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Overview on magnetically recyclable ferrite nanoparticles: synthesis and their applications in coupling and multicomponent reactions

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Nanocatalysis is an emerging area of research that has attracted much attention over the past few years. It provides the advantages of both homogeneous as well as heterogeneous catalysis in terms of activity, selectivity, efficiency and reusability. Magnetically recoverable nanocatalysts provide a larger surface area for the chemical transformations where the organic groups can be anchored and lead to decrease in the reaction time, increase in the reaction output and improve the atom economy of the chemical reactions. Moreover, magnetic nanocatalysts provide a greener approach towards the chemical transformations and are easily recoverable by the aid of an external magnet for their reusability. This review aims to give an insight into the important work done in the field of magnetically recoverable nanocatalysts and their applications in carbon–carbon and carbon–heteroatom bond formation.

1. Introduction

From the recent past, catalysis has emerged as a mature area of research supported by well explained theories and explanations. It is one of the twelve principles of green chemistry. Researchers are working on the development of new catalysts which either have advantages over the existing catalytic systems or can be used for the improvement of the emerging processes in terms of cost effectiveness and ease of reactions. Design of a catalyst having desired catalytic properties for a specific chemical transformation is an art

that requires the knowledge of optical, electronic, energetic and photonic efficiencies.^{1–3} Further, development of highly functionalized catalysts requires high-throughput technology.^{4,5} From the past few years, many fruitful efforts have been made in the area nanocatalysts that provide advantages of homogeneous as well as of heterogeneous catalysis in terms of activity, selectivity, efficiency and reusability.^{6–8} This can be attributed to the nanostructure, quantum size and electronic effects of the nanoparticles (NPs).^{9–11}

1.1. Nano-catalysis as a tool for green and sustainable chemistry

Green and sustainable chemistry is one of the key research areas which can pave a way to meet the continuously increasing

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cations in various synthetic reactions for the preparation of organic molecules of industrial and medicinal importance by using principles of green chemistry.



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moieties of medicinal interest and preparation of nanocatalysts for their applications in green chemistry.



demand of the population which is expected to be 9 billion by the year of 2050. Nano-catalysis is essential for sustainable and green chemistry in terms of use of green reagents which avoid the use of harmful and toxic chemicals, using solvent free reactions conditions which reduce the effluent treatment load, moderate reaction conditions, less reaction time and reusability of the catalysts. These characteristics of the nanocatalysts have led to their numerous applications in various organic transformations.^{12–17} Further, these nanocatalysts provide simple and eco-friendly methods for synthetic transformations with excellent yields and selectivity.^{18–23} Many attempts have been made for the synthesis of nanoparticles that can participate in green chemistry and can be reused for many cycles without appreciable loss in their catalytic activity.^{24–27} Heterogeneous nano-catalysts like zeolites, metal oxides, clay particles *etc.* have been widely used in the industrial sector for various organic transformations and have proven to be more effective than the homogeneous catalysts in terms of ease of work up after the completion of the reaction, fewer chances of formation of by-products and recyclability of the catalysts.^{28,29}

1.2. Fe_3O_4 nanoparticle catalyst and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ magnetic catalyst

From the last few years, preparation of ferrite nanoparticles has emerged as the key research area in the field of catalysis. In 1930, Frankel *et al.* reported that the conventional ferrite nanoparticles are of the size between 10–100 nm. Below 10 nm, ferrite nanoparticles possessed super paramagnetic properties.¹⁸ Ferrite nanoparticles have extensively been studied for their applications in biomedical field.^{30,31} medical diagnostic,^{32,33} multimodal imaging^{34,35} and medical therapy.^{36–39} The preparation of these nanoparticles has been achieved through various methods like co-precipitation, thermal decomposition reduction technique, and sol-gel method. Further, these nanoparticles have been coated by silica and various metals like TiO_2 , Cu, Zn, Ni, Co, Cu, Pd, Pt *etc.* to explore their catalytic activities in various important organic transformations.^{19–22}

1.3. Scope of the present review

Silica coated ferrite nanoparticles have been well known in literature for their catalytic activity to carry out various organic

transformations (Fig. 1). The main key features of these nanocatalysts include their high selectivity, excellent yields in lesser reaction time and hence these catalysts provide economical ways of synthesizing the target products with high selectivity. Further, these catalysts avoid the use of harmful chemical, reagents and solvents and thus are environment friendly. Also, due to their magnetic properties, these catalysts are easily separable after the completion of the reaction by applying external magnetic fields and can be reused for number of repeated cycles without any significant loss in their catalytic activity. Various review articles have been published from time to time on the applications of ferrite nanoparticles. Kharisov *et al.* have recently reported a mini review on the ferrite nanoparticles for the catalysis of the various processes like methanol decomposition, degradation of phenolic compounds, H_2O_2 decomposition, electrocatalyst for oxygen evolution reaction *etc.*,⁴⁰ Patil *et al.* have reported a review on the synthesis of various silica coated ferrite nanoparticles.⁴¹ Abu-Dief *et al.* have reported the development and functionalization of magnetic nanoparticles till 2010.⁴² Gwande *et al.* have reported a review in 2013 on Fe_3O_4 supported catalysts for the development of sustainable methodologies.⁴³ Lim *et al.* have reviewed the applicability of magnetically recyclable nanocatalysts for catalysing various organic reactions till 2010.⁴⁴ In 2009, Polshettiwar *et al.* have reported a review on the applications of palladium based silica supported nanocatalysts for various synthetic reactions like Heck reactions, Sonogashira reactions, Suzuki–Miyaura reactions *etc.*⁴⁵ The main scope of the present review is to compile the important research work done in the field of the magnetically recoverable ferrite nanoparticles from 2010 onwards. Further, the application of these nanocatalysts to catalyze various carbon–carbon and carbon–heteroatom bond formation reactions like Suzuki, Heck, Sonogashira, and A3 coupling reactions as well as multicomponent reactions like Strecker, Biginelli and Hantzsch reactions have been discussed in detail in the present review.

2. Synthesis of ferrite magnetic nanoparticles

2.1 Synthesis of Fe_3O_4 nanoparticles

Various synthetic methods are known in literature for the preparation of Fe_3O_4 nanoparticles (Fig. 2). Co-precipitation is



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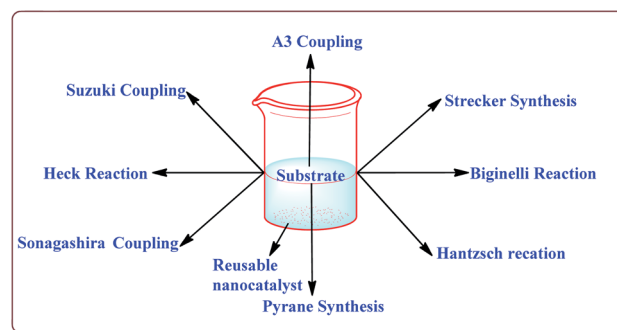


Fig. 1 Scope of the ferrite nanocatalysts.



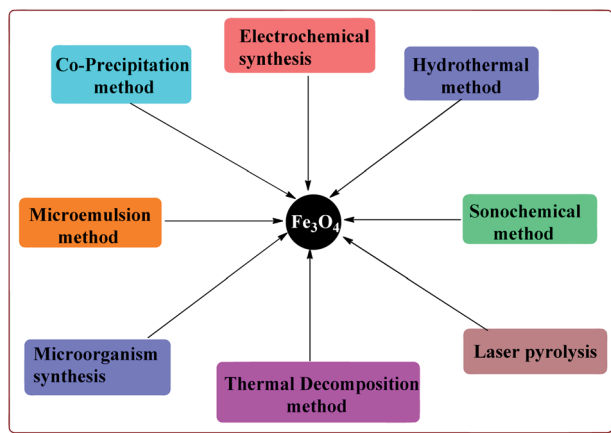


Fig. 2 General methods for the preparation of Fe_3O_4 nanoparticles.

one of the common methods used for the preparation of the Fe_3O_4 nanoparticles which consist of mixing ferric and ferrous ions in 1 : 2 molar ratios under basic conditions at room or elevated temperature. The properties like shape and size of the nanoparticles prepared by this method depend upon the pH of the reaction mass, type of iron salts used, stirring rate and temperature during the reaction. However, this method gives Fe_3O_4 nanoparticles with wide particle size distribution. The synthesis of monodispersed Fe_3O_4 nanoparticles have also been achieved either in the absence⁴⁶ or present of the surfactants.^{47,48} Another approach for the synthesis of monodispersed Fe_3O_4 nanoparticles with narrow size distribution is thermal decomposition of various salts like $\text{Fe}(\text{acac})_3$, $\text{Fe}(\text{Cup})_3$ and $\text{Fe}(\text{CO})_5$.^{49–52} In addition, microemulsion route can also be used for the synthesis of shape and size controlled Fe_3O_4 nanoparticles.^{53–55} Hydrothermal process is an alternate method to prepare the Fe_3O_4 nanoparticles with controlled size and shape that avoids the high temperature and complex reaction conditions required in the microemulsion process.^{56–61} Another versatile method used for the preparation of Fe_3O_4 nanoparticles is sonochemical synthesis which involve the sonication of various salts like $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2$ and $\text{Fe}(\text{acac})_3$.^{62–64} In addition to these methods, there are other reported techniques like electrochemical synthesis,^{65,66} microorganism or bacterial synthesis^{67,68} and laser pyrolysis techniques *etc.*⁶⁹ which can also be used for the preparation of Fe_3O_4 nanoparticles. These ferrite nanoparticles have found their applications in various fields like biomedical,^{70,71} healthcare,^{72,73} agriculture,⁷⁴ environmental remediation,⁷⁵ *etc.*

2.2. Synthesis of metal doped ferrite nanoparticle ($\text{Fe}_3\text{O}_4@ \text{metal}$)

Metal coated ferrite nanoparticles possess different properties. For example, He *et al.* have reported the one pot synthesis of platinum-coated magnetite nanoparticles to study their magnetosensitive catalytic applications.⁷⁶ Vaddula *et al.* have reported the synthesis of Fe_3O_4 -Dopa-Pd nanocatalyst for catalysing Heck type reactions by reacting aqueous mixture of Fe_3O_4 with dopamine under sonication followed by reaction

with methanolic solution of palladium.⁷⁷ Sá *et al.* have reported the synthesis of Fe_3O_4 doped with Pd by impregnation method followed by chemical reduction for its application in Buchwald–Hartwig reaction.⁷⁸ Neto *et al.* have reported an increase in the photocatalytic properties of Fe_3O_4 nanoparticles on its doping with Ce^{4+} , Mn^{2+} , CO^{2+} and Ni^{2+} metal ions by co-precipitation method.⁷⁹ Petrov *et al.* have used thermal decomposition method to synthesize Fe_3O_4 nanoparticles modified with Ag by reacting $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and AgNO_3 at high temperature. These prepared nanoparticles were further studied for their magnetic and magneto-optical properties.⁸⁰ Yang *et al.* have reported the synthesis of $\text{Fe}_3\text{O}_4/\text{Au}$ composites by seed deposition method for catalysing the reduction of 4-nitrophenols.⁸¹ Alzahrani *et al.* have reported the coating of Fe_3O_4 nanoparticles with Ag by using co-precipitation method from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and AgNO_3 and have explored its catalytic properties for photodegradation of eosin Y for the purification of industrial waste of dyes.⁸² Yang *et al.* have reported the effect of doping of magnesium on Curie temperature (T_c), Magnetic properties, and heating efficiency of Zn-Co-ferrite nanoparticles.⁸³ Mohamed *et al.* have reported green method for the preparation of CoFe_2O_3 nanoparticles as a sensor for the detection of Cu^{2+} in water samples and food products.⁸⁴ Rather *et al.* have reported the synthesis of aluminium doped zinc ferrite nanoparticles by thermal treatment method using polyvinylpyrrolidone (PVP) as capping agent.⁸⁵ Ishaq *et al.* have reported the synthesis of nickel ferrites nanoparticles by wet impregnation method to study their anti-bacterial activity (Fig. 3).⁸⁶

2.3. Ionic liquid supporting ferrite nanoparticle ($\text{Fe}_3\text{O}_4@ \text{IL}$)

Shikha *et al.* have reported the synthesis of manganese doped La-Ce ferrite nanoparticles by hydrothermal route using ionic liquid surfactant (ILS) by reacting $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, cerium(III) acetate and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ under sonication and observed that highly doped samples exhibited significant changes in their magnetic behaviour. Also, the

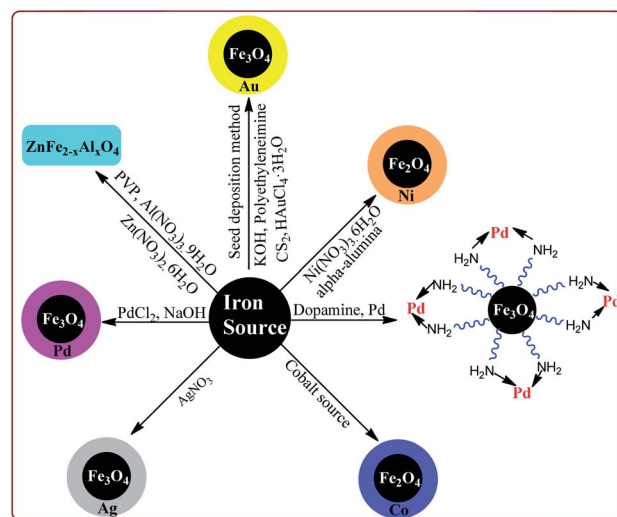


Fig. 3 Synthesis of metal doped ferrite nanoparticle.



transition from ferro to paramagnetism was observed for doped samples.⁸⁷ Zhang *et al.* have achieved the *trans*-esterification of glycerol trioleate catalyzed by 1-allyl-dodecylimidazolium hydroxide ([ADIm][OH]) ionic liquids immobilized on SiO₂/CoFe₂O₄ and CoFe₂O₄ magnetic nanoparticles. The targeted catalyst was prepared by free radical reaction between allyl groups of ionic liquid and sulfhydryl group of SiO₂/CoFe₂O₄ and CoFe₂O₄.⁸⁸ Dewan *et al.* have reported the use of ionic liquid stabilized magnetic cobalt nanoparticles as a catalyst to carry out aza- and thia-Michael reaction at room temperature. The catalyst was prepared by reaction of CoCl₂·6H₂O with NaBH₄ in the first step followed by reaction with ionic liquid [bmim]BF₄.⁸⁹

2.4. Silica coated Fe₃O₄ (Fe₃O₄@SiO₂) and metal coated Fe₃O₄@SiO₂ (Fe₃O₄@SiO₂@M)

Many attempts have been made in literature to prepare silica and metal coated nanoparticles to study their catalytic activity for various synthetic reactions (Fig. 4). Silica as a solid support has attracted the attention of various research groups because of its wide accessibility, high porosity which facilitates the anchoring of the organic groups on its surface to generate active catalytic sites and high stability.⁹⁰ Thangaraj *et al.* have reported the effect of the silica coating on Fe₃O₄ nanoparticles for lipase immobilization and further studied its application in biodiesel production. The catalyst was prepared by co-precipitation method by coating Fe₃O₄ nanoparticles with varying ratio of SiO₂ by using Stober method. These silica coated ferrite nanomaterials were further coated with 3-aminopropyltriethoxysilane and 3-mercaptopropyltrimethoxysilane to study their catalytic properties.⁹¹ Gad-Allah *et al.* have studied the role of silica content on the photocatalytic activity of TiO₂/SiO₂/Fe₃O₄ and have reported that the silica content higher than 10 wt% led to decrease in the catalytic activity. Silica and titanium coating on Fe₃O₄ nanoparticles was achieved by sol-gel technique.⁹² Similar types of studies have also been reported by Pang *et al.* wherein Fe₃O₄/SiO₂/TiO₂ catalyst was prepared by encapsulating Fe₃O₄ nanoparticles with silica followed by coating with TiO₂ by sol-gel method. The resulted catalyst exhibited high photocatalytic properties which was evident from the photodegradation of methylene blue in UV light.⁹³ The detailed synthesis and application of various silica and metal coated ferrite nanoparticles have been discussed in Section 4.

3. Characterization of ferrite nanoparticles

Various analytical techniques have been used in literature to characterize the magnetic nanoparticles. Surface characterization techniques are helpful to study the morphology, special distribution of the functional groups and chemical compositions.⁹⁴ Fourier transform infrared (FT-IR) spectroscopic technique has been used in literature to confirm the type of bonding between the atoms to find out the chemical composition of the sample. Further, X-ray diffraction (XRD) study gives the information about the crystal structure and size of crystallites by using well-known Scherrer formula. Transmission Electron Microscopy (TEM) technique is used to study the morphology of the crystallite structures in the sample. The magnetic properties of the ferrite nanomaterials can be studied with Vibrating Sample Magnetometer (VSM). In addition, weight loss steps in Thermal Gravimetric Analysis (TGA) studies and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) confirm the distribution of various atoms in the sample. Similar type of distribution studies can also be performed by using Scanning Electron Microscope (SEM) coupled with energy dispersive X-ray spectrometry which gives an idea about the chemical composition of the studied sample.^{95–104} Other characterization techniques include zeta potential measurement, ion-particle probe, electrophoresis, field flow fractionation, turbidimetry studies and laser microscopy *etc.*^{105,106}

4. Applications of magnetic nanoparticles

In recent years, magnetic nanoparticles (MNPs) have attracted an increasing interest for their utilization as catalysts for the development of various green and sustainable processes with excellent yields of the products and ease of work up of reaction. These reactions have been performed under moderate reaction conditions, avoid the use of harmful chemicals and reagents and catalysts can be reused for number of cycles.^{107,108} The next part of the review is aimed to provide the application of these catalysts to catalyse various coupling, oxidation and multi-component reactions.

4.1. Coupling reaction or C–C bond formation

The discovery of the homogeneous catalysis based upon transition metal elements began during the mid of 1960 and has resulted into number of important processes of industrial as well as academic importance.¹⁰⁹ It has now become an important tool to form carbon–carbon and carbon–heteroatom bond formation *via* different reactions like Suzuki coupling, Sonogashira coupling, Still coupling and Heck reaction.

4.1.1 Suzuki coupling reaction. The Suzuki coupling reaction, also referred as Suzuki–Miyaura reaction, is the most dominant reaction in the organic synthesis to evolve in the 20th century.^{110–112} It is the most efficient method for the synthesis of the styrenes, substituted biphenyls and poly olefins and is associated with many advantages like tolerability against the

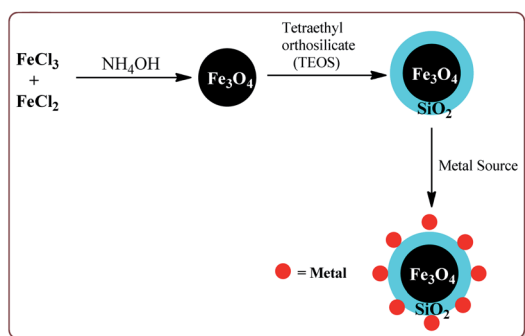


Fig. 4 General synthesis of Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂@M.



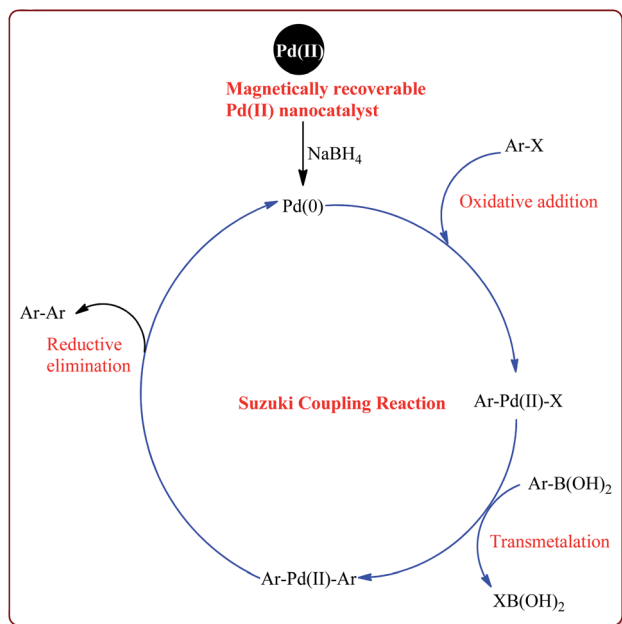
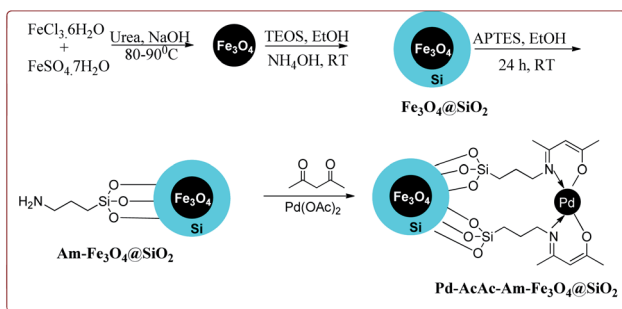


Fig. 5 Mechanistic pathway of Suzuki coupling reaction.

presence of water and broader range of functional groups, moderate reaction conditions, easily availability of the boronic acids, high regio and stereo selectivity.¹¹³ Also, the boronic acids are less toxic to environment and hence are safer to use than their organostannate and organozinc derivatives making this reaction a better choice for academicians and industrialist to manufacture various targeted products. Various reviews have been published in literature discussing the applicability of this reaction for the synthesis of natural products, polymers, active pharmaceuticals and fine chemicals.^{110,111,114,115} The typical catalytic cycle of the Suzuki coupling reaction is depicted in Fig. 5 where the Palladium catalyst cycles between Pd(0) and Pd(II) oxidation state during the catalytic cycle.

Many transition metal base homogeneous Schiff base catalysts have been developed in the literature to carry out the Suzuki–Miyaura cross-coupling reactions which gave excellent yields as compared to heterogeneous catalysts but suffered from the disadvantage of separation of catalyst from the reaction mass which prohibit catalyst recyclability.^{116–119} Vibhute *et al.*

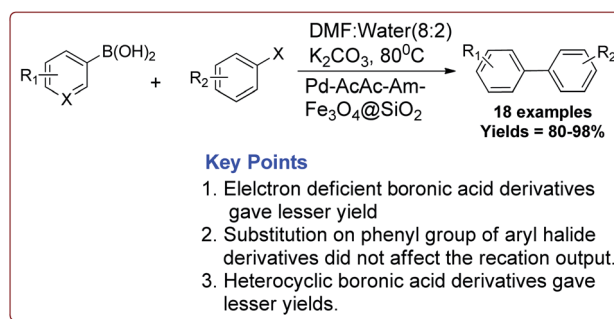


Scheme 1 Synthetic route for the preparation of Pd-AcAc-Am-Fe₃O₄@SiO₂ nanocatalyst.

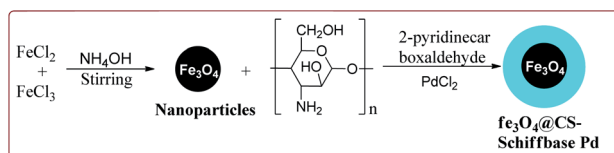
have reported the synthesis of ferrite supported silica coated amine functionalized Schiff base–palladium(II) nanocatalyst (Pd-AcAc-Am-Fe₃O₄@SiO₂) for catalysing Suzuki–Miyaura cross-coupling reaction between aryl halides and aryl or heteroaryl boronic acid derivatives which gave excellent yield in lesser reaction time under moderate reaction conditions. The catalyst was prepared by reacting FeCl₃·6H₂O and FeSO₄·7H₂O under basic conditions followed by reaction with tetraethyl orthosilicate (TEOS) to give Fe₃O₄@SiO₂. Further reaction with 3-aminopropyltriethoxysilane (APTES) and acetylacetone in the presence of palladium acetate gave target catalyst (Scheme 1). Only 30 mg of the catalyst was sufficient to catalyse the reaction. Further, the electron deficient aryl boronic acid took longer reaction time and gave lesser yields whereas heterocyclic boronic acid derivatives gave lesser yields. However, the nature of substitution on phenyl group of aryl halide did not affect the reaction output. Interestingly, the catalyst was recycled for 6 cycles and was found to be active without any significant loss in its catalytic activity (Scheme 2).¹²⁰

Naghipour *et al.* have reported the synthesis of Fe₃O₄@chitosan-Schiff base supported Pd nanocatalyst by using chemical co-precipitation method for carbon–carbon bond formation in Suzuki–Miyaura and Heck–Mizoroki reactions (Scheme 3).

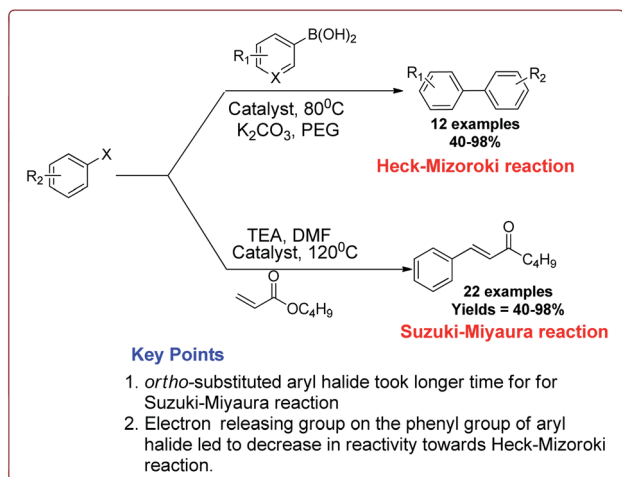
In general, the prepared catalyst gave excellent yields for Suzuki–Miyaura reaction irrespective of the substitution on the phenyl group of aryl halide. However, the *ortho*-substituted aryl halide derivatives took longer reaction time due to steric hindrance. On the other hand, in case of Heck–Mizoroki reaction, the presence of electron releasing group on the phenyl group of aryl halide led to decrease in the reactivity (Scheme 4). Further, 10 mg of the catalyst was sufficient to catalyse the reactions and the catalyst was used 5 times without change in its catalytic activity to much extent.¹²¹



Scheme 2 Synthesis of diarylation product of Suzuki–Miyaura cross-coupling reaction catalyzed by Pd-AcAc-Am-Fe₃O₄@SiO₂.



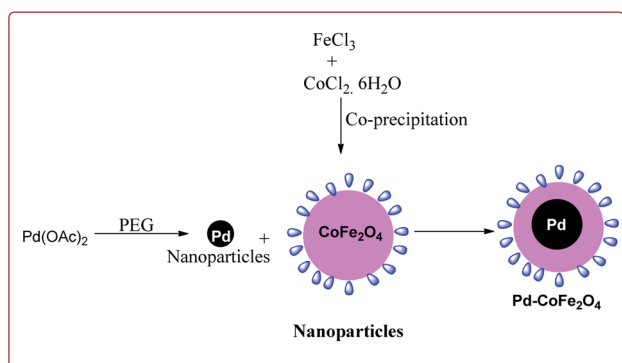
Scheme 3 Synthesis of Fe₃O₄CS-Schiff base-Pd nanocatalyst.



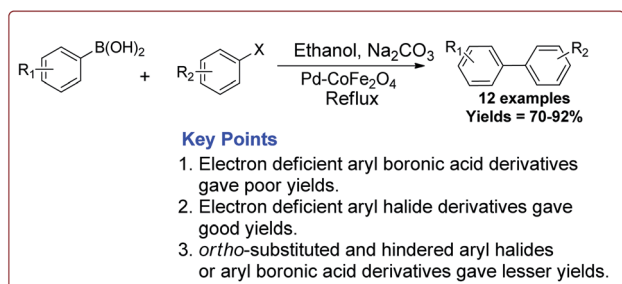
Scheme 4 Suzuki-Miyaura and Heck-Mizoroki reactions catalyzed by Fe₃O₄CS-Schiff base-Pd nanocatalyst.

Senapati *et al.* have reported the synthesis of Pd-CoFe₂O₄ nanocatalyst which involved the preparation of nanoparticles of palladium by stirring palladium acetate in polyethylene glycol followed by reaction with CoFe₂O₄ nanoparticles under ultrasonic irradiation (Scheme 5).

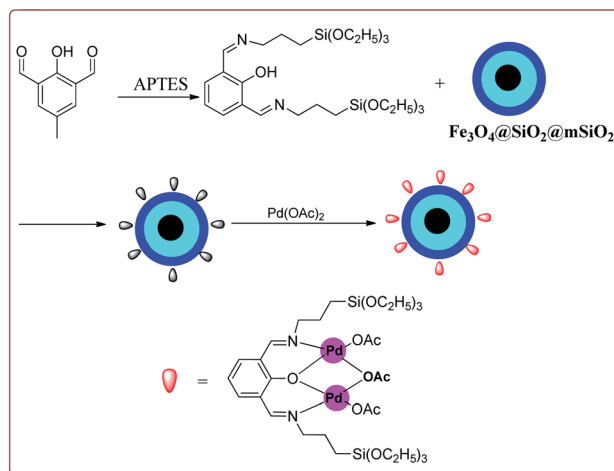
Only 1.6 mol% of the catalyst was required to catalyse the Suzuki coupling reaction between aryl boronic acid and aryl halide derivatives. It was observed that electron deficient aryl



Scheme 5 Synthesis of Pd-CoFe₂O₄ magnetic nanocatalyst.



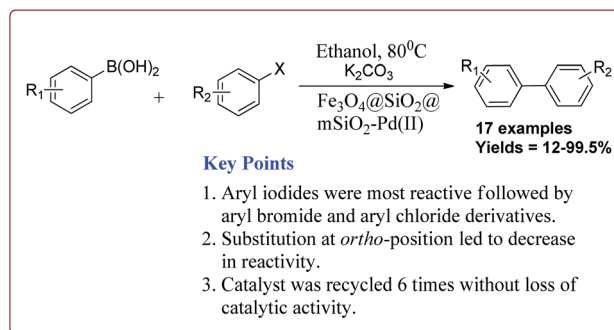
Scheme 6 Suzuki coupling reactions catalyzed by Pd-CoFe₂O₄ nanocatalyst.



Scheme 7 Synthesis of core-shell Fe₃O₄@SiO₂@mSiO₂-Pd(II) nanocatalyst.

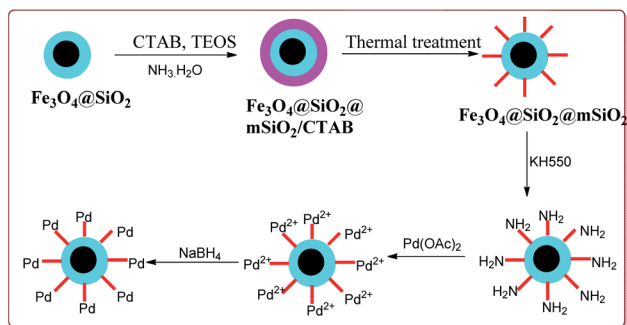
boronic acid derivatives gave poor yields whereas the electron deficient aryl halide derivatives gave good yields. Further, *ortho*-substituted and hindered aryl halides or aryl boronic acid derivatives gave lesser yields (Scheme 6). The catalyst was recovered by the external magnet after the completion of the reaction and was used multiple times without affecting its catalytic activity.¹²²

Le *et al.* have reported the cost effective synthesis of Pd(II) complex functionalized core-shell magnetic mesoporous catalyst Fe₃O₄@SiO₂@mSiO₂-Pd(II) having high surface area which exhibited excellent activity against Suzuki-Miyaura coupling reactions (Scheme 7). The catalyst was prepared by the reaction of 3-aminopropyltriethoxysilane (APTES) with mesoporous Fe₃O₄@SiO₂@mSiO₂ followed by reaction with Pd(OAc)₂. The best results were obtained in ethanol and K₂CO₃ at 80 °C by using 0.5 mol% of the catalyst. In general, aryl iodides were found more reactive than the aryl bromide derivatives and required lesser reaction time. Aryl chloride derivatives gave poor yields with larger reaction time. Further, the presence of electron withdrawing group at *ortho*-position led to decrease in the yield (Scheme 8). The catalyst was recycled for 6 times while retaining the yield of 91%.¹²³



Scheme 8 Suzuki coupling reactions catalyzed by core-shell Fe₃O₄@SiO₂@mSiO₂-Pd(II) nanocatalyst.



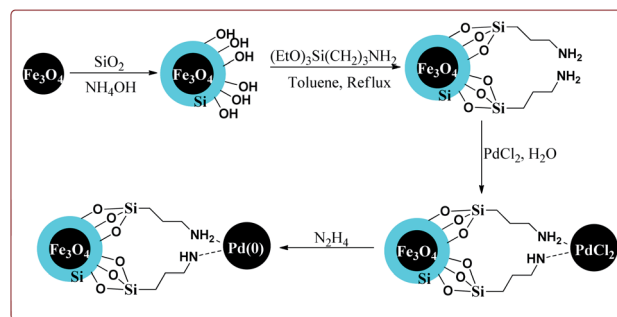


Scheme 9 Preparation of immobilized $\text{Fe}_3\text{O}_4@\text{SiO}_2@m\text{SiO}_2\text{-Pd(0)}$ nanocatalyst.

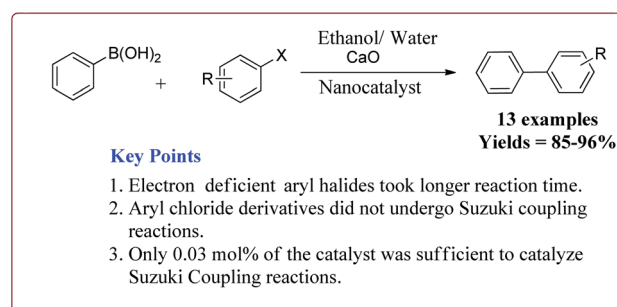
Li *et al.* have reported the synthesis of a core-shell magnetic mesoporous $\text{Fe}_3\text{O}_4@\text{SiO}_2@m\text{SiO}_2\text{-Pd(0)}$ microspheres having large pore-size mesoporous for catalysing Suzuki coupling reactions. Fe_3O_4 nanoparticles were coated on silica by using Stober method followed by reaction with hexadecyltrimethylammonium bromide (CTAB) and TEOS to give $\text{Fe}_3\text{O}_4@\text{SiO}_2@m\text{SiO}_2$. Further reaction steps involved the reaction with Pd(OAc)_2 and reduction with NaBH_4 to give the target catalyst (Scheme 9).

The catalytic activity of the catalyst was attributed to the dense inner shell which protected the magnetic core and the porous outer shell which provide large surface area for Pd loading which coordinated with the amine-modified core-shell magnetic mesoporous $\text{Fe}_3\text{O}_4@\text{SiO}_2@m\text{SiO}_2$ microspheres. Iodobenzene was found to give best results followed by bromo and chlorobenzene. Further, electron deficient aryl halide derivatives facilitated the Suzuki coupling (Scheme 10). Interestingly, only 0.075 mol% of the catalyst was sufficient to catalyse the reaction and it could be used six times without losing its catalytic activity.¹²⁴

Khazaei *et al.* have reported the synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles supported on Pd(O) for catalysing Suzuki coupling reactions. The catalyst was synthesized by using rice husk biomass as a source of biosilica. The synthesis of the desired catalyst involved the preparation of the Fe_3O_4 nanoparticles by co-precipitation method followed by reaction with silica in the presence of NH_4OH . Next steps involved the reaction with 3-(triethoxysilyl)propylamine followed by reaction



Scheme 11 Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Pd(0)}$ nanocatalyst.



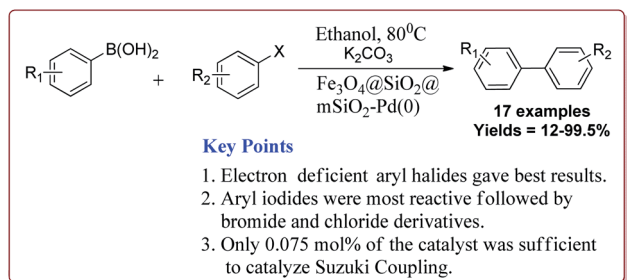
Scheme 12 Suzuki coupling reactions of phenyl boronic acid with aryl halides catalyzed by functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Pd(0)}$ nanocatalyst.

with PdCl_2 . Last step involved the reaction with N_2H_4 to get the desired functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Pd(0)}$ nanocatalyst (Scheme 11).

Only 0.03 mol% of the catalyst was sufficient of carry out Suzuki coupling reaction by using CaO as base in H_2O /ethanol mixture at high temperature. In general, excellent yields were observed in all the cases. However, electron deficient aryl halides took longer time for reaction completion. Interestingly, aryl chloride did not react under these conditions (Scheme 12). The catalyst was recovered and was reused for 5 times without any loss in its activity.¹²⁵

4.1.2 Heck coupling reaction. The arylation or vinylation of alkene derivatives was discovered by Mizoroki and Heck in 1970.^{126,127} Heck reaction involving the palladium catalyzed reaction between alkenyl or aryl halide is an another important class of reactions for carbon-carbon bond formation.¹²⁸ This approach has been widely used for the preparation of the biologically active compounds and natural products at small as well as at industrial scale.¹²⁹ Many studies have been reported in literature for the significance and practical importance of this method.^{130,131} The typical catalytic cycle of the Heck coupling reaction is depicted in Fig. 6.

Vibhute *et al.* have reported the synthesis of palladium supporting Schiff-base complex immobilized on magnetic nanoparticles, $\text{Pd-AcAc-Am-Fe}_3\text{O}_4@\text{SiO}_2$, to carry out Mizoroki and Matsuda Heck coupling reactions. The synthesis of $\text{Pd-AcAc-Am-Fe}_3\text{O}_4@\text{SiO}_2$ nanocatalyst was achieved as shown in Scheme 1. The results suggested that the catalyst tolerate



Scheme 10 Suzuki reactions catalyzed by $\text{Fe}_3\text{O}_4@\text{SiO}_2@m\text{SiO}_2\text{-Pd(0)}$ nanocatalyst.

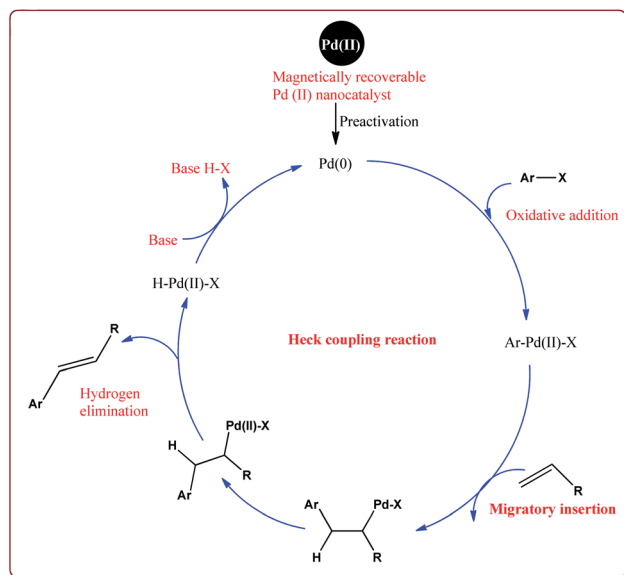
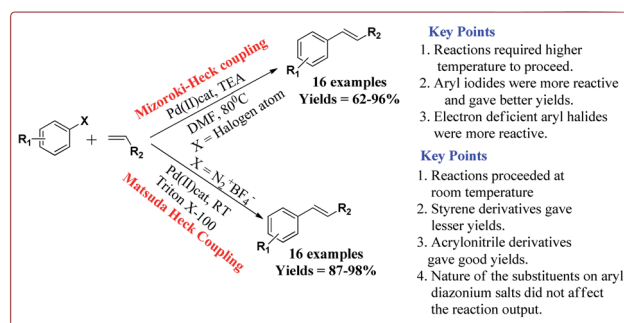


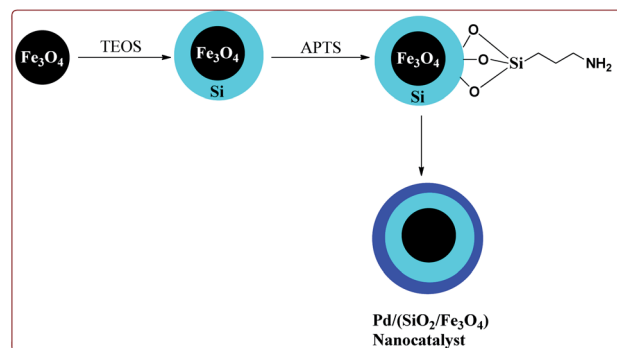
Fig. 6 Mechanistic pathway of Heck coupling reaction.

number of functional groups and *trans* products were formed in all the cases in Mizoroki–Heck coupling reactions of aryl halides with terminal olefins at higher temperature. Further, aryl iodides were found to be more active followed by aryl bromides and aryl chlorides. In addition, electron deficient aryl halides were more reactive than the electron rich aryl halides and gave better yields. On the other hand, Matsuda Heck coupling reactions between aryl diazonium salts and terminal alkenes were achieved at room temperature in aqueous medium. Moderate yields were obtained in case of styrene derivatives because of their low reactivity. However, excellent yields were obtained for the reactions of arenediazonium salts and acrylonitrile derivatives. Further, the nature of the group on the aryl diazonium salts did not affect the reaction output (Scheme 13). Only 0.3 mol% of the catalyst was required to complete the reaction and was reused for 6 cycles without loss of its activity.¹³²

Wang *et al.* have reported the synthesis of palladium catalyst based upon magnetic nanoparticles by using bottom up approach to explore its applicability in Heck coupling of acrylic acid derivatives with aryl halides. The Fe_3O_4 nanoparticles were



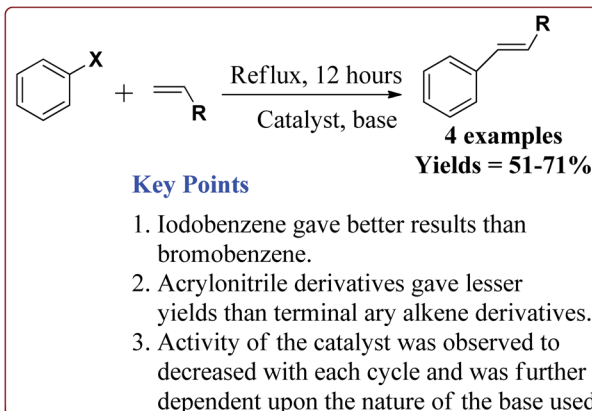
Scheme 13 Pd-AcAc-Am- Fe_3O_4 @ SiO_2 nanocatalyst catalyzed Mizoroki and Matsuda Heck coupling reactions.



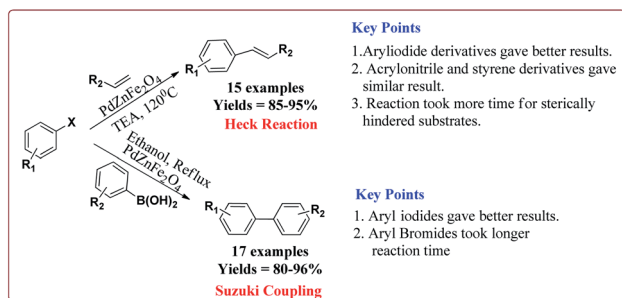
Scheme 14 Synthesis of $\text{Pd}/(\text{SiO}_2/\text{Fe}_3\text{O}_4)$ nanocatalyst.

prepared by chemical co-precipitation method which were further reacted with sodium silicate and TEOS to give Fe_3O_4 @ SiO_2 . Further reaction with 3-aminopropyl triethoxysilane (APTS) under vigorous stirring followed by reaction with H_2PdCl_4 gave the targeted $\text{Pd}/(\text{SiO}_2/\text{Fe}_3\text{O}_4)$ nanocatalyst (Scheme 14). The studies suggested that the aryl iodides gave better yields than the aryl bromides. On the other hand, acrylic acid derivatives gave lesser yield than the terminal aryl alkenes (Scheme 15). Only 30 mg of the catalyst was required for the reaction completion. However, the catalytic activity of the catalyst was found to decreased with each cycle and was further dependent upon the type of the base used.¹³³

Singh *et al.* have reported the synthesis of a super-paramagnetic palladium supporting zinc ferrite nanoparticles by ultrasound assisted co-precipitation method. The scope of the prepared catalyst was studied for Heck and Suzuki reactions of variety of aryl halides and alkene derivatives. In general, aryl iodides were found to be more reactive than bromo derivatives in both the reactions. Both, electron deficient as well as electron rich aryl halides gave similar results. For Heck reactions, acrylic and styrene derivatives gave similar results. However, hindered alkenes took more time for completion of the reactions. Only 4.2 mol% of the catalyst was found sufficient for the completion of the reactions and could be used for 5 times without any loss in its catalytic activity (Scheme 16).¹³⁴



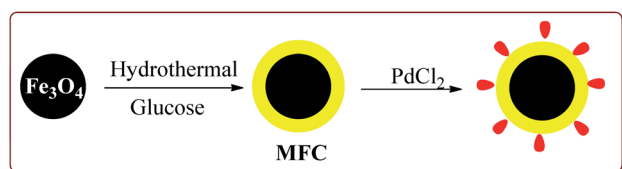
Scheme 15 $\text{Pd}/(\text{SiO}_2/\text{Fe}_3\text{O}_4)$ catalyzed Heck reaction.



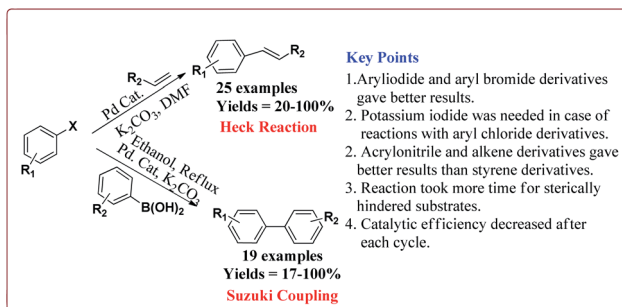
Scheme 16 Heck coupling reactions catalyzed by Pd-ZnFe₂O₄ nanocatalyst.

Zhu *et al.* have reported the synthesis of carbon nanocomposite supported Pd nanoparticles (Pd/Fe₃O₄@C) in three steps the first step of which involved the preparation of Fe₃O₄ nanoparticles by hydrothermal method. Second step involved the reaction of Fe₃O₄ nanoparticles with glucose under ultrasonic irradiation in autoclave to get MFC. In the last stage, Pd/Fe₃O₄@C catalyst was obtained by deposition-precipitation method under ultrasonication by reaction with PdCl₂ (Scheme 17).

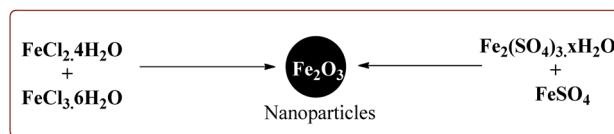
The prepared catalyst was used to perform Suzuki and Heck coupling reactions. The studies suggested similar observations for both type of reactions. Aryl iodide and aryl bromide derivatives gave good yields whereas the aryl chloride derivatives gave poor yields. Also, less hindered substrate gave better yields. In case of Heck reaction, acrylates and alkene derivatives gave better results as compared to styrene derivatives. Further, only 30 mg of the catalyst was sufficient to carry out the reactions. However, the yields of the reactions were found to decrease on reusing the catalyst (Scheme 18).¹³⁵



Scheme 17 Preparation of Pd/Fe₃O₄@C nanocatalyst.



Scheme 18 Pd/Fe₃O₄@C catalyzed Suzuki and Heck coupling reactions.



Scheme 19 Synthesis of Fe₃O₄ nanoparticles.

4.1.3 Sonogashira coupling reaction. The coupling between aryl, vinyl or pseudo halide derivatives with terminal acetylene derivatives by using Pd(0) catalyst in the presence of amine is called Sonogashira cross-coupling reaction.¹³⁶ It is one of the most important reactions for C(sp²)-C(sp) bond formation¹³⁷ and is widely used for its applications in the synthesis of natural products,¹³⁸ agrochemicals and pharmaceuticals,¹³⁹ polymers and nanostructures.¹⁴⁰⁻¹⁴³ Typical catalytic cycle of the Heck coupling reaction is depicted in Fig. 7.

Firozabadi *et al.* have reported the ligand free Sonogashira-Hagihara reactions of aryl iodides with terminal alkyne

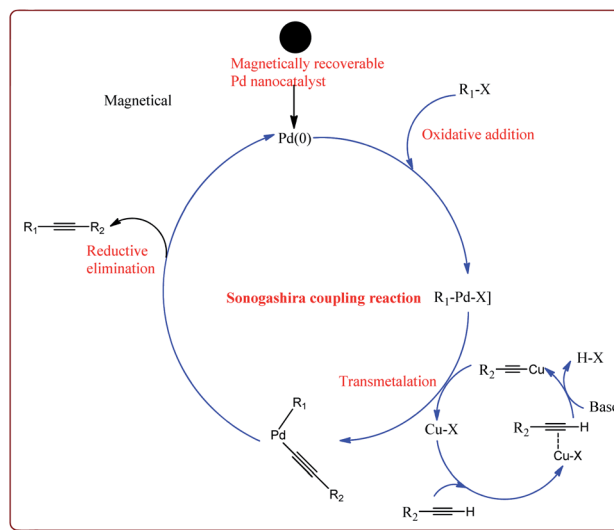
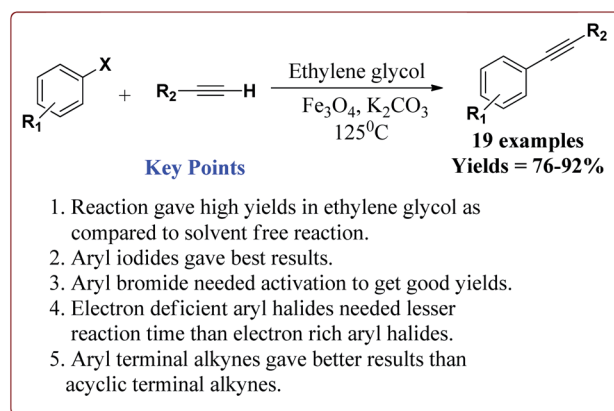
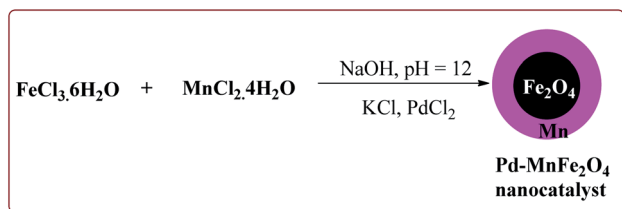


Fig. 7 Mechanistic pathway of Sonogashira coupling reaction.



Scheme 20 Fe₃O₄ nanoparticles catalyzed Sonogashira-Hagihara reactions.



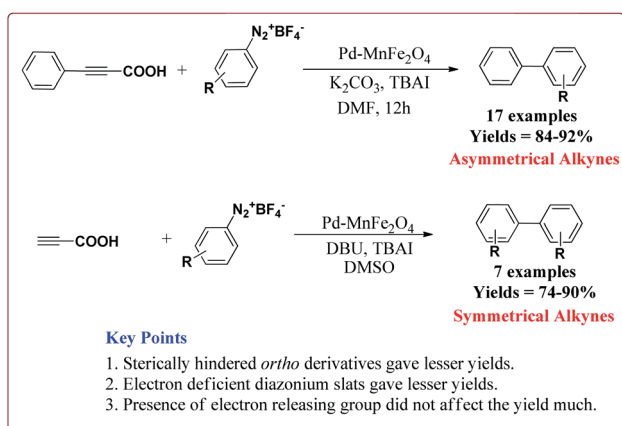
Scheme 21 Preparation of Pd-MnFe₂O₄ nanocatalyst by one pot sonochemical co-precipitation method.

derivatives in ethylene glycol in the presence of Fe₃O₄ nanoparticles to give corresponding arylalkyne derivatives. The nanoparticles of Fe₂O₃ were prepared either from the reaction of FeCl₂·4H₂O and FeCl₃·6H₂O or from the reaction of Fe(SO₄)₃·xH₂O and FeSO₄ by literature reported methods (Scheme 19).^{144,145}

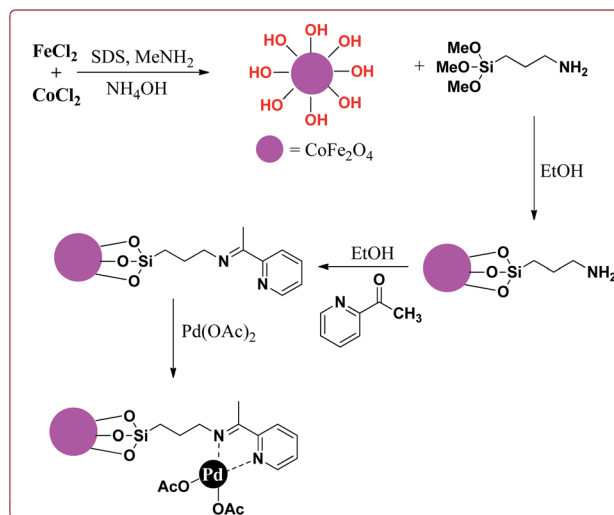
The structure activity relationship studies (SAR) showed that the electron rich aryl halides took longer reaction time as compared to electron deficient aryl halides. Further, aryl iodides were found to be reactive whereas aryl bromide needed activation to get the desired products. Also, the aryl terminal alkene gave better results than the acyclic terminal alkene derivatives (Scheme 20). Only 5 mol% of the catalyst was needed to carry out the reaction and was recycled for 5 cycles without any loss in its catalytic activity.¹⁴⁶

Jadhav *et al.* have prepared Pd-MnFe₂O₄ nanocatalyst by one pot sonochemical co-precipitation method for its application to carry out Sonogashira reactions for the synthesis of symmetric as well as asymmetric alkynes in good to excellent yields *via* decarboxylative coupling of terminal alkynes with arenediazonium salts (Scheme 21).

The studies suggested that the sterically hindered *ortho*-substituted diazonium salts gave lesser yields. Also, the electron deficient diazonium salts were found to be less reactive whereas the presence of electron releasing group did not affect the yield much. Only 1 mol% of the catalyst was sufficient to carry out the reaction and was reused for 5 cycles without any appreciable loss in its catalytic activity (Scheme 22).¹⁴⁷



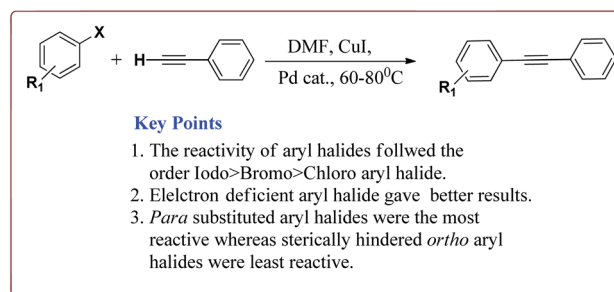
Scheme 22 Pd-MnFe₂O₄ nanocatalyst catalyzed Sonogashira reactions.



Scheme 23 Synthesis of superparamagnetic nanoparticles supported phosphine-free palladium catalyst.

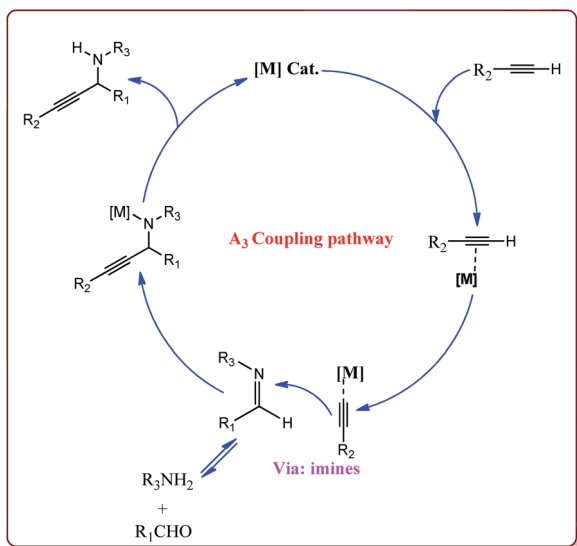
Bui *et al.* have reported the synthesis of superparamagnetic nanoparticles supported phosphine-free palladium catalyst for catalysing the Sonogashira coupling reactions. The target catalyst was prepared by following microemulsion method involving reaction of FeCl₂ and CoCl₂ in sodium dodecyl sulphate (SAD) to get superparamagnetic cobalt spinel ferrite nanoparticles which were further reacted with 3-(trimethoxysilyl)propylamine to give amino-functionalized magnetic nanoparticles. These were further reacted with 2-acetylpyridine followed by reaction with palladium acetate to give the target catalyst (Scheme 23).

It was observed that the catalyst was able to catalyse the Sonogashira reactions in 0.5 mol% ratio. Also, the aryl iodides were found to be more reactive than aryl chlorides which needed the presence of electron withdrawing groups on aryl ring to give the reactions in moderate yields. On the other hand, electron rich aryl halides gave lesser yields. Interestingly the *para* substituted aryl halides gave best yields followed by sterically hindered *meta* and *ortho* isomers. Interestingly, the catalyst could be used for 5 runs without loss of activity if purified in DMF at higher temperature before reuse (Scheme 24).¹⁴⁸



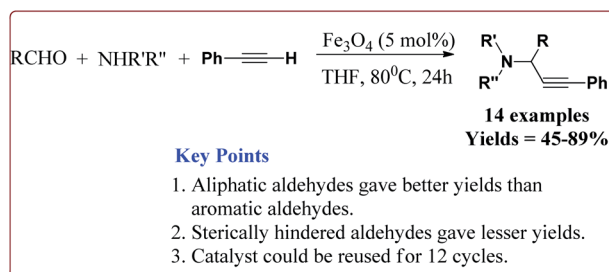
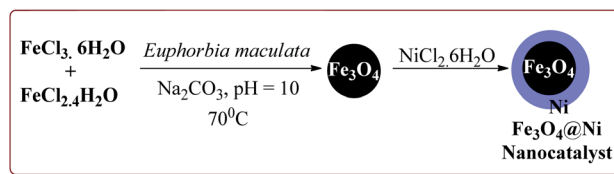
Scheme 24 Sonogashira reactions between phenyl acetylene and aryl halides catalyzed by palladium nanocatalyst.



Fig. 8 Mechanistic pathway of A₃ coupling reaction.

4.1.4 A₃ coupling reaction. A three component reaction between an aldehyde, an amine and an alkyne to give corresponding substituted alkyne derivatives is known as A₃ coupling. It involves the activation of C–H bond of alkyne by transition metal catalyst for *in situ* generation of metal acetylide which is a common step for Sonogashira and A₃ coupling reaction. The first example of A₃ coupling was reported in 1998 by Dyatkin *et al.*¹⁴⁹ After that, number of synthetic applications of this reaction for the synthesis of heterocyclic compounds, propargylamines, polycyclic pyrroles, 3-benzazepines, imidazole derivatives, lactones, thiazolidines and glyco-conjugates have been reported in literature.^{150–153} Typical mechanism of A₃ coupling is depicted in Fig. 8.

Zeng *et al.* have reported the use of Fe₃O₄ nanoparticles having size less than 50 nm as a nanocatalyst to carry out the A₃ coupling reaction between aldehyde, phenylacetylene and amine derivatives. The reaction gave moderate to good yields with various aliphatic and aromatic aldehydes. Aliphatic aldehyde derivatives gave better yields than aromatic aldehydes. Within aliphatic aldehydes, satirically hindered aldehyde derivatives gave lesser yields whereas straight chain aldehydes gave better yields. Also, six membered amine derivatives gave better yields as compared 5 membered amine derivatives.

Scheme 25 Fe₃O₄ nanoparticles catalyzed A₃ coupling reaction.Scheme 26 Synthesis of Fe₃O₄@Ni nanocatalyst.

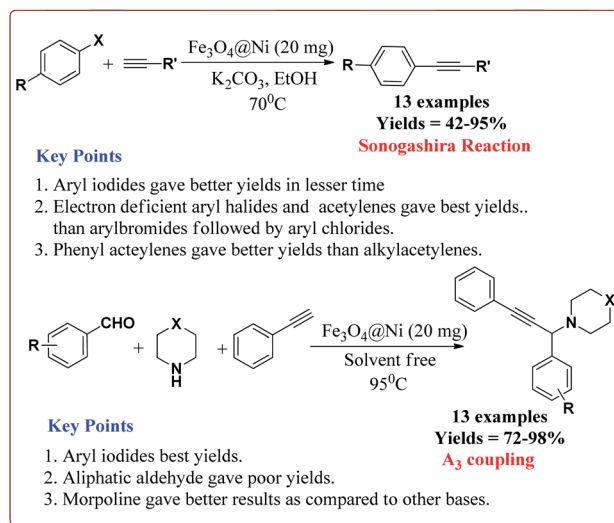
Further, only 5 mol% of the catalyst was necessary to catalyse the reaction and the catalyst could be used for 12 times without any loss in its catalytic activity (Scheme 25).¹⁵⁴

Alinezhad *et al.* have reported the biosynthesized Fe₃O₄@Ni nanoparticles catalyzed A₃ coupling and Sonogashira reactions. The catalyst was prepared by a green method the first step of which involved the reaction of FeCl₃·6H₂O and FeCl₂·4H₂O in *Euphorbia maculata* extracts at 70 °C by maintaining the pH of reaction mass at 10 by Na₂CO₃ to give Fe₃O₄ nanoparticles followed by with NiCl₂·6H₂O in *Euphorbia maculata* extracts at 60 °C to give target nanocatalyst (Scheme 26).

The prepared catalyst gave better yields in case of electron deficient aryl halides and acetylene derivatives for Sonogashira reaction. Further, aryl iodides gave best yields in lesser reaction time on reaction with aryl acetylene derivatives as compared to reaction with alkyl acetylene derivatives. In case of A₃ coupling, aryl iodides gave better yield in lesser time as compared to aliphatic aldehydes in the presence of morpholine as a base. Interestingly, the catalyst could be used 5 times without loss in its activity after being purified in ethyl acetate (Scheme 27).¹⁵⁵

4.2. Multicomponent reaction

4.2.1 Strecker reaction. The reaction between an aldehyde derivative and ammonium chloride in the presence of potassium cyanide and ammonia to afford α-amino acid derivative is commonly known as Strecker synthesis. It was first reported by

Scheme 27 Fe₃O₄@Ni catalyzed Sonogashira and A₃ coupling reactions.

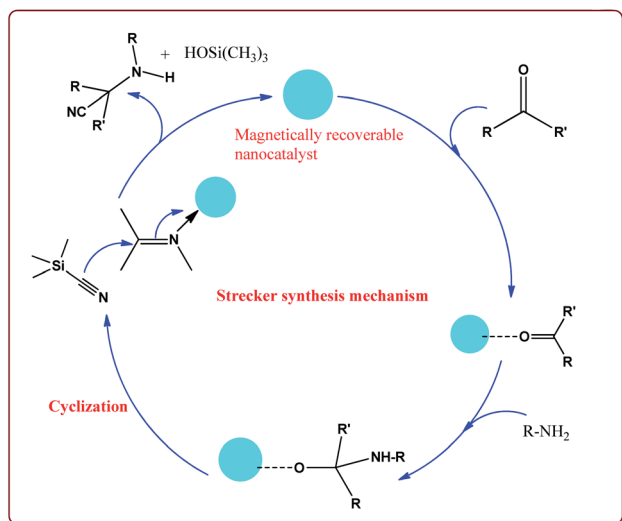
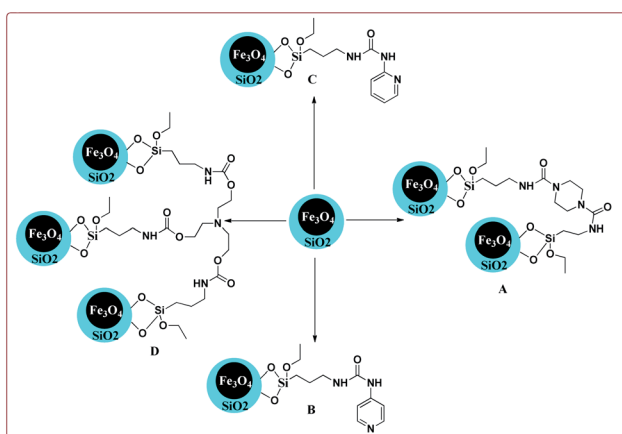


Fig. 9 Mechanistic pathway of Strecker synthesis.

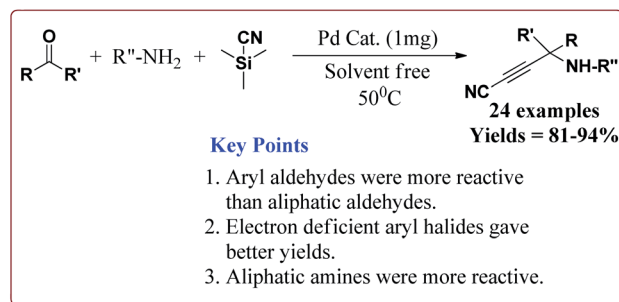
Adolf Strecker in 1850.¹⁵⁶ Since then, significant amount of the work has been reported in literature for the application of this reaction for the preparation of various racemic as well as chiral α -amino acids, α -amino nitriles and heterocyclic derivatives.^{157–163} Typical mechanism of Strecker synthesis is depicted in Fig. 9.

Bagheri *et al.* have reported urea and urethane based four novel magnetic nanocatalysts for the synthesis of α -amino nitriles under solvent free conditions at moderate temperature of 50 °C. The catalysts were prepared by the reaction of $\text{Fe}_2\text{O}_3\text{@SiO}_2$ nanoparticles with the corresponding urea and urethane derivatives in ethanol under ultrasonic vibrations (Scheme 28).

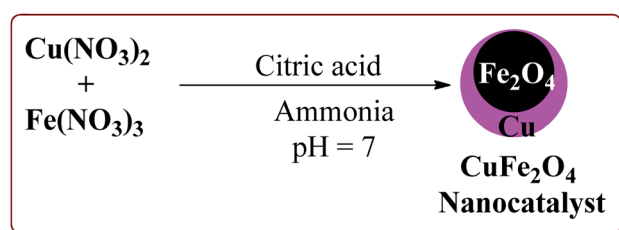
All the prepared catalysts were efficient in catalysing the Strecker synthesis. Catalyst **A** was found to be slightly more active followed by **B**, **C** and **D**. Also, aromatic aldehydes were found to be more reactive than aliphatic aldehydes with electron deficient aryl aldehyde derivatives giving better results



Scheme 28 Preparation of novel urea and urethane palladium nanocatalysts.



Scheme 29 Synthesis of α -aminonitriles derivatives by using urea and urethane based four novel magnetic nanocatalysts.

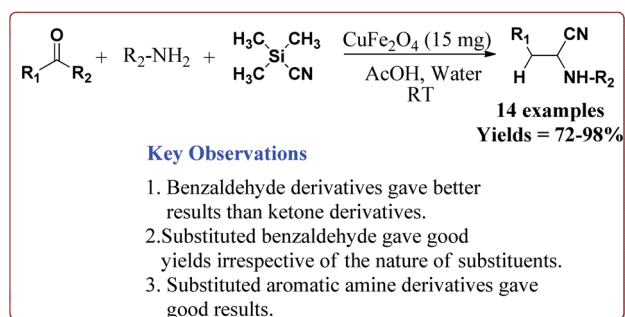


Scheme 30 Preparation of CuFe_2O_4 nanocatalyst by citrate gel precursor method.

than the electron rich aryl aldehydes. Further, aliphatic amines reacted in lesser time under Strecker conditions due to higher nucleophilicity. Only 1 mg of each catalyst was active enough to catalyse the reaction and could be used for 7 times without loss in catalytic activity (Scheme 29).¹⁶⁴

Gharib *et al.* have achieved the synthesis of α -aminonitriles using copper ferrite (CuFe_2O_4) nanocatalyst in one pot by the reaction of various aldehyde derivatives, amines and trimethylsilyl cyanide at room temperature by using water as a solvent. The catalyst was synthesized by citrate gel precursor method by reacting copper nitrate and iron nitrate in citric acid solution at pH = 7 maintained by adding ammonia at higher temperature (Scheme 30).¹⁶⁵

It was observed that the reaction of ketone derivatives proceeded with lesser yields as compared to the benzaldehyde derivatives which gave excellent yields irrespective of the type of



Scheme 31 CuFe_2O_4 nano catalyst catalyzed preparation of α -amino nitrile derivatives.

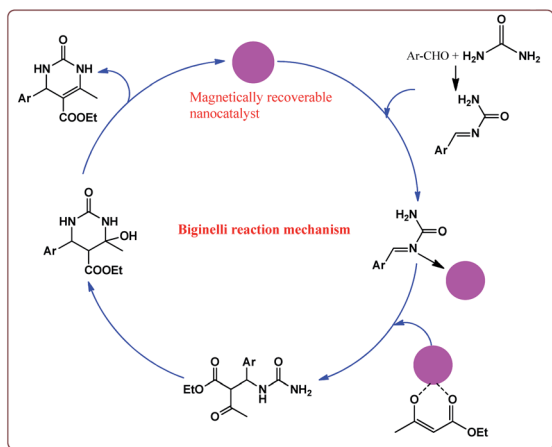
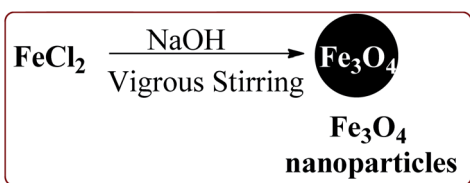
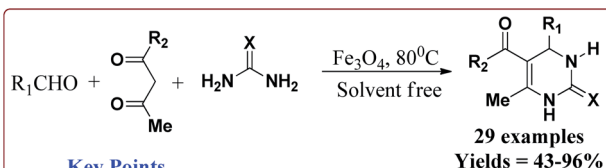


Fig. 10 Mechanistic pathway of Biginelli reaction.

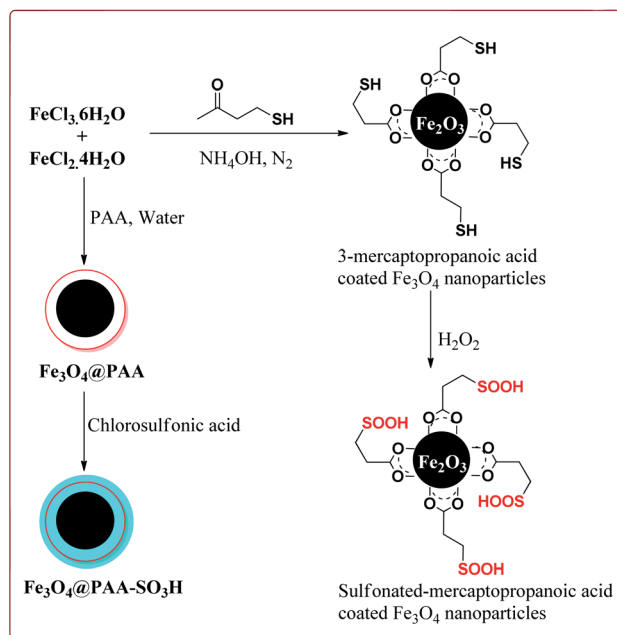
substitution on the aromatic ring system. Also, the substituted aryl amines gave good results for the formation of the products (Scheme 31).¹⁶⁶

4.2.2 Biginelli reaction. Biginelli reaction is one of the classical multicomponent reactions used for the synthesis of heterocyclic derivatives by three component condensation reaction between aldehydes, β-ketoesters and urea or thiourea moiety.¹⁶⁷ This reaction has found its applications for the synthesis of various biological active compounds^{88,168,169} and many reviews have been reported in literature for its synthetic applications.^{170–172} This reaction has also been used for the asymmetric synthesis of various derivatives of industrial use.¹⁷³ Typical mechanism of Biginelli reaction is depicted in Fig. 10.

Nasr-Esfahni *et al.* have reported the use of Fe_3O_4 nanoparticles for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones by using one pot Biginelli condensation of aromatic aldehydes,

Scheme 32 Preparation of Fe_3O_4 nanocatalyst.**Key Points**

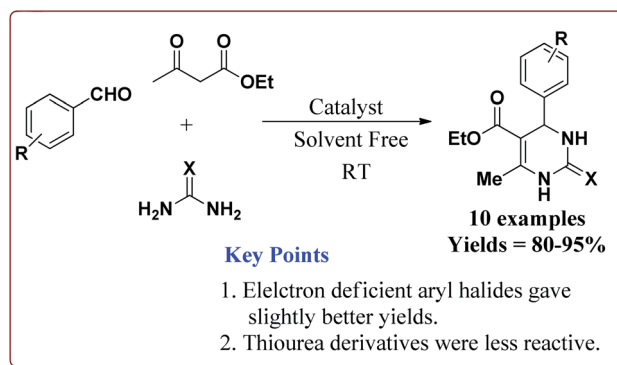
1. Aliphatic aldehydes have lesser yields than aryl halides.
2. Sterically hindered aromatic aldehydes gave lesser yields.
3. Reaction tolerated number of substitutions on aromatic ring.
4. Reaction gave good results with urea and thiourea derivatives.

Scheme 33 Fe_3O_4 nanocatalyst catalyzed Biginelli reactions.Scheme 34 Synthesis of sulfonated-mercaptopropanoic acid coated Fe_3O_4 nanoparticles.

urea or thiourea and β-dicarbonyl derivatives under solvent free conditions. The Fe_3O_4 nanoparticles were prepared by the reaction of FeCl_2 with NaOH under vigorous stirring (Scheme 32).

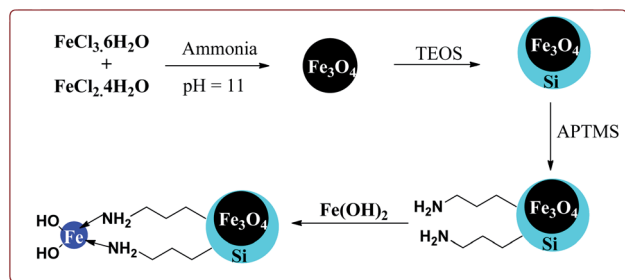
The reaction was well tolerated with various aromatic aldehyde derivatives and gave good yields whereas aliphatic aldehydes gave poor yields. In addition, sterically hindered *ortho* substituted aryl halides gave lesser yields. Also, the reaction gave good results with urea as well as thiourea derivatives and only 20 mol% of the catalyst was sufficient to catalyse the reaction (Scheme 33).¹⁷⁴

Zamani *et al.* have reported the synthesis of sulfonated-mercaptopropanoic acid coated Fe_3O_4 nanoparticles to carry out Biginelli reaction for the preparation of 3,4-dihydropyrimidin-2(1H)-ones in one pot synthesis. The catalyst was prepared by the reaction of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$

**Key Points**

1. Electron deficient aryl halides gave slightly better yields.
2. Thiourea derivatives were less reactive.

Scheme 35 Preparation of 3,4-dihydropyrimidin-2(1H)-ones by using sulfonated-mercaptopropanoic acid coated Fe_3O_4 nanocatalyst.

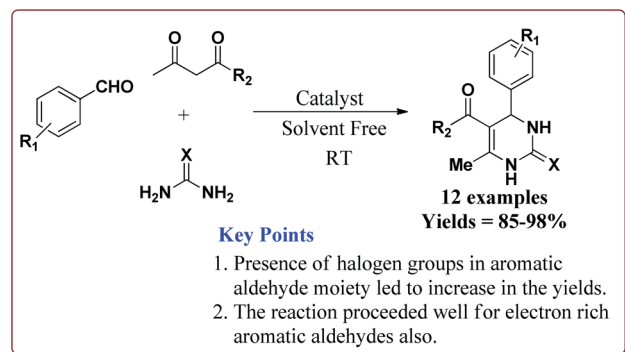


Scheme 36 Preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTMS-Fe(OH)}_2$ nanocatalyst.

followed by the reaction with 3-mercaptopropionic acid in the first step to give 3-mercaptopropionic acid coated Fe_3O_4 nanoparticles followed by oxidation of terminal thiol groups to sulfonic acid groups by H_2O_2 in the second step (Scheme 34). The presence of electron releasing groups on aromatic aldehyde led to slightly decrease in the yield whereas the electron withdrawing groups led to slightly increase in the yields as compared to benzaldehyde. In addition, the thiourea derivatives gave lesser yields as compared to urea derivatives. Further, 60 mg of the catalyst was sufficient to catalyse the reaction and could be used six times effectively (Scheme 35).¹⁷⁵

In one of the other communications, Zamani *et al.* have reported the synthesis of sulfonated-phenylacetic acid coated Fe_3O_4 nanoparticles ($\text{Fe}_3\text{O}_4@\text{PAA-SiO}_3\text{H}$) as a novel nanocatalyst for carrying of Biginelli reaction. The first step of catalyst preparation involved the reaction of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ with phenylacetic acid at $\text{pH} = 11$ followed by sulfonation step by reaction with chlorosulfonic acid to give target catalyst which gave the similar results (Schemes 34 and 35).¹⁷⁶

Sheykhan *et al.* have reported the use of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTMS-Fe(OH)}_2$ nanoparticles as an efficient catalyst for Biginelli reaction. The catalyst was prepared by reacting $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in ammonia followed by reaction with tetraethyl orthosilicate (TEOS) at high temperature to afford $\text{Fe}_3\text{O}_4@\text{SiO}_2$. Next step involved the reaction with 3-aminopropyltrimethoxysilane (APTMS) and Fe(OH)_2 to give target catalyst (Scheme 36).



Scheme 37 $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTMS-Fe(OH)}_2$ catalyzed Biginelli reactions.

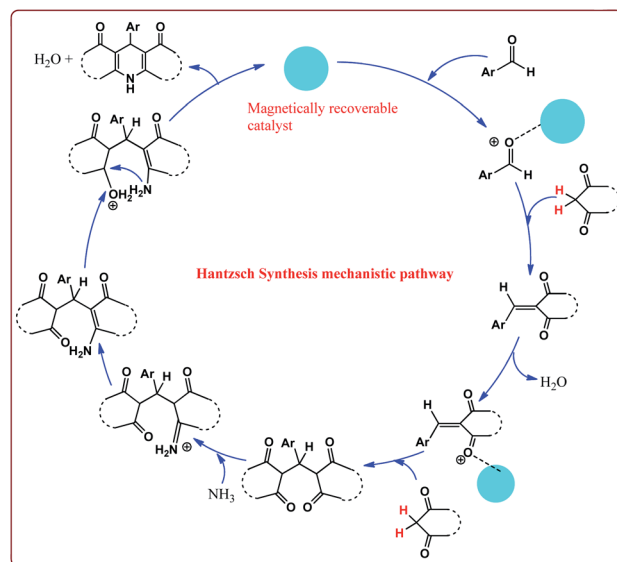
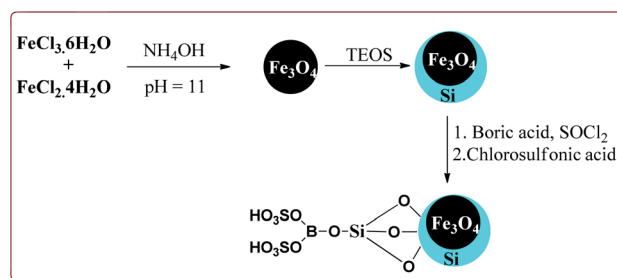


Fig. 11 Mechanistic pathway of Hantzsch reaction.

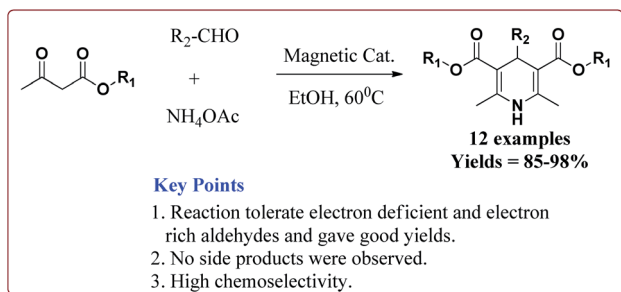
0.43 mol% of the catalyst could catalyse the Biginelli reaction at high temperature. The presence of halogen group on aromatic aldehyde moiety led to increase in the yields. Interestingly, electron rich aromatic aldehydes also gave good results under these conditions (Scheme 37).¹⁷⁷

4.2.3 Hantzsch synthesis. Hantzsch synthesis is one of the most important reaction for the synthesis of 1,4-dihydropyridines (1,4-DHPs) by the reaction of an aldehyde derivative with two equivalents of β -keto ester in the presence ammonia source like ammonium acetate. 1,4-Dihydropyridines (1,4-DHPs) exhibit significant biological as well as medicinal activity.^{178–181} This reaction was first reported in 1882 by Arthur Hantzsch.¹⁸² Various methods are reported in literature for the use of alternate catalysts to improve the Hantzsch synthesis towards greener chemistry.^{183–187} Mechanism of Hantzsch synthesis is depicted in Fig. 11.

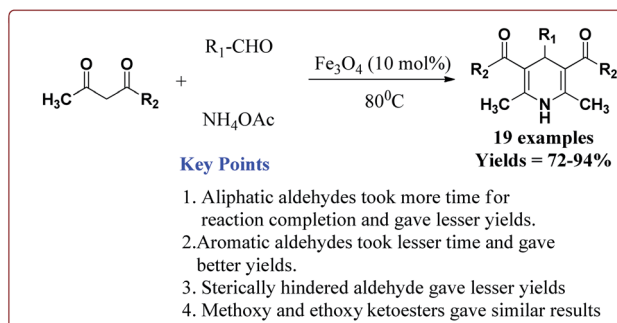
Azizi *et al.* have reported magnetically separable sulfated boric acid functionalized nanoparticles as a catalyst to carry out Hantzsch synthesis. Catalyst was prepared by the reaction of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ with boric acid in the presence of thionyl chloride to get boric acid–silica-coated magnetite nanoparticles which



Scheme 38 Synthesis of sulfated boric acid–silica-coated magnetite nanoparticles.



Scheme 39 Sulfated boric acid-silica-coated magnetite nanoparticles catalyzed Hantzsch synthesis.



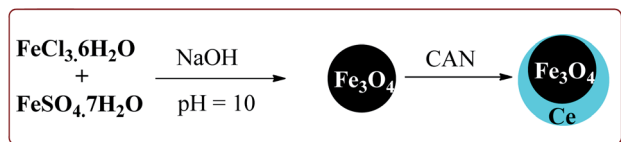
Scheme 42 Fe_3O_4 nanoparticles catalyzed synthesis of 1,4-dihydropyridine derivatives.

were further reacted with chlorosulfonic acid to afford sulfated boric acid-silica-coated magnetite nanoparticles (Scheme 38).

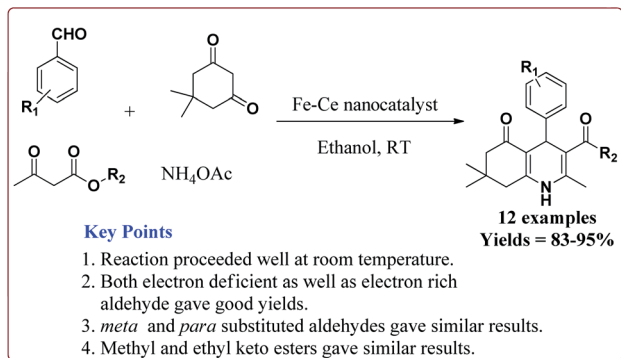
The prepared catalyst was found to very efficient in catalysing the Hantzsch reaction of electron rich as well as electron deficient aldehyde derivatives and gave good yields with high chemo selectivity. No side products were observed during the reactions and only 10 mg of the catalyst was sufficient to catalyse the reaction (Scheme 39).¹⁸⁸

Gawande *et al.* have reported the applications of magnetite-ceria (Nanocat-Fe-Ce) nanocatalyst for the synthesis of 1,4-dihydropyridines at room temperature by using greener protocol. Fe_3O_4 nanoparticles were prepared by already known method and were further reacted with ceric ammonium nitrate (CAN) at pH = 12 to get Nanocat-Fe-Ce catalyst (Scheme 40).

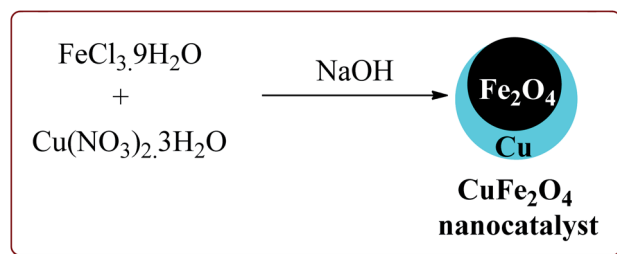
Only 5.22 mol% of the catalyst was sufficient to catalyze the reaction at room temperature and gave good yields for electron deficient as well as electron rich aldehyde derivatives. Further, both methyl as well as ethyl keto esters afforded good yields.



Scheme 40 Preparation of magnetite-ceria (Nanocat-Fe-Ce) nanocatalyst.



Scheme 41 Synthesis of 1,4-dihydropyridines catalyzed by Fe-Ce nanocatalyst.

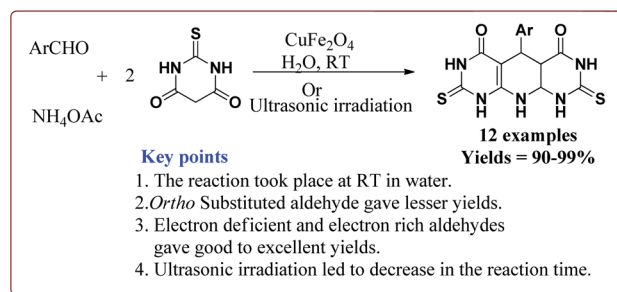


Scheme 43 Preparation of CuFe_2O_4 nanocatalyst.

The catalyst could be used six times without loss in its catalytic activity (Scheme 41).¹⁸⁹

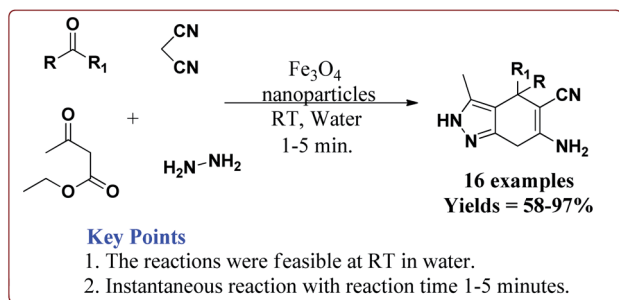
Nasr-Esfahani *et al.* have reported the synthesis of 1,4-dihydropyridines derivatives by using Fe_3O_4 nanocatalyst which was prepared by reported method.¹⁹⁰ Typical procedure involved the reaction of alkyl or aryl aldehyde derivatives, β -dicarbonyl derivatives and ammonium acetate at 80 °C in the presence of 10 mol% of the catalyst. In general, aromatic aldehydes took lesser reaction time than the aliphatic aldehydes and gave better yields. Also, the substitution on the phenyl ring of the aromatic aldehyde led to decrease in the yields. On the other hand, both methyl and ethyl keto ester gave similar results (Scheme 42).¹⁹¹

Naeimi *et al.* have reported one pot four components synthesis of pyrido[2,3-*d*:6,5-*d'*]dipyrimidines in water by the use of CuFe_2O_4 nanoparticles as catalyst which was prepared by



Scheme 44 CuFe_2O_4 catalyzed synthesis of pyrido[2,3-*d*:6,5-*d'*]dipyrimidines.





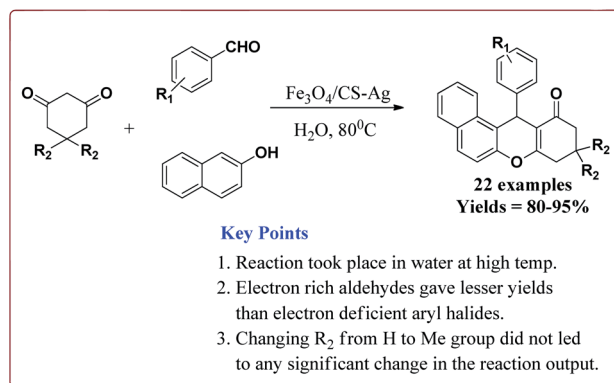
Scheme 45 Preparation of pyranopyrazole derivatives by using Fe_3O_4 nanoparticles.

co-precipitation method by the reaction of $\text{FeCl}_3 \cdot 9\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in the presence of sodium hydroxide (Scheme 43).

The prepared catalyst gave good to excellent yields in case of electron rich and electron deficient aldehyde derivatives. Interestingly, the reaction proceeded well in water at room temperature by using only 10 mol% of the catalyst which could be used for four cycles (Scheme 44).¹⁹² In another reported method, Naeimi *et al.* have reported the similar type of reactions by using the same catalyst under ultrasonic irradiation which resulted in decrease in the reaction time for the formation of the products.¹⁹³

4.2.4 Pyrane synthesis. Pyrane or oxine derivatives are monocyclic six-member oxygen-containing heterocyclic, non-aromatic ring compounds. The first reported pyrane derivatives were developed in 1962 by using pyrolysis reactions.¹³⁴ Pyrane derivatives have found their applications as fragrances and flavors,¹⁹⁴ possess antifungal and antibacterial activity,¹⁹⁵ anticancer activity¹⁹⁶ and are thus of industrial as well as medicinal importance.

Aleem *et al.* have reported the synthesis of pyranopyrazole derivatives in one pot four component reaction of hydrazine hydrate, ethyl acetoacetate, malononitrile and a carbonyl



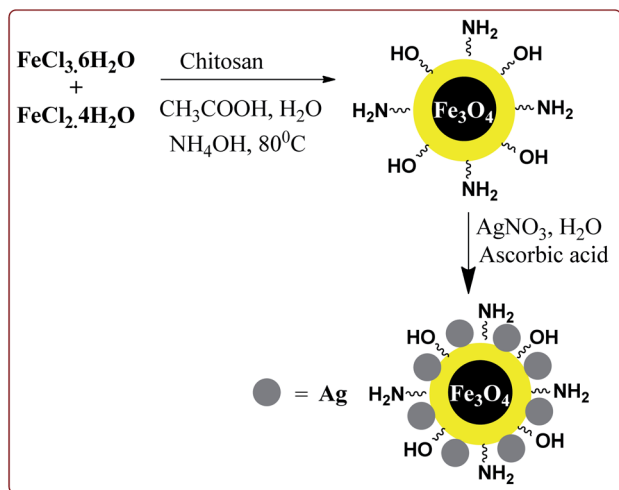
Scheme 47 $\text{Fe}_3\text{O}_4/\text{CS-Ag}$ catalyzed synthesis of tetrahydrobenzo[α]xanthene-11-ones.

derivative by using Fe_3O_4 nanoparticles as catalyst at room temperature by using water as a solvent. Interestingly, only 6 mol% of the catalyst was required for the completion of the reaction in only 1–5 minutes. Further, the catalyst could be used 14 times after purification from ethanol with slight loss of activity after 7th cycle (Scheme 45).¹⁹⁷

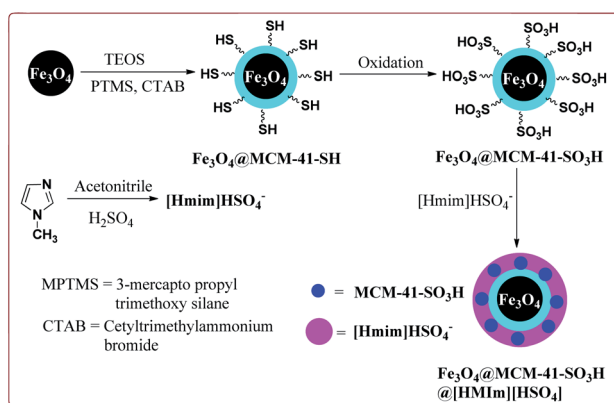
Mohammadi *et al.* have reported silver nanoparticles coated magnetic chitosan ($\text{Fe}_3\text{O}_4/\text{CS-Ag}$) catalyzed one pot three component green synthesis of tetrahydrobenzo[α]xanthene-11-ones. The first step of the catalyst preparation involved the reaction of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in the presence of chitosan to give chitosan-coated magnetic nanoparticles ($\text{Fe}_3\text{O}_4/\text{CS}$) followed by the reaction with silver nitrate in an ultrasonic bath to finally give $\text{Fe}_3\text{O}_4/\text{CS-Ag}$ (Scheme 46).

15 g of the prepared catalyst was sufficient for the reaction and could be reused for 7 cycles without any significant loss of its catalytic activity. Further, the reactions proceeded in water at high temperature where electron deficient aryl aldehyde derivatives gave better results (Scheme 47).¹⁹⁸

Kefayati *et al.* have reported the synthesis of $\text{Fe}_3\text{O}_4@\text{MCM-41-SO}_3\text{H}@\text{[Hmim][HSO}_4\text{]}$ as a magnetically separable catalyst for the preparation of spiro[benzochromeno[2,3-*d*]pyrimidin-indolines]. The catalyst was prepared by reacting

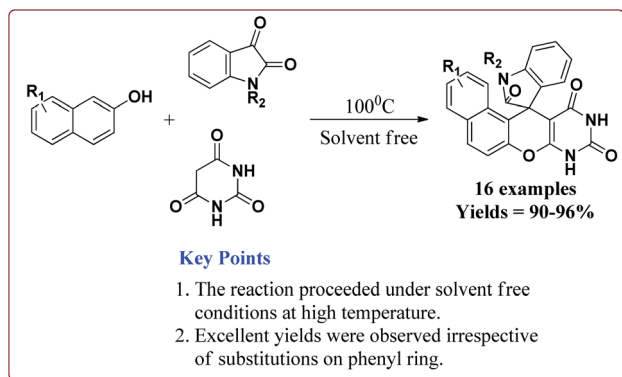


Scheme 46 Synthesis of $\text{Fe}_3\text{O}_4/\text{CS-Ag}$ nanocatalyst.

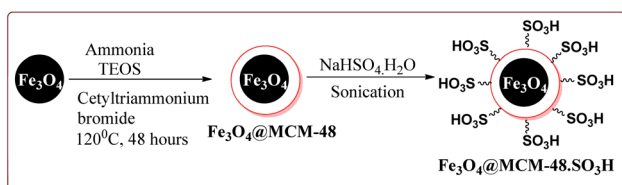


Scheme 48 Preparation of $\text{Fe}_3\text{O}_4@\text{MCM-41-SO}_3\text{H}@\text{[Hmim][HSO}_4\text{]}$ nanocatalyst.





Scheme 49 Preparation of spiro[benzochromeno[2,3-*d*]pyrimidin-4-indolines] catalyzed by $\text{Fe}_3\text{O}_4@\text{MCM-41-SO}_3\text{H}@\text{[Hmim][HSO}_4\text{]}$.

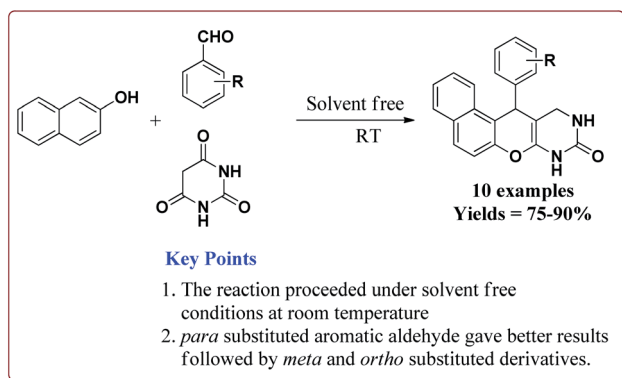


Scheme 50 Preparation of $\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$ nanocatalyst.

$\text{Fe}_3\text{O}_4@\text{MCM-41-SO}_3\text{H}$ and $[\text{Hmim}][\text{HSO}_4]$ at room temperature for 5 hours. Both the reactants were prepared by already reported methods (Scheme 48).^{199–201}

80 mg of the catalyst was able to catalyse the reactions under solvent free conditions at higher temperatures. The reactions gave excellent results irrespective of the substituents on the aromatic ring. Further, the catalyst could be reused for 5 cycles without loss of its catalytic activity (Scheme 49).²⁰²

In an another publication, Kefayati *et al.* have reported the use of $\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$ nanoparticles as a catalyst for the synthesis of benzo[*f*]chromeno[2,3-*d*]pyrimidinones. The catalyst was prepared by the reaction of Fe_3O_4 nanoparticles with TEOS and cetyltrimmonium bromide to give $\text{Fe}_3\text{O}_4@\text{MCM-48}$ which was then reacted with $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ under sonication to afford $\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$ (Scheme 50).



Scheme 51 Preparation of benzo[chromeno[2,3-*d*]pyrimidinones catalyzed by $\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$ nanocatalyst.

The catalyst could catalyse the synthesis of benzo[chromeno[2,3-*d*]pyrimidinones at room temperature using solvent free conditions where *para* substituted aromatic aldehyde derivatives gave better yields followed by *meta* and *ortho* substituted derivatives. Further, the only 50 mg of the catalyst was required to catalyze the reaction and could be used for 5 cycles without any loss in its activity (Scheme 51).²⁰³

5. Concluding remarks and outlook

As discussed in this review, a significant amount of research work has been done in the field of magnetically recoverable catalysts for carrying out various organic transformations. These catalysts offer many advantages such as excellent reaction output, stability, easily separability and reusability with minimal loss of activity. In addition, silica coated nanocatalysts offer the use of wide range of functional groups. However, there are number of reactions where the reaction mechanisms are still unknown and therefore more studies in this area could lead to explain any unexpected results which have been reported in this filed. In addition, there is a need to develop the catalysts which give required stereoselective products. Also, catalyst leaching is one of the important aspects that lead to decrease in the catalytic activity of the catalyst on repeated use in some cases and this area need much attention for future studies and therefore, this field will remain the focus of the research in the upcoming years also.

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Conflicts of interest

There are no conflicts to declare.

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