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Cobalt Ferrite Nanoparticles (CoFe_2O_4) As Catalyst and Support: Magnetically Recoverable Nanocatalyst in Organic Synthesis



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ABSTRACT

The recovery and reusability of catalysts is an important aspect of modern catalysis research, especially in organic synthesis. Compared to conventional separation, magnetic separation has emerged as a robust, highly efficient, easy, and rapid separation technique for products and catalysts. Cobalt ferrite nanoparticles are a well-known material, recognized as CoFe_2O_4 MNPs, and can be used as both catalyst and versatile support for the functionalization of metals, organocatalysts. In recent times, catalysis research has experienced a renaissance in the area of the utility of cobalt ferrite (CoFe_2O_4 MNPs) nanocatalysts based on their ability for recovery and reusability; the activity of these CoFe_2O_4 MNPs was investigated in a category of organic reactions. In this review, the fabrication, characterization, and application of cobalt ferrite (CoFe_2O_4 MNPs) nanocatalysts (CF-MNPs) in organic reactions have been well summarized.

1. INTRODUCTION:

1.1 Catalyst:

Catalysis plays an increasingly crucial role in chemical processes, and it is widely used at the heart of innumerable chemical processes from scientific research in academic laboratories to economical research in industrial laboratories¹. The catalyst is very important in chemistry science especially in organic synthesis; it can greatly promote the chemical processes and reactions and effectively and sustainably synthesize products². The development of new, sustainable chemical processes for the synthesis of natural products, drugs, and biologically active molecules is impossible without the use of catalysis. A catalyst ensures that a specific chemical reaction requires less energy (such as heat). In recent times, catalysts and catalytic reactions have attracted special attention to finding meaningful applications in the pharmaceutical and fine chemical industries³. Catalysis has possessed a key role in improving and developing organic synthesis especially in medical chemistry and has become one of the most economically and ecologically impacting technologies so far². The modern era of organic synthesis is shifting towards the path of creative strategies which fundamentally underline or focus on the concept of green chemistry especially the use of sustainable and green catalysts¹.

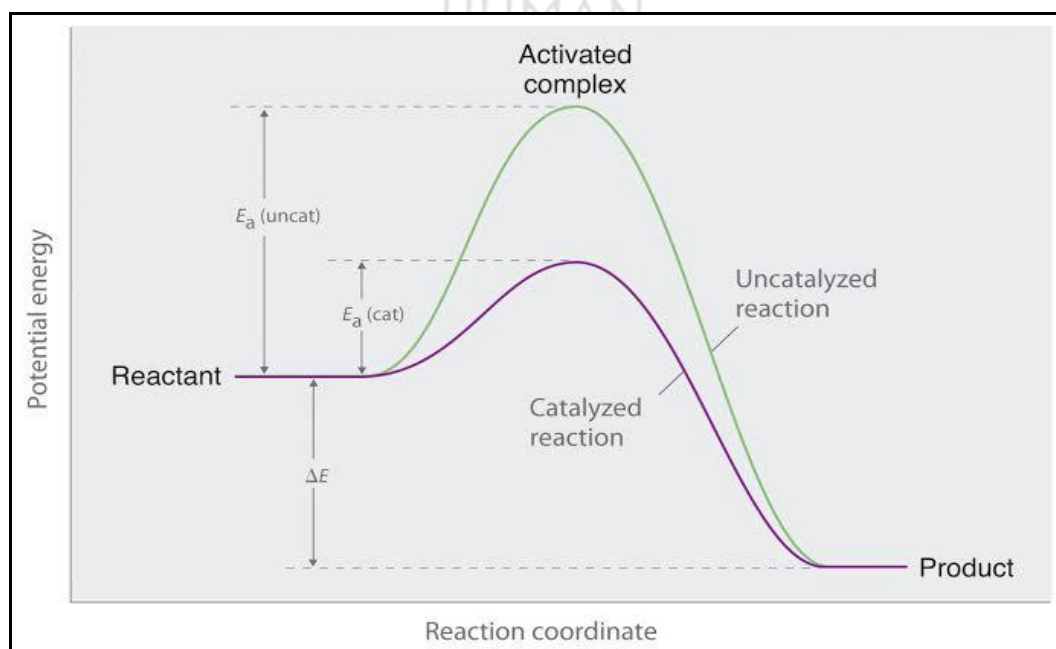


Figure No. 1 Effect of catalyst on activation energy

A catalyst accelerates a chemical reaction. It does so by forming bonds with the reacting molecules, and by allowing these to react to a product, which detaches from the catalyst, and leaves it unaltered such that it is available for the next reaction. We can describe the catalytic reaction as a cyclic event in which the catalyst participates and is recovered in its original form at the end of the cycle. Let us consider the catalytic reaction between two molecules A and B to give a product P. The cycle starts with the bonding of molecules A and B to the catalyst. A and B then react within this complex to give a product P, which is also bound to the catalyst. In the final step, P separates from the catalyst, thus leaving the reaction cycle in its original state.

2. Types of Catalyst:

There are mainly two types of catalyst homogeneous and heterogeneous catalyst.

2.1 Homogeneous Catalyst:

Catalysts can be divided into two types depending on the reaction phase that they occupy: homogeneous and heterogeneous. Homogeneous catalysis is a type of catalysis in which the catalyst operates in the same phase as the reactants, generally dissolved in the reaction medium; chemists are unanimous on this theory. In a homogeneous catalytic system, all catalytic sites are accessible because of their solubility in the reaction medium⁴; it is possible to tune the chemo-, region- and enantioselectivity of the catalyst⁵. Homogeneous catalysts have a series of other advantages such as high selectivity, better yield, high turnover numbers, and easy optimization of catalytic systems by modification of ligand and metals^{4, 6, 7, 8}. But here a notable disadvantage is glaring; separating homogeneous catalysts from the desired products or reaction medium is a difficult, tedious, and time-consuming task and needs a series of costly and specific techniques⁹. It is essential to remove the catalyst because metal contamination is highly regulated, especially in the drug and pharmaceutical industry⁶. Also, it is not compatible with the principles of green chemistry in modern catalysis science, especially from an economic standpoint⁹. To address the separation problems in homogeneous catalysis, chemists focused on designing new, green, and effective heterogeneous catalytic systems.

2.2 Heterogeneous Catalyst:

Heterogeneous catalysis is a type of catalysis in which the catalyst is present in a different or separate phase; normally the catalyst is a solid and the reactants are gas or liquid. In recent

times, heterogenization of active molecules on support materials (such as inorganic silica and organic polymers) has been introduced as an efficient strategy for developing eco-friendly catalytic systems that facilitate the recovery and reusability of the catalysts. However, the activities and selectivity of heterogeneous catalysts are generally lower than those of their homogeneous counterparts, due to the lower dimensionality of the interaction between the components and the catalyst surface¹⁰. This becomes the crucial factor that restricts it from developing well². In this respect, organic chemists are looking for new heterogeneous catalysts that possess the advantages of both homogenous catalysts (high activity and selectivity, etc.) and heterogeneous catalysts (easy catalyst separation, long catalytic life, thermal stability, and recyclability)¹.

3. Green and Sustainable Catalysis:

The development of green, sustainable, and economical chemical processes is one of the major challenges in modern chemistry science, especially in green chemistry. Green chemistry, also called sustainable chemistry, is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances¹¹. Green catalysis is a subchapter of green chemistry but probably the most important one, and one of the urgently indispensable challenges facing chemists now is the design and use of environmentally benign catalysts. The concept of green chemistry, which makes catalysis science even more creative, has become an integral part of sustainability⁶. From the perspective of green chemistry, an ideal and sustainable catalyst must possess a series of distinctive advantages such as low preparation cost, high activity, efficiency and selectivity, high stability, efficient recovery, and good recyclability¹⁰. Accordingly, the search for designing and using environmentally benign, sustainable, and efficiently reusable alternative catalytic systems has become an important challenge in modern catalysis science.

4. Magnetic Properties of Cobalt Ferrite Nanoparticles:

The magnetic nanoparticles with spinal structure MFe_2O_4 ($M = Fe, Co, Mn, Zn, Ni \dots$) have been widely studied for their properties compatible with various applications ranging from data storage to biomedical applications^{12, 13,14,15, and 16}. Recently, a special interest is devoted to magnetic nano-objects materials^{17, 18} because they endorsed interesting magnetic properties, with the possibility of tailoring their functionalities, by controlling the shape and morphology. Particularly, magnetic nanoparticles (MNPs) can be tuned straightforwardly by

the control of the size, monodispersity, chemical composition, as well as the adequate synthesis route, which is desirable for advanced magnetic nanodevices or magnetic hyperthermia. It is worthy to mention that a monodomain nanoparticle has a permanent magnetic moment, which is the sum of all magnetic moments of the atoms constituting it. However, during the structuring of the magnetic monodomain, the reduction of the total number of atoms (on the nanometric scale) leads to an increase in the contribution of surface atoms that do not have the same environment as in the core of the nanoparticle.

The contribution of surface effects affects the magnetic properties of the material. Indeed, in addition to the core spins as in the bulk material, the nanoparticles have surface spins, that create supplementary interactions. Therefore, for controlling the physical and chemical properties of nanoparticles, it is necessary to control the size, morphology, monodispersity, and chemical composition of the nanoparticles. For instance, cobalt ferrite has a ferromagnetic behavior at ambient conditions, with high magnetic core activity¹⁹, a high Curie temperature at the vicinity of 793 K, strong magnetocrystalline anisotropy²⁰, as well as a large magnetostriction coefficient²¹. These properties are very attractive for advanced technological devices, namely in data storage and biomedical applications. Magnetic order in cobalt ferrite arises from the superexchange interaction between the cations located in tetrahedral and octahedral sites through the oxygen anion. The induced antiferromagnetic coupling between the Fe³⁺ cations in the tetrahedral site and the Co²⁺ and Fe³⁺ cations in the octahedral sites is strong; although another weak antiferromagnetic coupling is present between tetrahedral Fe³⁺ cations^{22, 23}. In addition, a weak ferromagnetic coupling also exists between the cations of the octahedral sites. The two last couplings are masked by the interactions between tetrahedral and octahedral sites.

To date, several synthesis methods of MNPs have been developed^{24,25,26,27, 28, and 29} to improve the magnetic properties by controlling the size, morphology, and composition of the obtained nanoparticles. Among these different routes of synthesis, we have found the co-precipitations, solvothermal, hydrothermal, and thermal decomposition which are the most effective ones. The co-precipitation method has been used to synthesize crystals with different morphologies including spherical, cubic, and nanorods³⁰. Using solvothermal and hydrothermal methods, nanocrystals of iron oxide have been grown as spheres and hexagons^{27, 28}. The thermal decomposition method has produced monodispersed nanoparticles of spinel ferrite with narrow size distribution and good crystallinity³¹. In this respect, the present work reports on the synthesis of CoFe₂O₄ NPs by decomposition of acetylacetonate precursors at high

temperatures. Among many advantages of this synthesis route, the ability to control the particle size, size distribution, shape, and phase purity. The thermal decomposition approach has been chosen because the synthesis system is simple with one type of complex, one type of ligand, and a high boiling point organic solvent. The obtained nanoparticles are monodispersity with varied morphologies and sizes.

5. The procedure of Synthesis:

5.1. Synthesis of Cobalt Ferrite Nanoparticles:

Into a 100 mL three-necked flask under nitrogen flow, we placed 4 mmol of Fe(III) acetylacetonate, 2 mmol of Co(II) acetylacetonate, 20 mmol of 1,2-hexadecanediol, 12 mmol of oleic acid, 12 mmol of oleylamine, and 40 ml of benzyl ether. That is to say in proportions five times higher for the hexadecanediol compared to the Fe(III) acetylacetonate and six times higher for the surfactants (oleic acid and oleylamine) compared to the Fe(III) acetylacetonate. Thermal controlling is carried out using a thermocouple probe to control the temperature and the duration of the high-temperature treatment. The reaction mixture was magnetically stirred and degassed at room temperature for 60 min, then was heated and kept at 100 °C for 30 min to remove water. Subsequently, the temperature was increased and kept at 200 °C, for 30 min, then, heated (to reflux) and kept at 300 °C for 60 min. The final mixture is cooled to room temperature and purified three times with ethanol and hexane. A black magnetic precipitate is obtained after magnetic settling. The precipitate is redispersed in 20 ml of hexane and a ferrofluid composed of surfaced CoFe₂O₄ nanoparticles is obtained. The thermal decomposition process. It is interesting to note herein that the presence of the used surfactants helps the good dispersion of the obtained NPs in hexane. However, the presence of hexadecanediol helps to initiate the reaction by promoting the decomposition of the metal precursor's acetylacetonates. The choice of benzyl ether is an appropriate solvent for this process. Because its boiling temperature (298 °C) is higher than the decomposition temperature of precursors. The equation of the reaction is as follows³²:

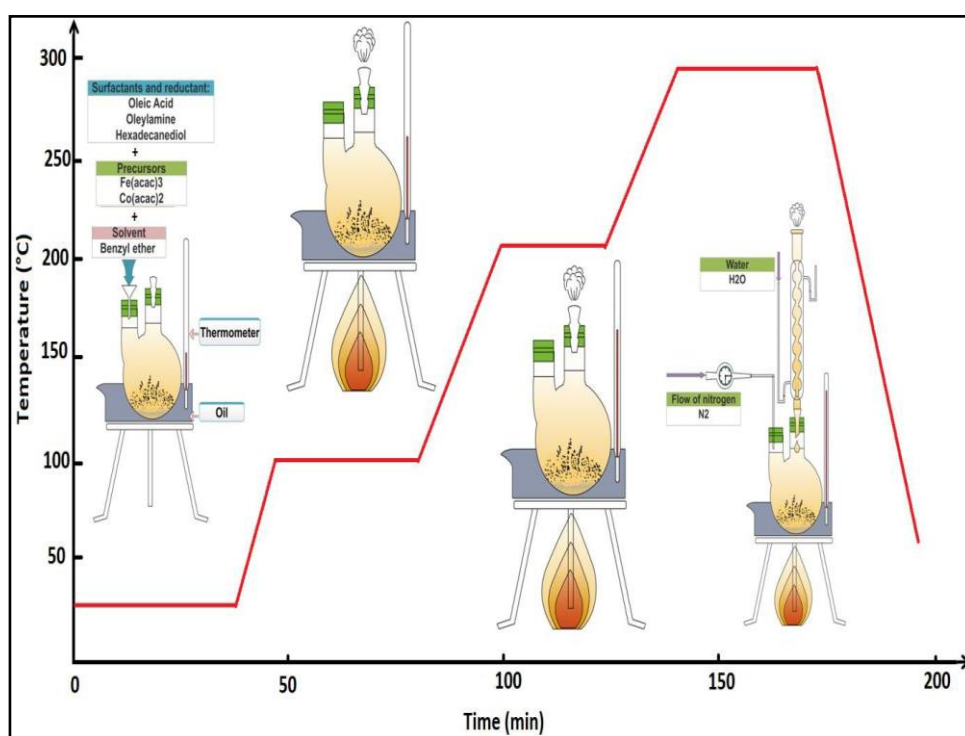
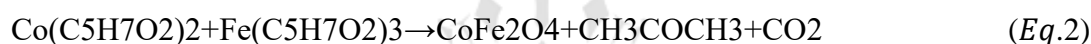


Figure No. 2 Synthesis of Cobalt Ferrite Nanoparticles



According to the equation (Eq. 2), in the presence of oleylamine, oleic acid, and 1,2-hexadecanediol, thermal decomposition of acetylacetonates of cobalt and iron produced cobalt ferrite nanoparticles, releasing acetone and carbon dioxide as by-products. Various synthesis parameters described above in the initial protocol have been modified to know the influence of synthesis parameters on the shape and size of nanoparticles: the decomposition temperature, the duration of the heat treatment, or the quantity of the reagents. This also allowed us to better understand the role of reagents such as hexadecanediol, oleic acid, or oleylamine in the synthesis³².

5.2. Characterization Techniques:

To get information about the mass loss of CoFe_2O_4 NPs, thermogravimetric analysis (TGA, TA Instrument Q500) was used to know the percentage and the degradation temperature of the organic molecules on the surface of nanoparticles. The sample was analyzed under an inert atmosphere, the heating rate is $10^\circ\text{C}/\text{min}$, the temperature range is between $25-600^\circ\text{C}$ and the mass used is between 10 and 30 mg.

Fourier Transform - Infrared Spectroscopy (FT-IR) spectra were recorded in the region from 250 to 4000 cm^{-1} by using ABB Bomem FTLA2000 on KBr-dispersed sample pellets. To avoid the signal saturation effects, the studied powders are diluted with KBr (transparent to infra-red radiation), and compressed into a disk with a diameter of 1 cm, in the form of pellets consisting of 30 mg of KBr and 1 mg of the sample. The spectra were recorded between 400 and 4000 cm^{-1} and processed using the Win-IR software.

X-ray powder diffraction (XRD) patterns of the nanoparticle assemblies were collected on a Bruker D8 Discover diffractometer under $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at 25°C . The scanning angle is ranging from 10° to 100° with a step of 0.1° . The objective of this analysis is the determination of the phases present in the samples, verification of the absence of secondary phases, the calculation of the unit cell parameter as well as the determination of the particle size.

Scanning transmission electron microscopy (STEM) studies and associated energy dispersive X-ray spectroscopy (EDS) microanalysis were performed using an FEI electronic microscopy operating at 30 KV. The nanoparticles were dispersed on holey carbon grids for STEM observation. EDS chemical analyses were also carried out on several zones to determine locally the quantity of the elements.

The magnetic properties of the CoFe_2O_4 nanoparticles were studied at various temperatures using a Quantum Design MPMS-XL-7CA SQUID magnetometer with a magnetic field strength up to 6 T. The principle of this measurement is based on the displacement of the sample within a set of superconducting detection coil. During the movement of the sample through the coils at a given temperature and magnetic field, the magnetic moment of the sample induces an electric current in the sensing coils. Any change of this current in the detection circuit induces a change of magnetic flux; therefore, by moving the sample on either side of the detection coils, the magnetic flux is integrated. A flux transformer is used to transmit the signal to the SQUID.

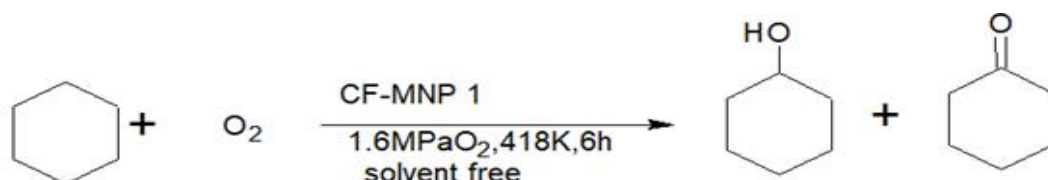
6. Cobalt Ferrite Nanocatalyst in Organic Synthesis:

Hydrocarbon Oxidation:

1. Aerobic oxidation under solvent-free conditions was considered as the standardized condition. As shown in Scheme 1, when pure CoFe_2O_4 was applied as catalyst (5 mg), 16.2% of cyclohexane conversion and 92.4% of selectivity for cyclohexanone and

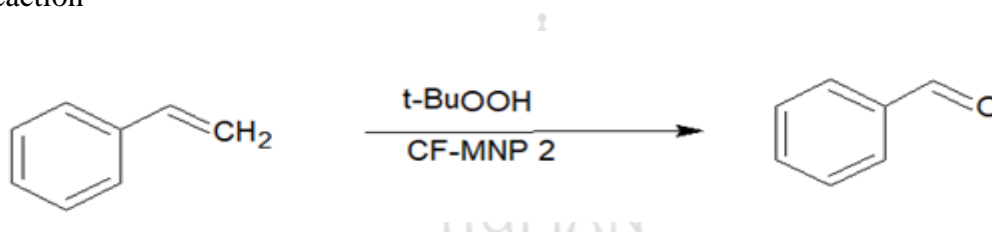
cyclohexanol were observed after 6 h. The catalyst can be readily recovered by an external magnet, and no significant loss of efficiency was observed when reused five successive times. CF-MNPs 1 was proved to be also efficient for oxidation of linear alkanes³³.

1. Reaction



2. Immobilization of a Schiff base molybdenum complex on silica-coated cobalt ferrite nanoparticles (CF-MNPs 2) as a novel heterogeneous catalyst for the oxidation of alkenes. The catalytic activity of CF-MNPs (50 mg) was then tested in the oxidation of various alkenes (1 mmol) using 30% t-BuOOH as an oxidant.

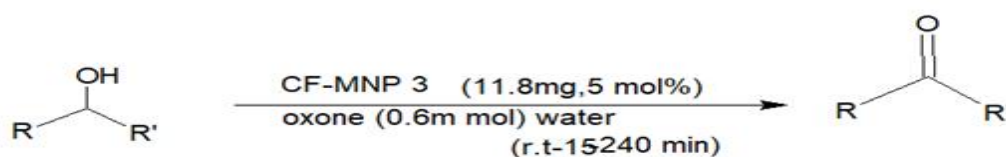
2. Reaction



Alcohol Oxidation:

1. Selective oxidation of alcohols is the straightforward and most common route for the preparation of carbonyl compounds^{34,35}. Alcohol oxidation reactions were performed under an aqueous medium at room temperature in the presence of oxone (potassium hydrogen monopersulfate) as an oxidant. Under the described conditions, a library of primary and secondary benzylic and aliphatic alcohols (1 mmol) was smoothly oxidized to the corresponding carbonyl products in good to excellent yields (Scheme 3) magnetically recovered and reused for six cycles without noticeable loss of catalytic activity.

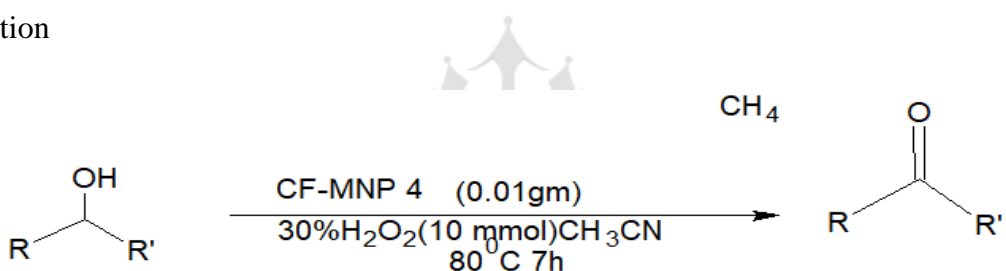
3. Reaction



R=Alkyl Phenyl Benzyl
R'=Alkyl Phenyl

2. Nickel hydroxide complex on magnetic cobalt ferrite nanoparticles modified with 3-aminopropyltriethoxysilane (CoFe₂O₄@APTES@Ni(OH)₂) (CF-MNPs 4) and successfully utilized this as a heterogeneous catalyst for the oxidation of alcohols to the carbonyl compounds. The best reaction conditions for the alcohol oxidation were found to be CF-MNPs 2 as the catalyst and H₂O₂ (30 wt% in water, 10.0 mmol) as the oxidant in acetonitrile at 80°C. This catalytic system was able to oxidize primary and secondary alcohols (1 mmol) efficiently (87%) to corresponding carbonyls in good yields.

4. Reaction



R=Alkyl,Pheny, Benzyl,Allyl

Heterocyclic Synthesis:

Heterocyclic chemistry is one of the most important and valuable branches in chemistry science [6]. Heterocycles are present in a broad library of drugs, most vitamins, many natural products, and biologically and industrially active molecules.

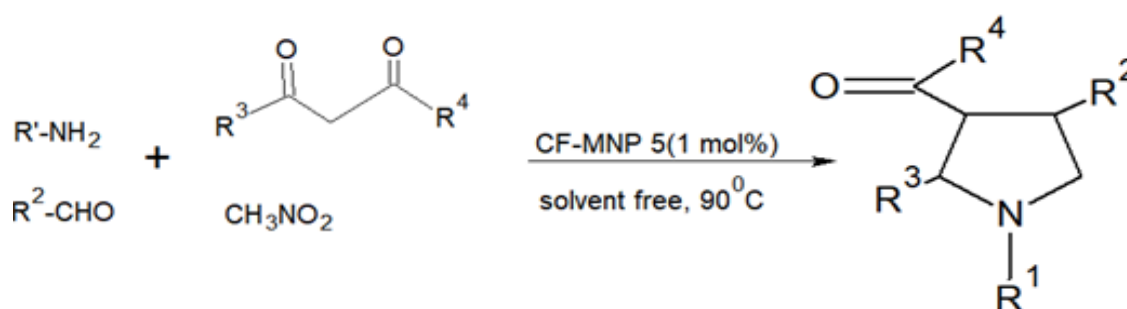
7. Five-Member Heterocycles:

7.1 Pyrroles:

Compounds containing pyrrole ring systems are an important class of biologically and pharmaceutically active molecules; pyrrole derivatives possess many pharmacological properties and can play important roles in biochemical processes^{36,37}. Novel magnetically

recoverable molybdenum catalyst via immobilization of molybdenum complex (Mo(acac)₂) on the surface of silica-coated cobalt ferrite nanoparticles (CoFe₂O₄@SiO₂) functionalized with 3-aminopropyltriethoxysilane under refluxing methanol conditions. As-prepared CoFe₂O₄@SiO₂-NH₂- Mo(acac)₂ (CF-MNPs 5). The activity of CF-MNPs 5 (1 mol%) was evaluated in a one-pot, four-component synthesis of functionalized pyrrole derivatives. As shown in, the four-component reaction of aldehydes (1 mmol), amines (1 mmol), 1,3-dicarbonyl compounds (1 mmol), and nitromethane (0.5 ml) have been conducted under thermal solvent-free conditions, and a nice category of polysubstituted pyrrole products was afforded in moderate to excellent yields. The CF-MNPs 5 can be recycled five times with negligible decrease in activity.

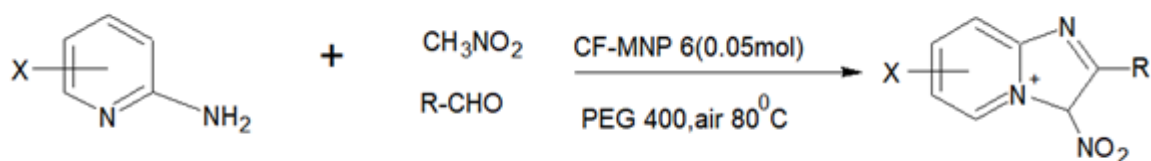
5. Reaction



7.2 Imidazols and Oxazoles:

Imidazole [1,2-a]pyridines are an important class of N-heterocyclic compounds from the points of view of biological and pharmacological activities³⁸. In this respect, a magnetically copper complex supported on magnetic CoFe₂O₄ CNT (CoFe₂O₄/CNT-C) and evaluated as a recoverable heterogeneous catalyst (CF-MNPs 6) for the synthesis of 3-nitro-2-arylimidazo[1,2-a]pyridines via one-pot three-component reaction of 2-aminopyridines (1 mmol), aldehydes (1 mmol), and nitromethane (1.1 mmol) in thermal PEG 400 under aerobic conditions. As shown in Scheme, the addition of the CuCl complex to a suspension of magnetic CoFe₂O₄ CNT in water led to the generation of the target catalyst. The reaction failed in the absence of the catalyst. Several solvents such as PEG 400, H₂O, EtOH, H₂O/EtOH, DMF, CH₃CN, CH₂Cl₂, toluene, and MeOH were tested, and water was found to be the best solvent. Under the described conditions, a nice collection of 3-nitro-2-arylimidazo[1,2-a]pyridines was synthesized in high yields. The recovered catalyst was able to be recycled at least eight times without loss of activity.

6. Reaction



CONCLUSION:

The results obtained in this work are likely to offer useful information about the preparation and the role of different parameters in this synthesis route of CoFe₂O₄NPs, promising for application in magnetically recoverable nanocatalyst, and synthesis of various organic materials. Cobalt ferrite nanoparticles possess a magnetic property that helps in easy recovery of catalyst and is used several times, this makes reaction very economic and ecofriendly. Magnetically recoverable nanoparticles play important role in green chemistry. They are used several times without loss of catalytic property this leads to the same catalyst being used several times, this automatically leads to environmental protection and support green chemistry.

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