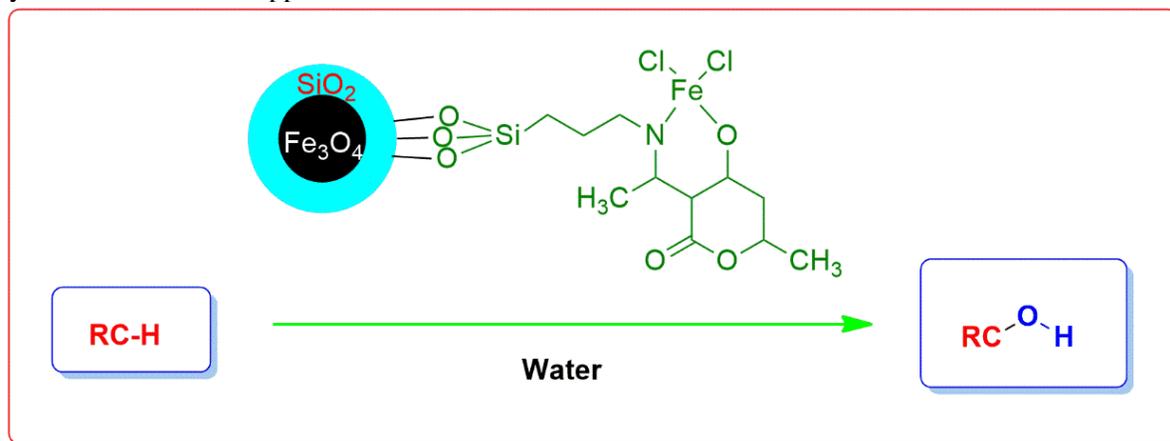


Scheme 59. Palladium-supported imidazolium organometallic complex on iron oxide nanoparticles used for the coupling reaction

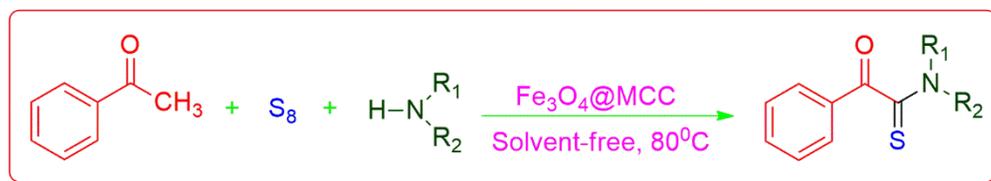
M. Majedi reported [87] the synthesis of novel magnetic nanoparticles and used for the oxidation reaction. The development, production, and analysis of the structure of a new iron (III) complex based on DHA attached to silica-coated magnetite nanoparticles are described by the researchers. The oxidation process involving C-H bonds in the benzylic position of aromatic substrates was described by the researcher using a newly manufactured unique magnetic nanocatalyst. (**Scheme 60**)

D. Shah and co-workers [88] reported the synthesis of microcrystalline cellulose supported with iron oxide

nanoparticles has been used for the synthesis of thioglyoxamide derivatives under microwave irradiation. As determined by XPS, PXRD SEM, TEM, EDS, FT-IR HR-TEM, and EDX studies, this produced catalyst exhibits constant iron oxide NP particle size. To get a decent yield quickly, a wide range of thioglyoxamides are synthesized under optimal reaction conditions. The described catalyst is similarly applicable for the gram-scale synthesis of thioglyoxamides and may be recycled up to five times without significantly losing activity (**Scheme 61**).



Scheme 60. Iron (III) complex based on DHA nanocatalyst used for oxidation reaction



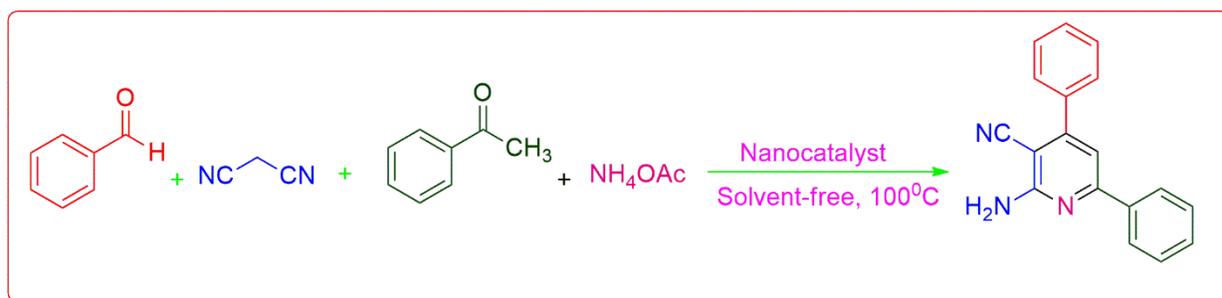
Scheme 61. Microcrystalline cellulose supported with iron oxide nanoparticles is used for the synthesis of thioglyoxamide derivatives

S. Motahari et reported [89] the synthesis of Co (II) supported on modified magnetic iron oxide nanoparticles and used for the synthesis of 2-Amino-3-Cyanopyridines. The reaction performed between aldehydes, acetophenones, malononitrile, ammonium acetate, and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Si}(\text{CH}_2)_3\text{NH}@CC@\text{Im}@\text{Co}$ nanocatalyst. The use of a straightforward set of easily accessible starting materials allowed for the efficient one-pot synthesis of 2-amino-3-cyanopyridines with high product yields and quick reaction times. The six times of recycling and recovery are possible for the developed green heterogeneous catalyst. (**Scheme 62**)

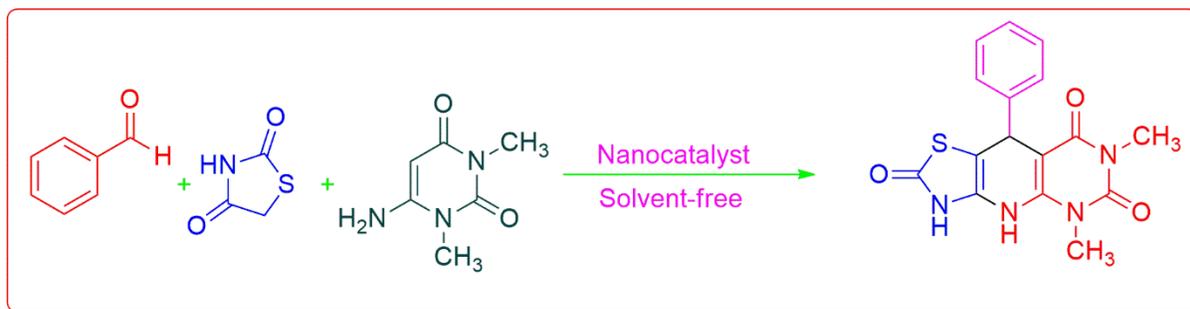
S. Alavinia [90] reported the synthesis of Ionic liquids (ILs) can be replaced by deep eutectic solvents (DESs), which are made by mixing the components and the hydrogen bonds that have formed between them. The melting point of DES components significantly

decreases as compared to their pure counterparts due to the strong hydrogen bond interactions. Fe_3O_4 nanoparticles' (NPs) function in lactic acid a new deep eutectic solvent, melamine: NH_4Cl , was used in the environmentally friendly synthesis of pyrido[2,3-d]pyrimidine derivatives (**Scheme 63**).

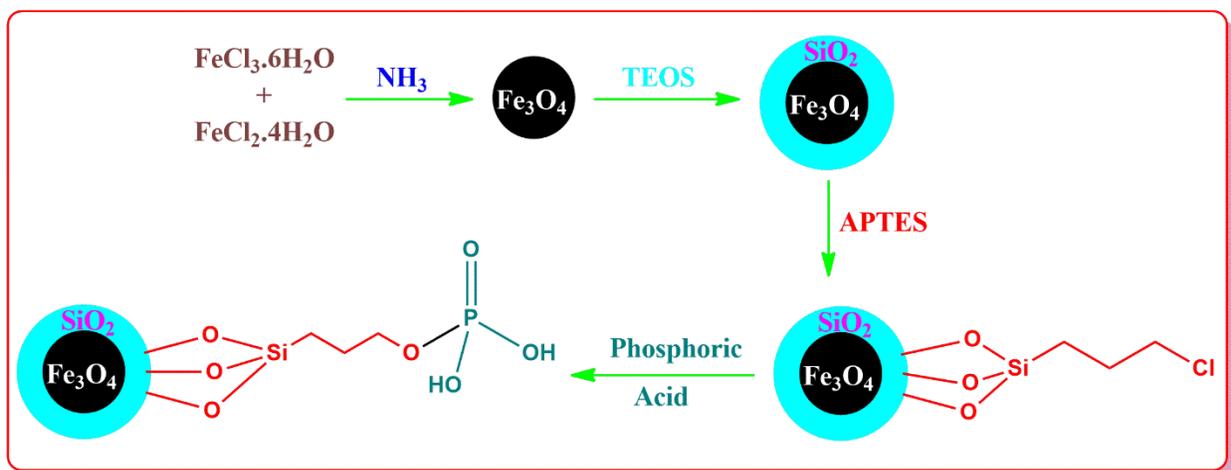
I. Sedighimehr and co-workers [91] reported the synthesis of novel pyrano [2, 3-F] chrome-done derivatives catalyzed by using phosphoric acid functionalized silica-coated iron oxide nanoparticles. The prepared nanoparticles were analyzed PXRD, FE-SEM, TGA, FT-IR, VSM, and EDS techniques (**Scheme 64**). The synthesized organic compounds were analyzed using FT-IR, NMR, CMR, and melting point. The reusability investigation of the newly developed nanosolid acid catalyst revealed that the catalytic stability is almost entirely preserved for up to five subsequent cycles (**Scheme 65**).



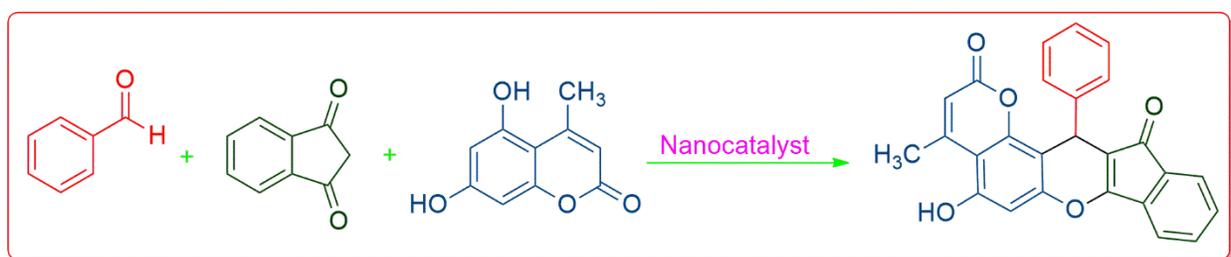
Scheme 62. Synthesis of Co (II) supported on modified magnetic iron oxide nanoparticles and used for the synthesis of 2-Amino-3-Cyanopyridines



Scheme 63. Synthesis of Co (II) supported on modified magnetic iron oxide nanoparticles and used for the synthesis of 2-Amino-3-Cyanopyridines.



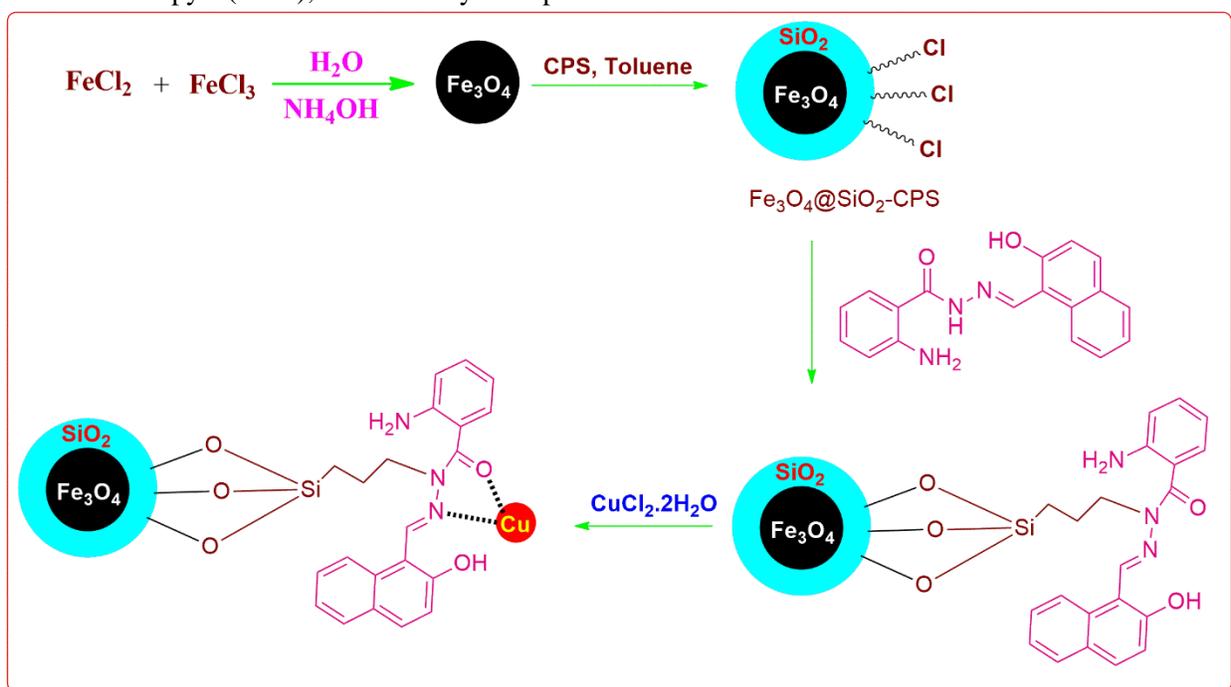
Scheme 64. Preparation of $\text{Fe}_3\text{O}_4@ \text{SiO}_2-(\text{CH}_2)_3\text{OPO}_3\text{H}_2$ nanoparticles



Scheme 65. $\text{Fe}_3\text{O}_4@ \text{SiO}_2-(\text{CH}_2)_3\text{OPO}_3\text{H}_2$ nanoparticles used for the synthesis of pyrano [2, 3-F] chrome-done derivatives

F. Rohmatpour et al [92] reported the synthesis of copper (II) Schiff base complex immobilized on Fe_3O_4 nanoparticles and used for the preparation of 2-amino-4*H*-benzo[*h*] chromenes derivatives as well as the reduction of 4-nitrophenol substrate. Scanning electron microscopy (SEM), Inductively coupled

plasma (ICP), vibrating sample magnetometry (VSM), powder X-ray diffraction (XRD), and energy-dispersive X-ray spectroscopy (EDX) techniques were used to thoroughly characterize the as-prepared $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ single bond CPS-CuL and its precursors (**Scheme 66**).



Scheme 66. Preparation of $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{CPS-CuL}$ nanoparticles

The prepared nanoparticles have been used for the synthesis of 2-amino-4*H*-benzo[*h*] chromenes derivatives. Similarly, the catalyst was used for the reduction of nitro group-containing compounds. Both reactions have been studied by various substrates like electron-donating as well as electron-withdrawing substrates. Some benefits of this work include high reaction conversion, rapid reaction times, and straightforward procedures. Additionally, by employing an external magnet to extract it from the reaction mixture, the nanocatalyst may be utilized again for both processes with no degradation in its catalytic performance (**Scheme 67**).

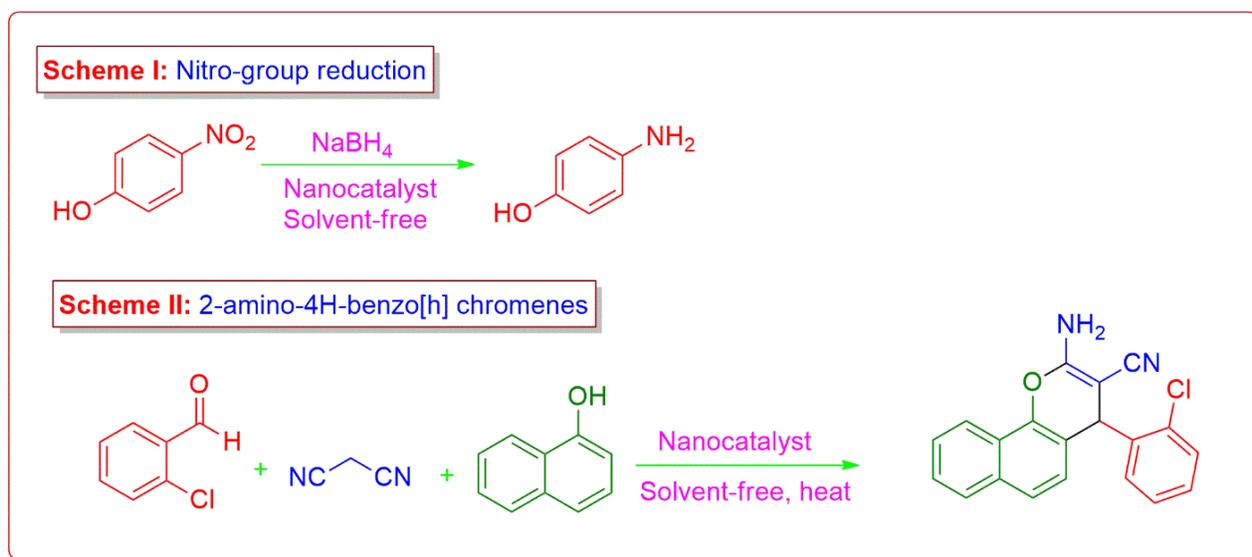
R. Rahimizadeh and co-workers reported [93] that the stabilization of the sulfonic group on the surface of the silica-coated Fe₃O₄ nanoparticles allowed for the synthesis of the unique functionalized silica-coated Fe₃O₄ nanoparticles, Fe₃O₄@SiO₂-TETA-SO₃H. The prepared nanoparticles were characterized by X-ray diffraction, field emission scanning electron microscopy, Fourier transform infrared spectroscopy, energy dispersive X-ray spectroscopy, thermal gravimetric analysis, and vibrating sample magnetometer techniques (**Scheme 68**).

For a safe one-pot synthesis of certain novel amido alkyl naphthols employing fatty acids as bio-based materials, the activity of the Fe₃O₄@SiO₂-TETA-SO₃H nanoparticles as a catalyst were examined. This reaction

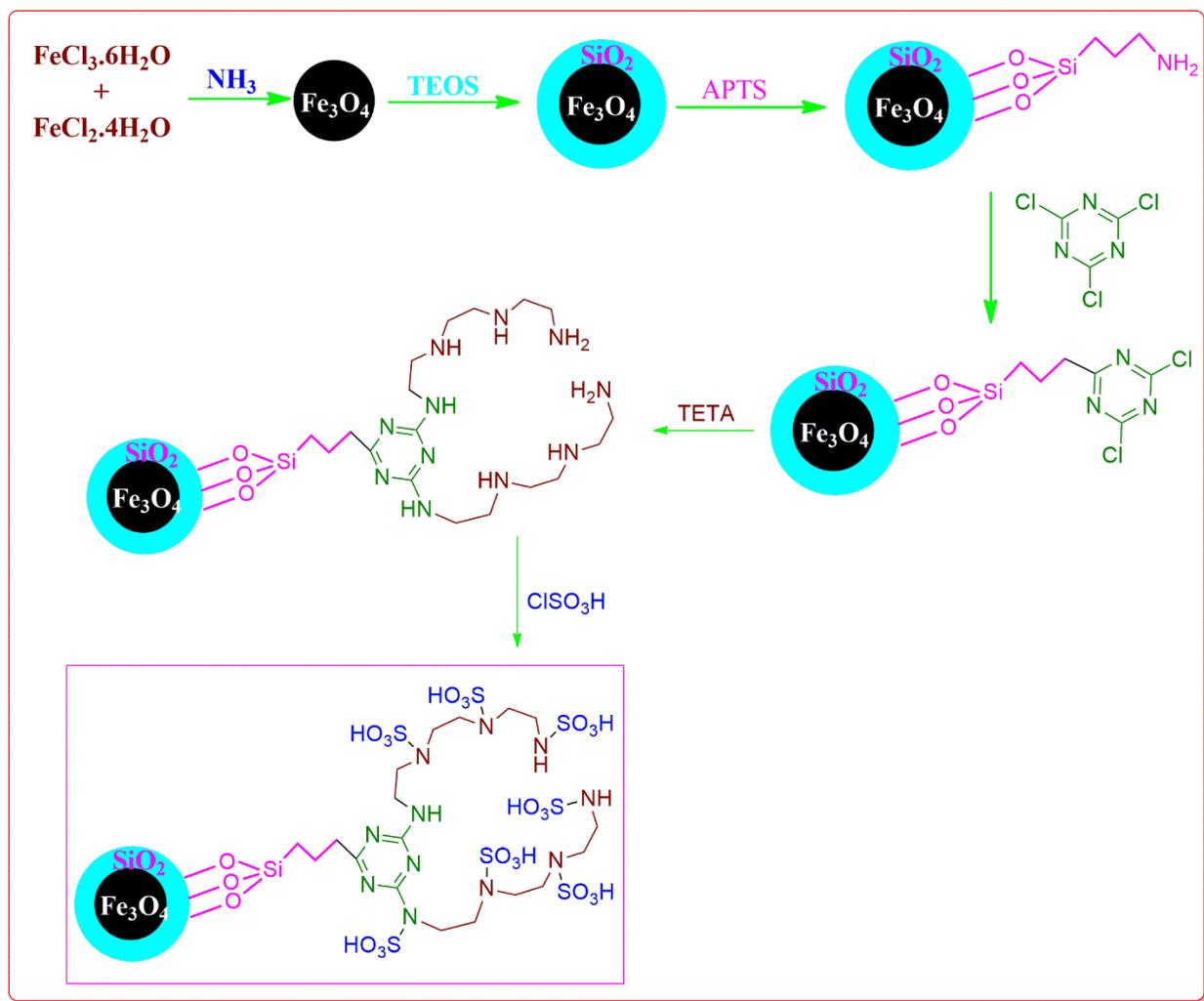
produced the necessary compounds with quick reaction times, excellent yields, and simple work-up procedures. Six cycles of recycling and reusing this acidic catalyst were possible without noticeably changing its activity. Additionally, *Staphylococcus aureus* (ATCC 25,923) and *Escherichia coli* (ATCC 25,922) bacteria were used to test the biological activity of the produced fatty amidoalkyl naphthols (**Scheme 69**).

4. Conclusions

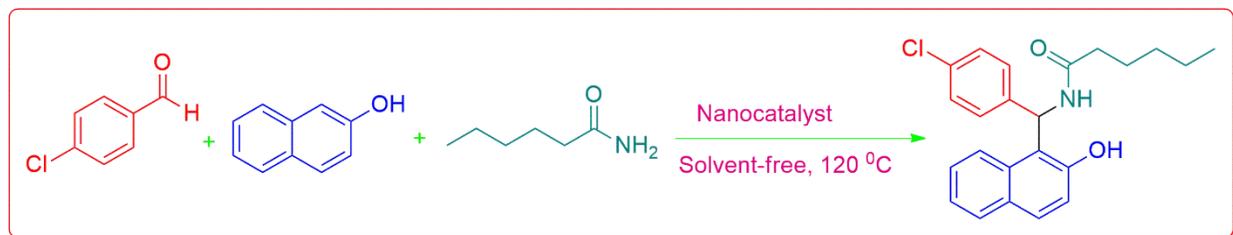
The synthesis of the magnetically recyclable nanoparticle by various functionalized compounds is useful in organic synthesis reactions. Nanocatalyst is used in the reaction and acts as a green acid catalyst, those nanocatalyst is highly active and also recyclable. Magnetic nanoparticle which was dopping by using green acids, metal oxides, ionic liquid, etc. This article briefly focuses on synthesized magnetic nanoparticles used for the coupling reaction and multicomponent reaction. The green chemistry approach is the synthesis of such catalysts which was the best to take catalyst for the organic reaction. To date, the best results are found with ferrite nanoparticles and silica-coated ferrite nanoparticles due to their activity and capacity to recycle. The advantages of this review article, we discussed recently synthesized and developed in ferrite nanoparticle is used in coupling reaction and multicomponent reaction. That novel catalyst will also be used for some other organic reactions.



Scheme 67. The Fe₃O₄@SiO₂CPS-CuL nanoparticles used in nitro group reduction and 2-amino-4*H*-benzo[*h*] chromenes



Scheme 68. Preparation of Fe₃O₄@SiO₂-TETA-SO₃H nanoparticles



Scheme 69. Betti base formation catalyzed under Fe₃O₄@SiO₂-TETA-SO₃H nanoparticles

Acknowledgements

The authors are grateful for significant support from the School of Chemical Engineering and Physical Sciences, Department of Chemistry, Lovely Professional University, Phagwara-144411 Punjab. Also thankful for the Rayat Shikshan Sanstha's, Principal of Dada Patil Mahavidyalaya, Karjat-414402, Maharashtra, India.

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