1. Catalysis: General introduction

The tranquilizing force behind the modernization of chemical industry is catalysis, which ensures more efficient use of finite natural resources, makes our industry safer and helps to prevent waste and air pollution, and thus promotes eco-friendly environment. Catalytic technologies play a key role in the economic development and growth of the chemical industry and contribute to around 20% of world GNP.¹ Catalysis ensures much more efficient use of raw materials and energy, and helps us reduce waste. Catalysts constitute only a tiny fraction of the total costs incurred by the chemical industry, but their added value is substantial because they can be used during many process cycles. Thus, catalysts are the key factors in reducing both the investment and operation costs of a chemical process.²

Conventional catalysis can be divided into homogeneous and heterogeneous catalysis. Homogeneous, where the catalyst is in the same phase as the reactants, and heterogeneous, where the catalyst is in the different phase than the reactants, with the reaction occurring on the surface. Homogeneous catalysts have the advantage of being dissolved in the reaction medium, thus rendering all catalytic sites accessible to reactants in solution. Hence, many homogeneous catalysts demonstrate high activity and selectivity.³,⁴ However, due to difficulties in separation from the products and reaction solvents, it is difficult to recycle such catalysts, especially when noble and/or toxic metals or metal complexes are used.⁵,⁶ As a consequence, there is substantial interest towards the use of heterogeneous and recyclable catalysts, since they eliminates the use of tedious procedures like distillation or extraction,⁵ and leads to greater activity and selectivity.

Immobilization of homogeneous catalysts on supports of nanometric dimensions is considered as a promising way for bridging homogeneous and heterogeneous catalysis because these nano-supports have a large surface area, as well as preserve the reactivity and selectivity of the immobilized catalysts. Moreover, when well dispersed, nanoparticulate catalyst forms a stable suspension in the reaction medium, leads to an elevated rate of reaction. In addition, nanoparticles can permit additional catalytic functionalities due to their unique properties, for example titania nanoparticles exhibit photooxidation on their surface,⁷ while other nanoparticles can utilize light energy as a
result of their photophysical properties. In this perspective, metal oxide nanoparticles supported catalytic systems are eye-catching candidates as they possess high activity and selectivity, remarkable efficiency, large surface-to-volume ratio, crystallinity, monodispersity, topological properties and tenability with improved recyclability. In particular, magnetic nanoparticles (MNPs) have received considerable attention as a viable support for homogeneous catalysts owing to their remarkably different and unique properties, which include high surface area, easy recovery, and nanosize (Fig. 1). The unique functional surface of MNPs allows the immobilization of homogeneous species, including metals, organoligands/organocatalysts, and N-heterocyclic carbenes (NHC).

From a sustainable chemistry viewpoint, MNPs are employed as relevant alternatives to conventional inert supports as these magnetic nanoparticles allow facile separation of the catalyst from the reaction mixture through an external magnet. This not only eliminates the requisite of cumbersome filtration and centrifugation procedures, but also reduces energy consumption, catalytic loss and saves time in achieving catalyst recovery.

**Fig. 1** Tedious and prolonged isolation processes (left); separation/isolation steps in MNPs (right) with respect to conventional systems.
2. Magnetic nanoparticles (MNPs) as a viable support in heterogeneous catalysis

Nowadays, magnetic nanoparticles (MNPs), a type of alternate support, have been extensively explored since they possess important advantages compared to conventional supported systems: i) versatility; ii) ease and simplicity of separation; iii) improved catalyst recyclability (more stable catalysts) and reduction of waste; iv) enhanced catalytic activities; v) different selectivities to products; and vi) access to previously challenging chemistries (e.g. aqueous processes). These characteristics make them more sustainable. Among the MNPs, magnetite (Fe₃O₄) has been identified as the ideal and most widely used support in catalysis because of its low cost and easy preparation. Magnetite is inert and possesses active surface for immobilization or adsorption of catalytic fragments including metal catalysts (Au, Pd, Pt, Cu, Ni, Co, Ir), organocatalysts and enzymes, resulting in the formation of remarkably sustainable catalysts. It has also been directly applied as catalyst in organic transformations.

Magnetite, Fe₃O₄, is a mixed iron(II) and iron(III) oxide in a cubic inverse spinel structure (Fig. 2). It is a ferrimagnetic mineral formed with the spinel structure containing the atoms of Fe(II) and Fe(III), occupying octahedral and tetrahedral sites of coordination, where the oxide anions are arranged as a cubic close packed lattice. The unit cell of Fe₃O₄ has interesting properties because the presence of non-equivalent cations (Fe²⁺ and Fe³⁺) in the crystal structure leads to the formation of a unique magnetic structure. Moreover, iron and oxygen atoms in magnetite confer in it a character of soft Lewis acid and base respectively, as a result, it can promote organic transformations by itself. A wide range of metals, acids and organic molecules can be effortlessly immobilized and supported on the surface of magnetite. The unique properties of magnetite such as non-toxicity and inertness, make it an excellent solid support candidate.
2.1 Synthesis of magnetite nanoparticles (MNPs)

Various synthetic methods have been reported in the literature for the development of magnetic nanoparticles (MNPs) with controlled size and shape\textsuperscript{11-24}. Generally, two important approaches were employed for the synthesis of magnetite nanoparticles, such as bottom up and top down methods (Fig. 3).

Bottom-up approaches for the synthesis of iron oxide nanoparticles includes thermal decomposition, co-precipitation and microemulsion techniques. One of the popular method is the thermal decomposition of iron complex precursors, such as [Fe(acac)\textsubscript{n}] (acac=acetylacetonate) or [Fe(CO)\textsubscript{m}], in the presence of organic solvents and surfactants\textsuperscript{11,12,25}. The reaction temperature and time, ratio of starting reagents, and aging periods are key parameters for controlling the size and morphology of the MNPs\textsuperscript{26}. Another frequently used method is co-precipitation\textsuperscript{26-28}, which is a simple and reproducible pathway to synthesize magnetite nanoparticles. In this, magnetite (Fe\textsubscript{3}O\textsubscript{4}) nanoparticles are synthesized from Fe\textsuperscript{2+}/Fe\textsuperscript{3+} salt solutions in the presence of base under an inert atmosphere\textsuperscript{13-15}. Nanoparticles with different sizes, shapes, and compositions can
be successfully synthesized by varying the type of salts, the Fe\textsuperscript{2+}/Fe\textsuperscript{3+} ratio, pH value, reaction temperature, and the ionic strength of the medium\textsuperscript{27-30}. Since nanoparticles synthesized by coprecipitation method have a tendency to polydisperse in size; thus addition of organic chelating agents, such as carboxylate or a hydroxycarboxylate ions (citric, oleic acid, gluconic) or polymeric agents (starch, dextran, polyvinyl alcohol) during the formation of magnetite nanoparticles, is necessary for producing monodisperse iron oxide nanoparticles.

To gain more control over nanoparticle size and morphology, microemulsion technique can also be used, wherein separate oil-water microemulsions containing the different salts can be combined.\textsuperscript{13} Given their dynamic nature, the micelles will continually coalesce and break apart, ultimately forming microreactors containing mixtures of the two metal salts.\textsuperscript{31} Micelle size can be tuned by controlling oil-water ratios, providing more control over the nanoparticle synthesis environment.\textsuperscript{32,33}

**Fig. 3** Synthesis of iron oxide nanoparticles.

Top-down or lateral approaches for the synthesis of iron oxide nanoparticles rely on transforming existing solid phase materials. The grinding of bulk iron oxide produces particles in the nanometer regime, depending on grinding time and frequency\textsuperscript{34}. Such processes often yield irregular and polydispersed particles. For more control of particle
morphology, pre-existing, well-defined reduced iron particles can be oxidized in a controlled environment to provide the desired iron oxide nanoparticles with a high degree of precision (Fig. 3)\textsuperscript{35}.

Sayed et al. have reported a facile and sustainable approach for the synthesis of six different shaped iron oxides, such as (a) nanorod, (b) nanohusk, (c) distorted cubes, (d) nanocubes, (e) porous spheres, and (f) self-oriented flowers (Fig. 4)\textsuperscript{36}. Interestingly, iron oxides with six different shapes have been synthesised using exactly same synthetic protocol by simply changing the precursor iron salts. Microwave (MW) assisted templated solvo-thermal technique has been used for the synthesis of six different shaped iron oxides. Moreover, all the synthesized iron oxides were fully characterized for their textural properties such as, size, shape, phases, surface area, etc by the Sayed et al. Besides, band gap measurements along with the magnetic properties evaluation were also reported.

\textbf{Fig. 4} SEM images of iron oxides with six different shapes: (a) nanorod, (b) nanohusk, (c) distorted cubes, (d) nanocubes, (e) porous spheres, and (f) self-oriented flowers.
Table 1. Synthesis of different shaped iron oxides from different iron salts precursors

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Precursor</th>
<th>Shapes</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Fe(II)sulphateheptahydrate</td>
<td>Nanorods</td>
</tr>
<tr>
<td>2</td>
<td>Fe(II)oxalate dihydrate</td>
<td>Nanohusks</td>
</tr>
<tr>
<td>3</td>
<td>Fe(III)chloride hexahydrate</td>
<td>Cubes</td>
</tr>
<tr>
<td>4</td>
<td>Fe(III)nitrate nonahydrate</td>
<td>Nanocubes</td>
</tr>
<tr>
<td>5</td>
<td>Fe(II)D-gluconatedehydrate</td>
<td>Porous spheres</td>
</tr>
<tr>
<td>6</td>
<td>Fe(0)pentacarbonyl</td>
<td>Self-arranged flowers</td>
</tr>
</tbody>
</table>

2.2 Functionalized MNPs and their applications in organic synthesis

Nowadays, magnetite nanoparticles or magnetite supported catalysts have been efficaciously deployed in organic synthesis for a range of reactions. Literature is full of variety of examples where magnetite nanoparticles or magnetite supported catalysts were used to carry out environmentally benign organic transformations; that are too in short time span and in more economical way (Fig. 5).

![Fig. 5 Applications of Fe₃O₄ supported catalysts.](image-url)
2.2.1 Fe$_3$O$_4$/ functionalized Fe$_3$O$_4$ as a catalyst

Fe$_3$O$_4$ is stable, economical, environmentally benign, experimentally convenient to handle, and safe reagent, which can be easily synthesized and employed for many organic syntheses. From an environmental point of view, magnetite offers advantages over other conventional supports due to their easy recovery from the reaction mixture via external magnet, avoids tedious workup processes, such as filtration or centrifugation. Some important organic reactions catalyzed by Fe$_3$O$_4$ are given below:-

Saadatjoo$^{37}$ et al. have reported ultrasound-assisted stereoselective synthesis of β-amino carbonyl compounds via Mannich reaction using Fe$_3$O$_4$. Here, Fe$_3$O$_4$ nanoparticles having size less than 40 nm, were prepared by chemical precipitation method. Moreover, the proposed methodology offered several advantages, such as good yield, short reaction time and recyclable catalyst (Scheme 1).

Scheme 1

\[
\text{FeCl}_3 + \text{FeCl}_2 + \text{NH}_3\cdot\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4
\]

Datta$^{38}$ et al. have reported a simplistic approach for the synthesis of magnetite microspheres with flower-like morphology from iron(III) oxalate via a simple two-step process (Scheme 2). Firstly, thermally induced solid state decomposition of iron oxalate was carried out to produce iron(III) oxide (Fe$_2$O$_3$) with ultra-small nanostructured particles; and secondly, the subsequent thermally induced reduction of the prepared iron(III) oxide under a hydrogen atmosphere afforded magnetite (Fe$_3$O$_4$). The proposed catalyst has been employed as a robust, chemoselective and magnetically reusable catalyst for the reduction of industrially valuable nitroarenes in the presence of other sensitive reducible functional groups. The superb catalytic performance, simple procedure, easy separation, and the recyclability have made this environmentally benign catalytic system a notable and useful alternative to other Fe-based catalytic systems.
Zeng et al. have demonstrated Fe$_3$O$_4$ nanoparticles as robust and magnetically recoverable catalyst for three-component coupling of aldehyde, alkyne, and amine. A diverse range of propargylamines have been obtained in moderate to excellent yields under mild conditions in air. Also, the separation and reuse of the magnetic Fe$_3$O$_4$ nanoparticles was simple and economical.

Gao et al. have reported a simple and non-toxic approach for the synthesis of Fe$_3$O$_4$ nanoparticles/hydrogel nanocomposites. Here, crystalline Fe$_3$O$_4$ nanoctahedra have been fabricated *in situ* within a negatively charged hydrogel matrix (Scheme 3). The proposed magnetic nanocomposites exhibited intrinsic peroxidase-like activities, which are related to the morphology of the Fe$_3$O$_4$ nanostructures *in situ* fabricated within the hydrogel. It has been shown that the magnetic nanocomposite loaded with Fe$_3$O$_4$ nanoctahedra has possessed a sensitive response towards H$_2$O$_2$ detection with a limit of $5 \times 10^{-6}$ molL$^{-1}$. Based on the simplistic, economical fabrication strategy, large-scale production of this magnetic nanocomposite with a tunable peroxidase-like activity can be expected to revolutionize catalysis applications in biotechnology and environmental chemistry.
Monodispersed superparamagnetic Fe₃O₄ nanoparticles impregnated with oleic acid were successfully synthesized by Patsula et al. via thermal decomposition of Fe(III) glucuronate. The size, shape and particle size distribution has been controlled by changing the reaction parameters, such as the concentration of the stabilizer, reaction temperature, and high-boiling solvents. As we know, for the potential use in biomedicine, the Fe₃O₄ nanoparticles must be dispersible in water.
Here, $\alpha$-carboxyl-$\omega$-bis(ethane-2,1-diyl)phosphonic acid-terminated poly(3-O-methacryloyl-$\alpha$-D-glucopyranose) (PMG-P) was used as surface modifying agent in order to get water dispersible Fe$_3$O$_4$ nanoparticles. For future biomedical applications, non-toxicity has played a key role. Thus, PMG-P&Fe$_3$O$_4$ nanoparticles have been tested on rat mesenchymal stem cells to determine the particle toxicity. MR relaxometry has confirmed that the PMG-P&Fe$_3$O$_4$ nanoparticles have high relaxivity. Therefore, the proposed PMG-P&Fe$_3$O$_4$ nanoparticles have the potential to be used in biomedical applications, especially as contrast agents for magnetic resonance imaging (Scheme 4).

An innovative and environmentally-friendly quick sonochemical method was used for the successful synthesis of Fe$_3$O$_4$ nanocubes (NCs) decorated on RGO nanosheets (NSs) by Abbas et al. (Fig. 6). Here, iron(II) sulfate heptahydrate and GO were used as precursors, water as reaction medium and NaOH as reducing agent. Besides, hydrothermal method was also employed to synthesize the same catalysts for the comparison with the ultrasonocation technique. Fe$_3$O$_4$ and RGO/Fe$_3$O$_4$ catalysts prepared via both sonochemical and hydrothermal approaches were tested for industrially relevant Fischer-Tropsch synthesis. It has been proposed that the catalysts produced using the sonochemical method had a better CO conversion rate [Fe$_3$O$_4$ (80%), RGO/Fe$_3$O$_4$ (82%)] than the hydrothermally synthesized catalysts. But, when compared with the naked-Fe$_3$O$_4$

![Image](image-url)
catalysts, the sonochemically and hydrothermally synthesized RGO-supported Fe₃O₄ catalysts showed better catalytic activity. Thus, the reported surfactantless-sonochemical method holds promise for the eco-friendly synthesis of highly efficient catalyst materials for Fischer-Tropsch reaction.

A facile method for the preparation of a novel and magnetically separable Fe₃O₄/graphitic carbon nitride (g-C₃N₄) nanocomposites were reported by Zhu et al. (Fig. 7). The photocatalytic ability and stability of the synthesized samples were studied by the degradation of Rhodamine B (RhB) in simulated sun irradiation. In addition to this, the degree of mineralization of RhB and the optimum conditions such as pH and dosage of catalyst were also explored. It has been reported that the synthesized Fe₃O₄/g-C₃N₄ nanocomposites not only have higher photocatalytic activity, but also possess significant magnetic property and stronger stability, which are vital for the reuse in water pollutant treatment. Moreover, photoelectrochemical activities of proposed Fe₃O₄/g-C₃N₄ were also investigated. The photocurrent enhancement indicated a higher separation efficiency of electrons and holes due to the heterojunction between Fe₃O₄ and g-C₃N₄. This study showed the potential of Fe₃O₄/g-C₃N₄ nanocomposites as heterogeneous photocatalysts to remove pollutants from water.

Fig. 7 Fe₃O₄/graphitic carbon nitride (g-C₃N₄) nanocomposites showing the degradation of Rhodamine B (RhB).
A facile and effective method for the synthesis of multi-walled carbon nanotubes Fe_3O_4 impregnated with melamine has been reported by Fahimirad et al. (Scheme 5). MWCNTs-Fe_3O_4@melamine has been used for the concurrent ultrasound-assisted magnetic dispersive microsolid-phase extraction of the toxic metal ions, such as Pb(II), Cd(II), and Ni(II) ions from organic and inorganic vegetables. Two foremost advantages of the synthesized nanoadsorbent are: i) simple separation via external magnet, and ii) coating of melamine particles on the surface of MWCNTs-Fe_3O_4 as a functional group. These advantages have resulted in short extraction time and faster pre-concentration process, which led to increased adsorption of the metal ions Pb(II), Cd(II), and Ni(II). Additionally, the nanoadsorbent could be used for six times in real samples with negligible changes in the recovery of these ions.

Scheme 5

A reduced graphene oxide supported magnetite nanoparticles, (nFe_3O_4/RGO) were successfully synthesized by Yan et al. (Scheme 6). For the first time, it was shown that the synthesized composite acts as an efficient persulfate activator to generate SO_4^{•−} for trichloroethylene (TCE) degradation. Trichloroethylene (TCE) is enumerated as a priority pollutant by the United States Environmental Protection Agency (USEPA), and chronic
exposure to TCE via inhalation of their vapours released from ground water may cause cancer and other adverse effects on human health. It is important to mention that here agglomeration of Fe$_3$O$_4$ nanoparticles has been successfully prevented by their dispersion on RGO surface. The redox effect coupled in nFe$_3$O$_4$ and the electron transfer occurred through functional groups containing oxygen on the surface of RGO has stimulated the generation of SO$_4^{•−}$. The activation of persulfate via nFe$_3$O$_4$/RGO has showed a promise alternative for the remediation of TCE contaminated water.

Scheme 6

Yu$^{46}$ et al. have demonstrated a simplistic approach for the fabrication of monodispersed Fe$_3$O$_4$ nanocrystals with different size and morphology (Scheme 7). The synthesized nanocrystals possessed face-centered cubic structure. Here, oleic acid has played a key role in the dispersion of Fe$_3$O$_4$ nanocrystals. It has been shown that in order to reduce the surface free energy, the morphologies of Fe$_3$O$_4$ nanocrystals in the presence of oleic acid were changed from cubic to octahedral. Moreover, the coercive force, the saturation
magnetization and the blocking temperature of the samples are size-dependent. The proposed Fe₃O₄ nanocrystals possessed good magnetic property and excellent dispersion, which endowed the materials with a promising application in magnetic fluid fields including shock absorption, sealing, mineral processing, medical equipment and other aspects.

**Scheme 7**

Dutta⁴⁷ *et al.* have reported the synthesis of novel nanocarriers via self-assembly of anionic surfactant, SDS on the surface of oleic acid grafted MNPs, and examined their potential applications in drug delivery and hyperthermia therapy (**Scheme 8**). TEM and XRD analyses have shown that crystalline Fe₃O₄ nanoparticles so synthesized were of average size of 10 nm. Further, coating of oleic acid and self-assembly of SDS on Fe₃O₄ nanoparticles were confirmed from FT-IR and TGA studies. These nanocarriers have showed good magnetic field responsivity, colloidal stability and protein resistance characteristics, and also have capability of loading dual anticancer drugs (DOX and CUR). It has been observed that the interfacial modification of Fe₃O₄ nanoparticles with SDS creates functionalized exteriors with high densities of sulphate moieties for electrostatic binding of DOX, whereas the hydrophobic interlayer has provided sites for encapsulation of CUR. These nanocarriers possess good therapeutic efficacy upon conjugated/encapsulated with DOX and CUR. Moreover, these nanocarriers can also be used as effective heating source for hyperthermia therapy.
2.2.2 Acid functionalized MNPs

Homogeneous acid catalysts such as Lewis and Bronsted acids are applicable to a plethora of industrial organic transformations, such as Aldol condensations, hydrolysis, acylations, nucleophilic additions and others. However, reactor corrosion, difficult separations, waste neutralization and the inability for reuse are the major drawbacks associated with soluble, liquid acids. Moreover, some of the acid catalysts are moisture sensitive, which necessitates specialized reaction equipment and increases operating difficulty. The facile recovery and reuse of homogeneous acid catalysts via covalent tethering to a heterogeneous support, while maintaining high catalytic activity, has long been a goal in catalysis research. Therefore, there is a need for the development of novel, low cost, eco-friendly, non-toxic, recyclable solid catalysts with high efficiency that can replace highly corrosive, hazardous and polluting acid catalysts. For an efficient solid acid catalyst, there is an imperative need for excellent support material which possess high surface area and well-defined nanopores with a narrow pore size distribution. Recently, mesoporous solid supports such as silica, SBA-15, MCM-41, etc have been extensively used for the immobilization of acids, due to their high surface area and well defined structure. However, these materials can suffer from decreased catalytic activity resulting from diffusion limitations, as chemicals diffuse through the porous silica networks or through swollen polymeric resins.
Nowadays, nanoparticles have received increasing attention as an alternative support for catalysts. As the diameter of the particle decreases to the nanometer scale, ample external surface area becomes available for surface modifications. In addition, these particles can be dispersed into solvents, forming stable dispersions. However, the problem associated with these nanoparticles is the difficulty in their separation from reaction mixture. In this perspective, catalysts supported on magnetic nanoparticles (MNPs), usually iron oxides, have emerged as an suitable alternate to the conventional supports. MNPs can be quickly and easily recovered from the reaction mixture in the presence of external magnetic fields for reuse. Further, internal diffusion limitations can be avoided, because all of the available surface area of the nonporous MNPs is external\textsuperscript{57}. Moreover, the surface of the MNPs can be easily functionalized to accommodate a wide variety of organic and organometallic catalysts\textsuperscript{58}. Below, we are citing some important synthetic methods for the preparation of acid functionalized magnetite nanoparticles and their applications in organic synthesis.

Liu\textsuperscript{59} et al. have successfully synthesized triflic acid functionalized silica coated magnetic nanoparticles [\(\gamma\)-\(\text{Fe}_2\text{O}_3\@\text{SiO}_2\)-\(\text{TfOH}\)] and its catalytic activity was evaluated for the conversion of aldehydes or ketones into their corresponding gem-dihydroperoxides in the presence of 30% aqueous hydrogen peroxide (Scheme 9). The catalyst was found to be highly efficient and can be easily separated from the reaction mixture via magnetic decantation. Further, it can be recyclable up to seven runs without significant loss of catalytic activity.

**Scheme 9**
Naeimi et al. have reported sulfonic acid-functionalized silica coated magnetic nanoparticles with core shell structure (Fe₃O₄@silica sulfonic acid) as an novel and efficient catalyst for the cost-effective synthesis of 1-substituted-phenyl-1H-tetrazoles under solvent-free conditions. Here, the magnetite nanoparticles were prepared by a co-precipitation method, whereas modified stober method was used for the coating of SiO₂ composite over the Fe₃O₄ nanoparticles (Scheme 10).

**Scheme 10**

One-pot synthesis of Fe₃O₄@C core shell magnetic nanoparticles with an average size of about 190 nm were successfully reported by Zheng et al (Scheme 11). The grafting of sulfonic groups onto the surface of Fe₃O₄@C nanoparticles was successfully achieved by the method of vapor-phase sulfonation. The magnetically recyclable solid acid catalyst was studied for the condensation of benzaldehyde and ethylene glycol, and showed high

**Scheme 11**
catalytic activity with a conversion rate of 88.3% under mild conditions. Besides, the synthesized catalyst was easily separated via magnet and reusable upto eight times without any significant decrease in catalytic activity.

Mobarak et al. have developed a novel and efficient procedure for the three-component Strecker reaction of a series of aldehydes or ketones, amines, and trimethylsilyl cyanide for the synthesis of α-aminonitriles under solvent-free conditions using magnetic solid sulfonic acid modified with hydrophobic regulators, Fe$_3$O$_4$@SiO$_2$@PhSO$_3$H (Fig. 8). The combination of hydrophobicity and acidity on the Fe$_3$O$_4$@SiO$_2$ core–shell of the magnetic nanobeads, as well as its water-resistant property, has enabled easy mass transfer and catalytic activity in the Strecker reaction. The reported catalyst was easily separable via magnet and can be reused upto six runs without any significant loss of activity.

![Diagram](image-url)

**Fig. 8** Fe$_3$O$_4$@SiO$_2$@PhSO$_3$H for the Strecker reaction.

Naeimi et al. have reported Fe$_3$O$_4$@SiO$_2$-SO$_3$H as a reusable, inexpensive and efficient catalyst for the one-pot synthesis of 1,8-dioxo-octahydroxanthenes (Fig. 9).
A new and highly efficient nano-structured and magnetically recoverable catalyst, Fe₃O₄@FSM-16-SO₃H was developed successfully by Uderji et al.⁶⁴ The synthesized catalyst showed excellent catalytic activity for the synthesis of polyhydroquinolines via four-component reaction of various aldehydes, ethyl cyanoacetate, dimedone and ammonium acetate. The main advantages of this protocol were higher yields, high reusability and short reaction time. In addition, the magnetic nano-catalyst could be separated via external magnet and was reusable many times without any significant loss of activity (Scheme 12).

Scheme 12

Fig. 9 Fe₃O₄@SiO₂-SO₃H for the synthesis of 1,8-dioxo-octahydroxanthenes.
Koukabi et al.\textsuperscript{65} have reported the convenient method for the loading of sulfonic acid groups onto magnetite nanoparticles. Here, chlorosulfonic acid was used as sulfonating agent. The key advantages of this method are solvent-free conditions, room temperature, easy immobilization technique, and low cost precursors for the synthesis of highly active and stable MNPs with high densities of functional groups. The catalyst was active for the Hantzsch reaction and the products were isolated in good to excellent yields (Scheme 13).

**Scheme 13**

![Diagram of the loading of sulfonic acid groups onto magnetite nanoparticles.](image)

\[= \text{g-Fe}_2\text{O}_3 \text{ or g-Fe}_2\text{O}_3@\text{SiO}_2\]

### 2.2.3 Organocatalyst functionalized MNPs

During the past decade, organocatalysis has become a rapid emerging area in organic chemistry. This metal-free approach to the synthesis of biologically important organic molecules has attracted worldwide attention\textsuperscript{66–69}. It has served as an attractive technology for chemists, particularly in industry and results in disposal of metal analogues, and gives inexpensive source of catalysts. A diverse set of reactions, including enantioselective C–C, C–N, C–O bond formation,\textsuperscript{70} Diels–Alder,\textsuperscript{71,72} Baylis–Hilman,\textsuperscript{73,74} Mannich,\textsuperscript{75–77} Michael,\textsuperscript{78,79} Friedel–Crafts alkylation,\textsuperscript{80} oxidation,\textsuperscript{81,82} and carbohydrate synthesis,\textsuperscript{83} have benefited from the developments in this area.\textsuperscript{84–86}This relatively green approach has been rendered even greener by efforts in immobilization and recycling of the immobilized organocatalysts, which involve their adsorption, covalent linkage, and dissolution in various matrices\textsuperscript{87–90}. There is a considerable interest in the immobilization of organocatalysts onto heterogeneous supports. In this concern, magnetic nanoparticles
offer a number of advantages as a substrate enabling the retrieval and recycling of organocatalysts, which are normally impossible to remove from the reaction mixture. Literature is full of examples of immobilization of organocatalysts onto magnetic support and their applications in catalyzing important organic transformations. Some of which are listed below:

Polshettiwar et al. have reported a novel concept of immobilization of totally benign and naturally abundant nano-organocatalyst, glutathione onto magnetic nanoparticles (Fig. 10). The catalyst showed excellent activity for microwave-assisted Aza-Michael reactions, Paal-Knorr and pyrazole synthesis. Moreover, use of aqueous medium instead of organic solvent, for the Paal–Knorr reaction of amines has made the reported process greener and more economic. Also, this novel nano-organocatalyst bridges the gap between homogeneous and heterogeneous catalysis, thus preserving the desirable attributes of both the systems. 

![Glutathione immobilized onto magnetic nanoparticles](image)

**Fig. 10** Glutathione immobilized onto magnetic nanoparticles for the Aza-Michael reactions, Paal-Knorr and pyrazole synthesis.

Nasseri et al.\textsuperscript{92} have reported the synthesis of methylene dipyridine immobilized onto silica shell coated Fe\textsubscript{3}O\textsubscript{4} nanoparticles using a triethoxysilane derivative as a linker. The
nanocatalysts showed high efficiency for the synthesis of biologically active pyrazolophthalazinyl spirooxindoles. Moreover, the synthesized catalyst was easy to recover via magnet and is recyclable up to five runs (Fig. 11).

![Methylene dipyridine immobilized onto silica shell coated Fe₃O₄ nanoparticles for the synthesis of pyrazolophthalazinyl spirooxindoles.](image)

**Fig. 11** Methylene dipyridine immobilized onto silica shell coated Fe₃O₄ nanoparticles for the synthesis of pyrazolophthalazinyl spirooxindoles.

Direct binding of organocatalytic species to the surface of magnetic iron oxide nanoparticles was successfully achieved by Toprak et al.⁹³. They have reported the synthesis of 4-piperidine carboxylic acid functionalized magnetite nanoparticles directly via base catalyzed precipitation reaction. This magnetic organocatalyst was used for the synthesis of nitro-alkenes from aldehydes and nitroalkanes via Knoevenagel condensation (Scheme 14).

**Scheme 14**

\[
\begin{align*}
\text{FeCl}_3\cdot6\text{H}_2\text{O} & \quad \text{NH}_3\text{OH, N}_2 \\
+ \quad 80 \, ^\circ\text{C}, 120 \, \text{min}
\end{align*}
\]
Dangolani et al.\textsuperscript{94} have reported an efficient and simple strategy for the chemical modification of MNPs with DMAP (Scheme 15). The MNP-DMAP was used as a proficient heterogeneous organocatalyst for the one-pot synthesis of 2-amino-4H-chromene-3-carbonitrile via three-component coupling reaction of aldehydes, \(\beta\)-diketones and malononitrile under mild and green conditions. The developed organocatalyst system was recyclable up to ten times without any change in catalytic activity.

\textbf{Scheme 15}

\[\text{Fe}_3\text{O}_4@\text{SiO}_2 \rightarrow \text{Fe}_3\text{O}_4@\text{SiO}_2@\text{vinyl} \]

\[\text{HN} \quad \text{NH} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Oxiran} \]

Nezhad et al.\textsuperscript{95} have unveiled an efficient and novel method for the immobilization of L-cysteine onto silica coated magnetic nanoparticles. Here, the vinyl group on the surface of VMNP material was reacted with the SH group of L-cysteine in the presence of azobisisobutyronitrile (AIBN). The synthesized organocatalyst was used as an efficient heterogeneous organocatalyst for one-pot synthesis of 2-amino-4-(1H-indol-3-yl)-4H-chromene-3-carbonitrile under mild, green and heterogeneous conditions. Moreover, this magnetic recyclable organocatalytic system was reusable for seven times without any significant decreased in catalytic activity (Scheme 16).
2.2.4 Transition metal functionalized MNPs

MNPs have emerged as a versatile solid support for the immobilization of transition metal nanoparticles (Ag, Pd, Cu, Co, Au, Rh etc). However, aggregation of the naked MNPs is virtually unavoidable because of their small interparticle distances, high surface energy, and the existence of Vander Waals forces. To solve this problem, modification of MNPs using suitable stabilizing ligands or coating materials (including small molecules, silica, polymers, carbon, ionic liquids, metal or metal oxide NPs, and their layer-by-layer combinations) has been proved to be the best solution to date. It is also noteworthy to mention that in many cases, coating of protective layer over the naked MNPs not only stabilize them but also provide sites for the immobilization of active species, such as metal nanoparticles, organocatalysts, acids etc.

Long et al.\textsuperscript{96} have reported the synthesis of three core–shell supports i.e. pyrrole, glucose, and tetraethyl orthosilicate (TEOS), respectively, encasing magnetic Fe\textsubscript{3}O\textsubscript{4}
nanoparticles using different “green” approaches (Scheme 17). After that, Pt nanoparticles (NPs) were uniformly immobilized onto these supports using NaBH₄ as the reducing agent. It has been reported that the coating of pyrrole or glucose or tetraethyl orthosilicate (TEOS) over MNPs have remarkably affected the distribution of Pt NPs and its catalytic activity. It has also been reported that Pt NPs dispersed more uniformly on the surface of Fe₃O₄@C and Fe₃O₄@PPy as compared to Fe₃O₄@SiO₂. Among them, Pt immobilized on polypyrrole (PPy) coated MNPs showed the best catalytic activity for the selective oxidation of glycerol to glyceric acid, and ethanol to acetic acid in the presence of molecular oxygen. Moreover, it could be recyclable up to four times without any significant loss in activity.

Scheme 17

Girija et al.⁹⁷ have reported the synthesis of nickel(II) complex supported onto functionalized magnetite nanoparticles (Fig. 12). Studies revealed that Fe₃O₄@[Ni(bpy)₂(py-tmos)] is a new and highly efficient green catalyst for the synthesis of a diverse range of 3,4-dihydropyrimidin-2-(1H)-ones under solvent-free conditions.

Fig. 12 Fe₃O₄@[Ni(bpy)₂(py-tmos)] for the synthesis of 3,4-dihydropyrimidin-2-(1H)-ones.
Moreover, Fe₃O₄@[Ni(bpy)₂(py-tmos)] could be easily recovered by a simple magnetic separation and recycled at least five times without deterioration in catalytic activity.

Superparamagnetic\(^9^8\) Ag@Fe₃O₄ nanospheres with core–shell nanostructure have been successfully synthesized by Jiang et al. via a facile one-pot method (Scheme 18). They reported that particles with tunable core size can be easily synthesized by varying the synthesis parameters. Further, they found that the diameter of the as-synthesized nanospheres was near 200 nm and the core sizes were between 50 and 100 nm. Moreover, the saturated magnetization of Ag@Fe₃O₄ nanospheres was found to be in the range of 27.4 emu g⁻¹ at room temperature, which facilitated them to be separated from the solution via magnet.

**Scheme 18**

\[
\text{Fe(NO}_3\text{)}_3\cdot9\text{H}_2\text{O} + \text{C}_6\text{H}_5\text{O}_7\text{Na}_3\cdot2\text{H}_2\text{O} + \text{NH}_2\text{CONH}_2 + \text{AgNO}_3 \rightarrow \text{Ag@Fe}_3\text{O}_4
\]

A novel and efficient antimony grafted magnetic nanoparticles catalyst was successfully prepared by Ma et al.\(^9^9\) and its catalytic activity was studied for the Clauson-Kaas reaction. It was reported that the reaction proceeded efficiently in aqueous medium to give the corresponding \(N\)-substituted pyrroles in high yield and the catalyst is recyclable for six times without any significant loss in its catalytic activity (Fig. 13).

**Fig. 13** Antimony grafted magnetic nanoparticles for the synthesis of \(N\)-substituted pyrroles.

Sharma et al.\(^1^0^0\) have reported the synthesis of magnetically retrievable catalytic system, Cu-2QC@Am-SiO₂@Fe₃O₄ via the immobilization of quinoline-2-carboxaldehyde
(2QC) onto amine functionalized silica coated ferrite nanosupport, followed by metallation with copper acetate (Fig. 14). The synthesized nanocatalyst exhibited remarkable catalytic activity for the synthesis of industrially and pharmaceutically significant carbamates via the C-H activation of formamides under solvent-free conditions. Moreover, the activity of the Cu-2QC@Am-SiO₂@Fe₃O₄ nanocatalyst has been found to be far more superior in comparison with the literature precedents in terms of the cost, product yield and recyclability. Apart from this, ambient reaction conditions, wide substrate scope, simple workup procedure and cost effectiveness are some of the other outstanding features of this protocol that made it more economical and sustainable.

**Fig. 14** Cu-2QC@Am-SiO₂@Fe₃O₄ for the synthesis of industrially and pharmaceutically significant carbamates.

Baig et al.¹⁰¹ have reported the synthesis of novel magnetic carbon-supported Pd catalyst via *in situ* generation of nanoferrites and incorporation of carbon from renewable cellulose via calcination. The catalyst efficaciously catalyzed oxidation of alcohols, amination reaction and arylation of aryl halides (cross-coupling reaction) (Scheme 19).

**Scheme 19**

Yinghuai et al.¹⁰² have developed nanopalladium supported magnetic catalysts for both Suzuki and Heck cross-coupling reactions (Scheme 20). The supported catalysts can be well dispersed in both aqueous and organic phase to produce a pseudo-homogeneous
catalytic system. In addition, the catalyst can be easily separated using a magnet and reused several times with sustained activity.

**Scheme 20**

Polshettiwar *et al.* have also developed a Pd catalyst supported on dopamine-functionalized nanoferrite, which displayed high catalytic activity in the oxidation of alcohols and olefins with high turnover rates. Here, dopamine has appeared as an excellent interparticle linker and prevents the leaching of nanosized Pd nanoparticles. Moreover, the reported catalytic system is magnetic in nature and can be easily separated from the reaction mixture effortlessly using external magnet, thus avoids the tedious workup procedures (*Fig. 15*).
A nanosized catalytic system possessing high magnetic responsivity and excellent dispersibility, Fe₃O₄-NH₂-Pd was successfully prepared by Zhang et al.¹⁰⁴ using one-pot template free method. Here, functionalization of amino group onto the surface of magnetite nanoparticles has played significant role in increasing the stability of Pd(0) nanoparticles. It has been reported that using amine functionalized magnetite nanoparticles, loss of Pd(0) nanoparticles has been greatly reduced during recyclability. The synthesized catalytic system has been proved to be an excellent catalytic system for the hydrogenation and Heck reactions (Fig. 16).

![Fig. 16 Fe₃O₄-NH₂-Pd for the hydrogenation and Heck reactions.](image)

Sarrafi et al.¹⁰⁵ have reported novel and efficient synthesis of magnetically recoverable nano-catalyst based on bis-imidazole Cu(I) complex. The catalyst was prepared by covalent grafting of bis-imidazole onto functionalized silica grafted magnetite

![Fig. 17 Bis-imidazole Cu(I) complex supported onto SiO₂-Fe₃O₄ composite for the synthesis of imidazo[1,2-alpyridines.](image)
nanoparticles, followed by metalation with CuI. Nanoparticles were mostly spherical in shape and have an average size of 20 nm. Besides this, loading amount of functionalized organic groups on the magnetic material was experimentally found to be 1.4 mmol g⁻¹. The synthesized nanocatalyst showed excellent activity for the synthesis of imidazo[1,2-a]pyridines in aqueous medium and also recyclable for at least ten runs without any deterioration in its catalytic activity (Fig. 17).

Xiong et al.¹⁰⁶ have developed a facile synthetic method for insitu growth of Au nanoparticles onto magnetic γ-Fe₂O₃@carboxylated cellulose nanospheres using 2,2,6,6-tetramethylpiperidiny1-1-oxyl radical oxide cellulose as reducing agent. Here, only one step was needed to synthesize the magnetic γ-Fe₂O₃@cellulose nanospheres. The reported γ-Fe₂O₃@carboxylated cellulose@Au is dispersible in aqueous solution and its potential as a magnetic catalyst was proved by the reduction reaction of 4-nitrophenol to 4-aminophenol. Besides, there occurred no significant decrease in the catalytic activity of the reused catalyst even after being recycled five times. Moreover, both the synthesis steps and the reaction cost were remarkably decreased due to the absence of any other reducing agent during the synthesis process, which further made it very suitable for industrially important processes (Scheme 21).

Scheme 21

A novel, water dispersible and proficient magnetic catalyst based on copper nanoparticles immobilized onto ethylene diamine functionalized inorganic/organic composite [Cu(0)–Fe₃O₄@SiO₂/NH₂cel] was reported by Bhardwaj et al.¹⁰⁷ (Scheme 22). Here, authors reported that grafting of ethylene diamine onto organic/inorganic composite have
generated active sites for the immobilization of Cu(0) nanoparticles and prevents their leaching. Further, Cu(0)–Fe3O4@SiO2/NH2cel was found to be highly efficient catalytic system for the one-pot synthesis of 1,4-disubstituted-1,2,3-triazoles via 1,3-dipolar cycloaddition of terminal acetylenes to azides, generated in situ from anilines in water and one-pot three component reaction of 2-iodoaniline, aldehyde and thiourea as sulphur source for the synthesis of 2-substituted-benzothiazole derivatives in water.

Scheme 22

Pd(0) nanoparticles immobilized onto ethylene diamine functionalized inorganic/organic magnetic composite [Fe3O4@SiO2/EDAC–Pd(0)] was reported by Bhardwaj et al.108 The amine functionalized silica/cellulose support has been found to be an efficient host for the immobilization of palladium nanoparticles. The reported catalyst has displayed remarkable catalytic activity towards the selective C–H bond oxidation using TBHP and reductive amination of aldehydes with nitroarenes using atom efficient molecular hydrogen (Scheme 23).

Scheme 23

Yang et al.109 have reported the synthesis of a novel magnetic nanocatalyst, Pd/Fe3O4@PMAA-Met by anchoring palladium nanoparticles onto the surface of
metformin-functionalized magnetic polymer nanohybrid. The proposed nanocatalyst has displayed excellent catalytic activity for the Suzuki-Miyaura cross-coupling reaction of aryl halides with arylboronic acids. Besides, the synthesized catalyst could be easily separated with the help of external magnet and reusable up to twelve times (Scheme 24).

Scheme 24

Shylesh et al.\textsuperscript{110} have reported the preparation of heterogeneous magnetic nanocatalytic system by covalent grafting of palladium dichloride complex of the type (L)\textsubscript{2}PdCl\textsubscript{2} (L=trimethoxysilyl-functionalized triphenylphosphine) onto silica-coated magnetite nanoparticles (Scheme 25). This catalytic system displayed excellent activity for the Suzuki–Miyaura cross-coupling reaction. Moreover, the catalyst could be easily separated from the reaction mixture via external magnetic field and recyclable many times without any significant loss of activity.

Scheme 25
Niu et al. have reported one-pot template-free method for the preparation of palladium nanoparticles supported onto water-dispersible magnetite nanoparticles functionalized with amino and carboxyl groups (Fig. 18). Here, the magnetic nanomaterial has played important role, i.e., it has increased the stability and water-dispersibility of the synthesized catalyst because of the presence of amino and carboxyl groups on their surface. The developed catalyst exhibited excellent catalytic activity for Suzuki and Heck cross-coupling reactions in water. Additionally, the catalyst is easy to be recovered via magnetic separation from aqueous phase reactions. The catalyst could be used consecutively six times without any significant loss in the catalytic activity.

![Fig. 18 Palladium nanoparticles supported onto magnetite nanoparticles functionalized with amino and carboxyl groups for the Suzuki and Heck reaction.](image)

Safari et al. have reported the synthesis of Cu nanoparticles immobilized on polyethylene glycol grafted Fe₃O₄ nanocomposite (Cu@Fe₃O₄/PEG) (Scheme 26). The PEG-Cl₄ so formed by using cyanuric chloride, was grafted onto Fe₃O₄ nanoparticles via formation of covalent bonds (Fe₃O₄/PEG). Finally, Cu nanoparticles were immobilized by reducing copper ammonia complexes with hydrazine hydrate onto the surface of the
nanocomposite. The highly active and green Cu@Fe₃O₄/PEG catalyst showed excellent catalytic activity for the synthesis of 2,4,5-trisubstituted imidazoles and 1,2,4,5-tetrasubstituted imidazoles. The developed catalyst has displayed paramagnetic properties, which allowed their quick separation from the reaction mixture using a simple magnet.

**Scheme 26**

Khojasteh *et al.*[^113] have reported tree like palladium catalyst immobilized onto Schiff base functionalized silica coated superparamagnetic nanoparticles (Fig. 19). It has been found that the presence of pendant Schiff base groups onto the catalyst support have

![Diagram](image-url)

**Fig. 19** Palladium catalyst immobilized onto Schiff base functionalized silica coated superparamagnetic nanoparticles for the Suzuki cross-coupling.

[^113]: Khojasteh et al.
played a special role in enhancing the catalytic activity of the Pd NPs for Suzuki cross-coupling reaction, resulting in higher selectivity, conversion and reusability. Here, amine and oxygen groups of Schiff base are donor atoms, which form coordinate bond with Pd thereby enhancing the catalytic activity and prevent leaching. Moreover, the recovery of the catalyst was easily done by simple magnetic decantation using an external magnet.

Doustkhah et al.\textsuperscript{114} have reported the synthesis of a new and efficient copper catalyst based on apple pectin encapsulated Fe\textsubscript{3}O\textsubscript{4} nanoparticles. Here, carboxylate functionality present in pectin biopolymer has played a key role in coordination of copper (II) species. This process led to the formation of magnetite nanoparticles within the network of pectin. The developed catalyst showed excellent activity for the three-component synthesis of triazoles via click chemistry. Moreover, the catalyst was recyclable up to eight runs without any deterioration in its catalytic activity (Fig. 20).

![Fig. 20: Copper catalyst immobilized onto apple pectin encapsulated Fe\textsubscript{3}O\textsubscript{4} nanoparticles for the synthesis of triazoles.](image)

Nasrollahzadeh et al.\textsuperscript{115} have reported a simple, greener and eco-friendly method for the preparation of stable Pd/Fe\textsubscript{3}O\textsubscript{4} nanocomposites via Hibiscus tiliaceus Leaf extract in the absence of any specific capping agent. Hibiscus tiliaceus is a source of useful bioactive and antioxidant flavonoids, which possess both reducing as well as capping/stabilizing
properties. Here, Pd NPs were synthesized via reduction of Pd$^{2+}$ ions to Pd(0) using Hibiscus tiliaceus L. extract as a reducing agent as well as capping ligand without addition of any other external reducing agent. In this method, Fe$_3$O$_4$ played an important role as a stabilizing agent and also prevents the agglomeration of Pd NPs. The synthesized catalyst showed excellent catalytic activity in the reduction process of Cr(VI), 4-NP and 2,4-DNPH in aqueous medium. This methodology possesses several advantages such as clean reaction, short reaction time, and elimination of toxic and dangerous reagents. Further, the catalyst was recyclable and reused six times without any deterioration in its catalytic activity (Scheme 27).

**Scheme 27**

Oxidant-free dehydrogenation of alcohols is attention-grabbing from the perspectives of environmental concerns and atom economy, as this process is accompanied by the evolution of hydrogen gas, which is one of the most promising energy fuels for the future. In order to achieve this aim, Bayat *et al.*$^{116}$ have reported the synthesis of a heterogeneous and recyclable catalyst with a high loading of silver nanoparticles. Here, 4-vinylpyridine (polymer) was functionalized onto the surface of Fe$_3$O$_4$ magnetic nanoparticles to increase the basicity and ease of elimination of hydrogen atoms from alcohols. Besides, it also played an important role to stabilize and increase the loading of silver nanoparticles onto the magnetic nanoparticles. The catalyst was used in the dehydrogenation of alcohols to corresponding carbonyl compounds. Additionally, the catalyst was easily recovered by using an external magnet and could be reused for seven reaction cycles without any significant loss of activity (Scheme 28).
Moghaddam et al.\textsuperscript{117} have reported a novel and efficient synthesis of gold nanoparticles supported onto poly ionic-liquid magnetic nanoparticles (MNP@PIL@Au) by the reduction of HAuCl\textsubscript{4} with sodium borohydride (Scheme 29). The catalytic activity of the synthesized catalyst has been investigated for the reduction of nitroarenes with NaBH\textsubscript{4}.

Scheme 29
The catalyst has showed excellent catalytic activity for the reduction of various nitroarenes in water and mild conditions even in the presence of other functional groups such as halides and alkynes. The key advantages of this protocol were simple synthesis, excellent reusability (up to eight runs), easy magnetic recovery, and high loading of gold nanoparticles on the catalyst surface.

Au NPs immobilized on magnetic graphene oxide modified with polyaniline (PANI) was successfully developed by Pourjavadi et al.\textsuperscript{118} (Scheme 30). The key advantages of the catalyst were large surface area, firm anchoring of Au NPs, uniform dispersal in water and facile recovery of catalyst via external magnet. The catalyst showed excellent activity for the reduction of different analytes (Congo red, methylene blue, rhodamine B and 4-nitro phenol) in the presence of NaBH\textsubscript{4}.

**Scheme 30**

\[ \begin{align*}
\text{Graphene oxide} & \xrightarrow{\text{Fe}^{2+}, \text{Fe}^{3+}} \text{Magnetic graphene oxide} \\
\text{Au@PANI/m-GO} & \xrightarrow{\text{PANI}} \text{PANI@m-GO}
\end{align*} \]

Nowadays, the ultimate goal of the chemists is to synthesize cost-effective heterogeneous catalytic systems for carrying out a range of critical chemical transformations. Transition
metal immobilized onto magnetic support not only serve as an overview of the fast growing field of transition-metal catalysis, but also provide inspirations for the future discovery of more efficient and practical catalysts to work under harsh conditions by tackling the economic and ecological challenges. In this section, we have presented an introduction to the metal nano catalysts grafted onto multifunctionalized magnetite support, focusing on their preparation and applications in different areas. Further, we believe that such approaches to reaction engineering will help catalytic systems to become more practical on a larger scale.
3. Scope of the present work

Over the previous few years, nanotechnology based procedures have aided the development of economic and environmentally benign synthetic pathways to produce efficient and highly active catalytic nanomaterials. Recently, efforts of the scientific community have been directed towards the preparation of superparamagnetic nanoparticles for the design of magnetically retrievable nanocatalytic systems, due to their exceptional physico-chemical properties and quick response to the applied magnetic field. Additionally, these magnetite-based nanocatalysts are robust, non-toxic, easy to prepare, magnetically recoverable, inexpensive and also recyclable. Subsequently, they have emerged as worthwhile alternatives to existing solid-supported heterogeneous catalysts. Synthetic approaches for the synthesis of magnetite materials with controlled size, composition and structure are presently undergoing rapid development and open enormous possibilities for the synthesis of magnetic catalysts (or non-magnetic material grafted onto magnetite supports). Development of different strategies for the stabilization of magnetite nanoparticles also opens up enormous number of options for the immobilization of catalytically active transition metal species. The combination of magnetic nanoparticles and catalytic active transition metal species presents the opportunity to solve array of catalyst recovery problems to which no other filtration technique is easily applicable. The utmost applications of catalysts immobilized onto magnetite supports are the easy recovery of the catalyst from reaction mixture, large surface area, inexpensive and non-toxic nature, easily functionalized with desired functional groups.

Though remarkable progress has been achieved in the area of magnetite nanoparticles based catalysts, yet the major challenge lies in the detailed understanding of the mechanistic aspects of the catalytic processes that would eventually help in tuning and tailoring the properties of the newly designed catalysts. In future, the design of novel magnetite nanoparticles supported active metal species will find major applications in industrially significant organic transformations, as they have the capability to effectively perform multiple catalytic reactions with higher atom-efficiencies, yields, chemoselectivities and enantioselectivities.
From a practical viewpoint, the development of simple, inexpensive, widely applicable and environmentally benign catalysts/procedures is still a challenge for the chemists. Keeping in view the importance of magnetic nanoparticles in heterogeneous catalysis and green procedures in organic synthesis, we have developed a series of biomaterial, inorganic material and polymer functionalized magnetic metal nanoparticles, such as Pd(0) nanoparticles immobilized on amine functionalized starch substrates [Pd(0)-Fe₃O₄-NH₂/L-dopa]; Cu(0) immobilized on TiO₂ grafted on magnetite nanoparticles [Cu(0)-Fe₃O₄-TiO₂/L-dopa]; and Co(0) nanoparticles immobilized on magnetite graphene oxide [Co(0)-GO/Fe₃O₄/L-dopa].

Different stabilizing agents such as starch, titania and graphene oxide were used in order to avoid the agglomeration of magnetite nanoparticles. Further, excellent interparticle linkers such as hexane-1,6-diamine and L-dopa were functionalized over the surface of stabilized magnetite nanoparticles in order to prevent the leaching of active metal species such as palladium, copper and cobalt. All the synthesized catalysts were fully characterized by various techniques such as SEM, HR-TEM, FTIR, VSM, EDX, XPS, XRD, CHN, ICP-AES and TGA studies. After the successful synthesis of novel and efficient catalytic systems, the catalytic activity of Pd(@Fe₃O₄-NH₂/Starch has been evaluated for the selective oxidation of substituted benzyl alcohols, reduction of substituted nitroarenes and reductive amination of aldehydes with nitroarenes; Cu@Fe₃O₄-TiO₂-L-dopa has been used for the Chan-Lam cross-coupling reaction and one-pot synthesis of substituted acridines; and finally the synthesized Co@GO/Fe₃O₄/L-dopa has been employed for Suzuki cross-coupling, oxidation of hydrocarbons and secondary alcohols into corresponding carbonyl compounds and one-pot synthesis of 5-substitutedphenyl-1H-tetrazoles. The synthesized catalytic systems have showed excellent catalytic efficiency for the tested organic transformations and afforded products in good to excellent yields. All the synthesized products were fully characterized by ¹H, ¹³C NMR and mass spectral data.
REFERENCES


