Summary

The thesis entitled “Development of magnetic metal nanoparticles and their applications in organic synthesis” has been divided into four chapters:

Chapter 1

This chapter includes a general introduction to catalysis, magnetic nanoparticles as viable support in heterogeneous catalysis, different procedures for the synthesis of magnetic nanoparticles, applications of MNPs based catalysts in organic synthesis and scope of the present work.

1. Catalysis: General introduction

The tranquillizing 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. Conventional catalysis can be divided into homogeneous and heterogeneous catalysis. 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. 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. 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, leads to greater activity and selectivity. Further, 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. Different nanometric supports were used for the immobilization of homogeneous catalysts. In this perspective, metal oxide nanoparticles supported catalytic systems are the eye-catching candidates as they possess high activity, remarkable efficiency,
selectivity, large surface-to-volume ratio, crystallinity, monodispersity, topological properties and tenability with improved recyclability.

2. Magnetic nanoparticles (MNPs) as a viable support in heterogeneous catalysis

Recently, 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. 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. 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, Fe₃O₄ is a mixed iron(II) and (III) oxide in a cubic inverse spinel structure. Magnetite is inert and possesses a very active surface for the 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.

2.1 Synthesis of magnetic nanoparticles (MNPs)

Various synthetic methods have been reported in the literature for the synthesis of magnetite nanoparticles (MNPs) with controlled size and shape. Generally, two important approaches were employed for the synthesis of magnetite nanoparticles, such as bottom up and top down methods. Bottom-up approaches for the synthesis of iron oxide nanoparticles includes thermal decomposition, co-precipitation and microemulsion techniques. Top-down or lateral approaches for the synthesis of iron oxide nanoparticles rely on transforming existing solid phase materials by applying grinding techniques.

2.2 Functionalized MNPs and their applications in organic synthesis

MNPs have appeared a worthwhile support in heterogeneous catalysis. 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. Meanwhile, the modification procedures provide reaction sites or active groups for covalently or non-covalently grafting the active catalytic units onto the coated MNPs to construct magnetically recoverable catalysts. In this section, we are under giving some examples of functionalized MNPs such as functionalized Fe$_3$O$_4$, acid functionalized MNPs, organocatalysts functionalized MNPs and transition metal functionalized MNPs, and their applications in some important organic transformations.

3. Scope of the present work

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 on 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. 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 onto starch stabilized amine functionalized magnetite nanoparticles [Pd@Fe$_3$O$_4$-NH$_2$/Starch]; Cu(0) nanoparticles immobilized on L-dopa grafted TiO$_2$ stabilized magnetite nanoparticles [Cu@Fe$_3$O$_4$-TiO$_2$-L-dopa]; and Co(0)
nanoparticles immobilized on L-dopa functionalized magnetic graphene oxide [Co@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 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.

CHAPTER 2

This chapter deals with the synthesis, characterization and applications of palladium(0) nanoparticles immobilized onto starch grafted amine functionalized magnetite nanoparticles [Pd@Fe₃O₄-NH₂/Starch]. It is divided into four sections, which are briefly discussed below:

Section 2.1 Synthesis and characterization of palladium(0) nanoparticles immobilized onto starch grafted amine functionalized magnetite nanoparticles

Palladium nanoparticles are well-known to catalyze a number of important organic transformations such as hydrogenations, oxidations, reductions, C-C, C-N and C-S cross-coupling reactions etc. But, unsupported palladium nanoparticles are very
expensive and cannot be used as such, owing to their coagulating properties and non-recyclability. Immobilization of palladium nanoparticles onto the suitable support material prevents their leaching into the reaction mixture and also permits them to be simply recovered and recycled. Recently, magnetic nanoparticles have appeared as a viable alternative to other solid supports due to their superior magnetic properties, high surface area, easy recovery, relative inertness and apparent simplicity of post synthetic surface functionalization. It is pertinent to mention that bare magnetic nanoparticles cannot be used as such owing to their strong tendency to agglomerate. In order to make it efficient support for noble metal species, surface modification of magnetite nanoparticles is required which can be achieved by functionalization with active groups (biomaterial, polymers and inorganic material).

Scheme 1. General scheme for the synthesis of Pd@Fe$_3$O$_4$-NH$_2$/Starch.

In this section, we have reported the synthesis of novel and efficient magnetic catalyst, Pd@Fe$_3$O$_4$-NH$_2$/Starch (Scheme 1). Here, magnetite nanoparticles were
used as core particles owing to its high surface area, relative inertness, superior magnetic properties and easy recovery. In order to prevent the agglomeration of magnetite nanoparticles, hexane-1,6-diamine was functionalized onto the surface of magnetite nanoparticles using solvothermal technique. In order to further enhance the catalytic efficiency of amine functionalized magnetite nanoparticles, starch possessing microfibril structure, was incorporated over the surface of amine functionalized magnetite nanoparticles. Finally, Pd(0) nanoparticles were successfully immobilized over the surface of starch stabilized amine functionalized magnetite nanoparticles using aqueous solution of NaBH₄. The synthesized catalyst was fully characterized by various techniques such as FTIR, VSM, SEM, HR-TEM, EDX, XRD, CHN, ICP-AES and TGA studies.

Section 2.2 Pd@Fe₃O₄-NH₂/Starch catalyzed selective oxidation of benzyl alcohols using H₂O₂ as an oxidant and EtOH: H₂O as solvent

The selective oxidation of substituted benzyl alcohols to corresponding aldehydes is widely recognized as one of the most essential transformations in organic synthesis. In recent years, particular attention has been paved on the development of green methodology for the selective oxidation of benzyl alcohols, and in this perspective, transition metal nanoparticles immobilized on heterogeneous support have been shown to be effective for catalyzing selective oxidation of benzyl alcohols. Literature is full of various reported methods for the selective oxidation of benzyl alcohols. Despite these recent advances, catalytic oxidation of benzyl alcohols has often suffered from several drawbacks such as low yield, poor selectivity, harsh reaction conditions and difficulty in separation of the catalyst at the end of the reaction. Moreover, selective oxidation of alcohols becomes trickier in case of compounds containing more than one oxidizable functional groups. Further, few magnetic heterogeneous metal catalysts have been reported in the literature, which mediates oxidation reactions in an aqueous phase. Hence, there is an immense necessitate to develop novel magnetically separable heterogeneous metal catalysts for the selective oxidation of benzyl alcohols.

In order to overcome these drawbacks, we report a mild and efficient approach to oxidize selectively a broad range of benzyl alcohols to their corresponding aldehydes in good to
excellent yields under mild reaction conditions (Scheme 2). Four different catalytic systems were prepared such as Pd@Fe₃O₄, Pd@Fe₃O₄-NH₂, Pd@Fe₃O₄-NH₂/Cellulose and Pd@Fe₃O₄-NH₂/Starch and tested for the selective oxidation of 4-methoxybenzyl alcohol into 4-methoxybenzaldehyde using H₂O₂ (1.5 eq.) as an oxidant in EtOH: H₂O (3:1, 8 mL) at 70 °C. After performing different experiments, it was found that Pd@Fe₃O₄-NH₂/Starch (2.36 mol% Pd, 0.1 g) was the appropriate catalyst for carrying out the desired oxidation.

**Scheme 2**

![Scheme 2](image)

After optimization of the reaction conditions with respect to temperature, solvent and oxidant, scope of the reported protocol was evaluated for a wide range of substrates and obtained products in good to excellent yields. All the products were characterized using ¹H NMR, ¹³C NMR and mass spectral data. The salient features of the reported methodology embrace operational simplicity, easy recyclability, a cleaner reaction profile, which lead to short reaction time and high yields, thus adding a credit towards the development of greener methodologies for organic synthesis.

**Section 2.3 Pd@Fe₃O₄-NH₂/Starch as a sustainable catalyst for the hydrogenation of nitroarenes under mild conditions**

Reduction of nitroarenes is of immense importance as the amino compounds act as important feedstock for the synthesis of valuable organic compounds. Numerous catalytic methods have been reported in the literature for the selective reduction of nitroarenes, but these methodologies suffer from many limitations. Though, a variety of catalytic hydrogenation methods have been reported using different transition metal catalysts, but their inadequate availability and high cost increased the overall expenditure. This has led the researchers to search for more economical, greener and environmentally acceptable alternatives.
In order to carry out such industrially significant reactions under mild and environment-friendly conditions, there is an imperative need to develop appropriate catalysts for the reduction of nitro compounds to the corresponding amines under mild, cost-effective and green conditions. In this section, we report the reduction of a variety of nitroarenes in the presence of Pd@Fe₃O₄-NH₂/Starch as a catalyst and molecular hydrogen as a source of hydrogen (Scheme 3).

**Scheme 3**

![Scheme 3](image)

Different experiments were performed in order to obtain suitable reaction conditions to carry out reduction of nitroarenes smoothly. After optimization of the reaction conditions, 0.1 g of Pd@Fe₃O₄-NH₂/Starch (2.36 mol% Pd) and water:ethanol mixture (3:1) were selected as the optimal amount and appropriate solvent system for carrying out the hydrogenation of nitroarenes smoothly. To check the compatibility of this reaction in the presence of other functional groups, we examined an array of synthetically valuable aromatic nitroarenes using Pd@Fe₃O₄-NH₂/Starch under the optimized reaction conditions. The synthesized products were characterized using ¹H NMR, ¹³C NMR and mass spectral data. Moreover, the usual side products of hydrogenation of nitroarenes such as azoxy, azo and hydrazo compounds were not observed in this method. The simplicity of the proposed method, easy workup procedure, recyclability of the Pd@Fe₃O₄-NH₂/Starch and excellent yields makes it an environmentally acceptable and greener alternative for the hydrogenation of nitroarenes.

**Section 2.4 Pd@Fe₃O₄-NH₂/Starch as a magnetically recoverable catalyst for the one-pot reductive amination of aldehydes with nitroarenes under mild conditions**

Synthesis of functionalized amines is one of the most significant organic transformations as amines are constructive intermediates for the synthesis of numerous functional materials. Recently, domino reductive aminations using nitroarenes is particularly very
attractive as it does not require preliminary reduction of nitroarenes, avoids separation of intermediates and purification steps, and minimizes waste production, thus, fulfilling one of the requirements of green chemistry. In the reductive amination, the selection of reducing agent plays significant role in the success of the reaction, in which the imine intermediates formed insitu need to be reduced selectively in the presence of other functional groups under the same reaction conditions. A more useful method is to utilize molecular hydrogen as a reducing agent in the presence of a catalyst, as it is the most atom-economical and environmentally benign method, particularly in large-scale reactions.

Considering the enormous importance of functionalized amines, our foremost focus was to develop a simple and greener approach for the reductive amination reaction using Pd@Fe₃O₄-NH₂/Starch as a magnetically recoverable catalyst under hydrogen atmosphere. In this section, a simple and environment-friendly protocol has been reported for the one-pot synthesis of functionalized amines via reductive amination of carbonyl compounds with nitroarenes in the presence of Pd@Fe₃O₄-NH₂/Starch (0.1 g, 2.36 mol% Pd) using molecular hydrogen as source of hydrogen at room temperature (Scheme 4).

Scheme 4

A variety of substituted aldehydes bearing either electron-donating or electron-withdrawing groups undergoes reduction smoothly. Different functional groups such as chloro, bromo, methyl and methoxy at para position in arylaldehydes were tolerated fairly well and afforded the desired products in good to excellent yields. The synthesized products were characterized using ¹H NMR, ¹³C NMR and mass spectral data. This methodology is clean and highly selective for the synthesis of secondary amines in high yields. Moreover, the reported catalyst was magnetic in nature, avoids the tedious process of separation and was also recyclable upto five runs.
CHAPTER 3

This chapter deals with the synthesis, characterization and applications of copper(0) nanoparticles immobilized onto L-dopa grafted TiO$_2$ stabilized magnetite nanoparticles [Cu@Fe$_3$O$_4$-TiO$_2$-L-dopa]. It is divided into three sections, which are briefly discussed below:

3.1 Synthesis and characterization of copper(0) nanoparticles immobilized onto L-dopa grafted TiO$_2$ stabilized magnetite nanoparticles

Currently, supported Cu NPs are attracting more attention than other transition metal NPs, namely Pd, Pt, Au and Ag, because of their low cost and broad applications in synthetic organic chemistry. Different supports were used for their immobilization, but recently, titanium oxide (TiO$_2$) has gained much impetus as a viable support for noble metal NPs owing to its exceptional characteristics, namely non-toxicity, good biological compatibility, easy preparation and cost effectiveness. Another major concern linked with heterogeneous catalysis is the leaching of noble metal NPs from the catalytic support. Hence, strong binding agents were required for the firm anchoring of active metal NPs onto the catalytic support.

This section deals with the synthesis and characterization of nanosized and water-dispersible heterogeneous Cu catalyst, Cu@Fe$_3$O$_4$-TiO$_2$-L-dopa (Scheme 5). In order to develop a more efficient and unique catalyst, magnetite nanoparticles were chosen as core particles owing to their distinctive characteristics, such as large surface to volume ratio, magnetic nature, non-toxicity and easy separation. In order to avoid the agglomeration of magnetite nanoparticles, TiO$_2$ nanoparticles were grafted over the surface of Fe$_3$O$_4$ nanoparticles using ultrasonication technique. Although, Fe$_3$O$_4$ embedded TiO$_2$ spheres are relatively stable yet the aggregation and leaching of active metal species from their surface remains the drawback. Thus, to get firm anchoring of active metal nanoparticles onto the support and prevent their leaching, L-dopa was used as a binding agent. So, Fe$_3$O$_4$-TiO$_2$ nanoparticles were functionalized with L-dopa and finally Cu(0) nanoparticles were immobilized onto the support material via reduction with aqueous NaBH$_4$ solution. The synthesized catalyst, Cu@Fe$_3$O$_4$-TiO$_2$-L-dopa was
fully characterized by diverse techniques such as SEM, HR-TEM, XPS, ICP-AES, CHN analysis, EDX, XRD, FTIR, VSM and TGA studies.

Scheme 5. General scheme for the synthesis of Cu@Fe₃O₄-TiO₂-L-dopa.

Section 3.2 Cu@Fe₃O₄-TiO₂-L-dopa as a novel and efficient catalyst for the Chan-Lam cross-coupling reaction in ligand-free conditions

The aromatic C-N bond containing organic moiety possesses indispensable importance in the field of synthetic organic chemistry due to the ubiquity of N-arylamine derivatives in numerous molecules of biological importance. Chan, Evans and Lam, individually attempted and developed a mild procedure for Cu-mediated oxidative amination of aryl boronic acids. However, the use of excess Cu(OAc)₂, aryl boronic acid, additives such as pyridine-N-oxide, TEMPO, molecular oxygen and harsh reaction conditions are
considered as major limitations associated with this cross-coupling method; regardless of the quite stable and non-toxic nature of aryl boronic acids. Thereafter, several modifications were employed to improve the yield and efficiency of Chan-Lam reaction using various copper salts in the presence of different ligands. However, high reaction temperature and long reaction time are still some of the curtailment concomitant with these methods towards Chan-Lam coupling. Thus, endeavouring efforts for finding better methods for Chan-Lam coupling are gaining much impetus recently.

Herein, we report the C-N cross-coupling reaction between diversely substituted anilines and phenyl boronic acid using water as a reaction medium, K$_2$CO$_3$ (1.2 eq, 0.165 g) as base and Cu@Fe$_3$O$_4$-TiO$_2$-L-dopa (1.9 mol% Cu, 0.05 g) as catalyst (Scheme 6).

Scheme 6

\[
\begin{align*}
\text{NH}_2 \quad \text{B(OH)}_2 & \quad \text{Cu@Fe}_3\text{O}_4\text{-TiO}_2\text{-L-dopa (1.9 mol% Cu)} \\
R \quad R & \quad \text{K}_2\text{CO}_3, \text{H}_2\text{O}, 80 \, ^\circ\text{C}
\end{align*}
\]

The cross-coupling was found to proceed with high regiospecificity and substituted diarylamines were obtained as a single regioisomer in good to excellent yields. An interesting observation was noticed when C-N cross-coupling reaction was performed with halide substituted arylamines. It was observed that when C-N cross-coupling reaction was performed with chloroaniline, 4-bromoaniline and 2-iodoaniline, yields of C-N cross-coupling products decreases. It was occurred due to the formation of C-C cross-coupling product along with C-N cross-coupling product. Whereas in case of 4-fluoroaniline and 2-fluoroaniline, only C-N cross-coupling products were obtained exclusively. It was concluded that pure C-N cross-coupling in the case of fluoro substituted aniline might occur owing to the the poor leaving nature of fluoro group. The structures of the products were further confirmed by $^1$H NMR, $^{13}$C NMR and mass spectral data.
Section 3.3 One-pot synthesis of decahydroacridine-1,8-diones using Cu@Fe$_3$O$_4$-TiO$_2$-L-dopa in aqueous medium

Acridine and its derivatives are essential structural motifs possessing antiviral, antimalarial and antiallergic properties. Varied methods have been reported in the literature for the synthesis of hexahydroacridine-1,8-diones, possessing several advantages. But on the other hand, also suffers from numerous disadvantages such as, the use of corrosive acid catalysts or expensive ionic liquids, nano-TiO$_2$ and In(OTf)$_3$, platinum nanoparticles, use of polar organic solvents, harsh reaction conditions, long reaction times, unsatisfactory yields and tedious workup procedures.

Scheme 7

To overcome these problems, in this section, we have reported an efficient and green method for the synthesis of hexahydroacridine-1,8-diones by the one-pot reaction of aromatic aldehydes, dimedone and aromatic amine or ammonium acetate in water at 80 °C using magnetically recoverable, Cu@Fe$_3$O$_4$-TiO$_2$-L-dopa catalyst (Scheme 7). The method offers numerous advantages such as short reaction time, mild reaction conditions, use of water as green solvent, simple work-up procedure, good yields of products and recyclability upto five reaction cycles. The structures of the products were further confirmed by $^1$H NMR, $^{13}$C NMR and mass spectral data.

CHAPTER 4

This chapter deals with the synthesis, characterization and applications of cobalt(0) nanoparticles immobilized onto L-dopa functionalized magnetic graphene oxide
[Co@GO/Fe₃O₄/L-dopa]. It is divided into four sections, which are briefly discussed below:

**Section 4.1 Synthesis and characterization of Co(0) nanoparticles immobilized onto L-dopa functionalized magnetic graphene oxide**

Majority of the important organic syntheses were usually catalyzed by precious and costlier second and third row transition metals. 3d Transition metal based catalysts represented a suitable substitute to precious and costlier second and third row transition metals for carrying out important organic transformations, because of their natural abundance and cost-effectiveness. Moreover, the use of environmentally benign nanocarbon materials in chemical industries have also attracted cumulative attention in the field of catalysis due to their attractive electronic, mechanical, catalytic, thermal, optical, and magnetic properties; easy recovery and large surface area.

In this section, we have reported the synthesis of graphene oxide based magnetic cobalt nanoparticles and fully characterized with different techniques such as SEM, HR-TEM, XPS, XRD, TGA, FTIR, VSM, CHN analysis, EDX and ICP-AES studies. Here graphene oxide was used as a support material due to its unique properties, perfect two-dimensional carbon nanostructure, high surface area, excellent stability and amazing tunability in supporting a range of metallic and bimetallic nanoparticles. In order to further enhanced its stability and make it magnetically recoverable, Fe₃O₄ nanoparticles were grafted over the surface of graphene oxide using ultra sonication technique. Further, in order to prevent the leaching of active metal species, excellent interparticle linker i.e. L-dopa was functionalized over the surface of magnetic graphene oxide. Finally, Co(0) nanoparticles, which recently appeared as appropriate substitute to costlier 4d and 5d transtition metals in catalyzing important organic synthesis, were immobilized over the surface of L-dopa functionalized magnetic graphene oxide using aqueous solution of NaBH₄ (Scheme 8).
Section 4.2 Co@GO/Fe$_3$O$_4$/L-dopa as an inexpensive and water dispersible magnetically recoverable catalyst for the Suzuki coupling in aqueous medium

The Suzuki cross-coupling reaction is one of the most effective tools in organic synthesis for C-C bond formation. These reactions have been widely used for the synthesis of substituted biaryls, which possess broad range of applications in the chemical and pharmaceutical industries. Palladium based catalysts are considered as the most competent catalysts for C-C cross-coupling reaction, offering high turnover frequency, fast reaction rates and good selectivity in various synthetic protocols. But, due to the high cost of palladium catalysts, development of cost-effective alternative to palladium based catalysts for the C-C cross coupling reaction, which can also be easily separated from the reaction medium and recycled, is highly enviable in catalysis industry.
3d Transition metals such as Ni, Rh and Co have been reported to catalyze the C-C cross-coupling reactions. Out of three, Co represented an appropriate substitute to carry out C-C coupling reaction owing to its non-toxic nature and availability. Very few methods were reported in the literature for the Suzuki coupling catalyzed by Co metal. Therefore, there is a lot of scope of improvement in the Co catalyzed C-C cross-coupling reactions. So, keeping in view the importance of Suzuki cross-coupling for the synthesis of diversely substituted biaryls and to avoid tedious workup procedures, we have developed a cost-effective and magnetic catalytic system for C-C cross-coupling reactions. In this section, Co@GO/Fe₃O₄/L-dopa has been reported as a suitable and stable catalyst for the synthesis of biaryls/polyaryls in aqueous medium in ligand-free conditions, and products were obtained in good yields (Scheme 9).

**Scheme 9**

In the reported method, both bromo as well as chloro substituted aryl halides reacted smoothly with the phenyl boronic acid to give the desired products. It has been observed that even the presence of amino, hydroxyl and cyano groups in aryl halides were fairly tolerated in the proposed method. The structures of the prepared products were further confirmed by ¹H NMR, ¹³C NMR and mass spectral data. To the best of our knowledge, this is the first kind of report for Suzuki cross-coupling reaction catalyzed by heterogeneous cobalt nanoparticles.

**Section 4.3 Co@GO/Fe₃O₄/L-dopa catalyzed selective C-H bond oxidation of aryl alkanes and secondary alcohols to corresponding carbonyl compounds in an aqueous medium**

Catalytic oxidation of benzylic C-H bond and secondary alcohols is one of the fundamental transformations in organic syntheses and has a wide application in the production of agrochemicals and medicines. Further, transition metal catalyzed oxidation
reactions are particularly attractive in this field, owing to their environmentally benign and economic nature. Several procedures have been reported in the literature using transition metals (Ru, Co, Cu, Pt, and Rh) as catalysts for the oxidation reactions. Nowadays, use of magnetic nanoparticles as support for the oxidation reactions has increased due to their high catalytic activity, arising from their high surface area. Inspite of this, only handful reports of C-H bond oxidation reactions catalyzed by heterogeneous magnetic metal catalysts are known. Thus, development of novel and efficient magnetically separable metal catalysts to carry out oxidation reactions smoothly became one of the main objective in synthetic chemistry.

In this section, we have reported the catalytic efficiency of novel and efficient magnetic catalytic system, Co@GO/Fe₃O₄/L-dopa for the oxidation of hydrocarbons and secondary alcohols to corresponding carbonyl compounds under mild reaction conditions (Scheme 10).

**Scheme 10**

In the developed methodology, even the unreactive hydrocarbons such as ethyl benzene, p-xylene etc. were also successfully oxidized to corresponding carbonyl compounds. The products were obtained in good to excellent yields and fully characterized using $^1$H NMR, $^{13}$C NMR and mass spectral data. Moreover, the catalyst is magnetic in nature, can be easily separated from the reaction mixture, thus avoids the tedious workup procedures and is also recyclable upto five runs.

**Section 4.4 Co@GO/Fe₃O₄/L-dopa catalyzed one-pot multi-component synthesis of 5-substituted-1H-tetrazoles under mild reaction conditions**

The development of novel multi-component protocols for the synthesis of fundamental scaffolds i.e. 5-substituted-1H-tetrazoles are receiving considerable attention in the synthetic organic chemistry as these are the integral part of wide range of synthetic drugs,
bioactive natural products and pharmaceuticals. Most of the reported methods for the synthesis of 5-substituted-1H-tetrazoles suffer from several drawbacks such as strong acidic conditions, expensive reagents, toxic metals, long reaction times, unrecoverable catalysts, low yields, \textit{insitu} generation of highly toxic and explosive hydrazoic acid, use of toxic nitriles, difficult work up procedures etc. To avoid these limitations, different attempts have been made for the development of more efficient and cost-effective protocols for the synthesis of 5-substituted-1H-tetrazole accompanied with higher yields and milder reaction conditions.

In this section, we have reported the one-pot multi-component reaction of various aldehydes, hydroxylamine and sodium azide to give corresponding 5-substituted-1H-tetrazoles in the presence of Co@GO/Fe$_3$O$_4$/L-dopa as magnetically recyclable heterogeneous catalyst (Scheme 11).

\begin{center}
\textbf{Scheme 11}
\end{center}

\begin{center}
\begin{tikzpicture}
\node at (0,0) [draw, shape=rectangle, rounded corners, align=center] {$\text{R} \quad \chem{\text{H}} + \text{NaN}_3 + \text{NH}_2\text{OH.HCl}$ \makebox[1cm][c]{$\xrightarrow{\text{Co@GO/Fe}_3\text{O}_4/\text{L-dopa}}$} \makebox[4cm][c]{$\text{H}_2\text{O, 100}^\circ\text{C}$} \makebox[1cm][c]{$\text{HN-N}$ \makebox[2cm][c]{$\text{R}$}}};
\end{tikzpicture}
\end{center}

The desired products were obtained in good to excellent yields, with no pre-requisite of inert or anhydrous reaction conditions. Another novelty of the developed method is the replacement of toxic and expensive nitrile precursors by aldehydes. Moreover, there is no \textit{insitu} formation of potentially explosive compounds. Being magnetic in nature, catalyst can be easily separated from reaction mixture and thus avoids the tedious workup procedure.
5-6,11-12
1-4,7-10,13-18
1. Cu@Fe$_3$O$_4$-TiO$_2$-L-dopa: A novel and magnetic catalyst for the Chan-Lam cross-coupling reaction in ligand free conditions.


2. Highly efficient magnetic Pd(0) nanoparticles stabilized by amine functionalized starch for organic transformations under mild conditions


3. Ionic liquid coated sulfonated carbon@titania composites for the one-pot synthesis of indeno[1,2-b]indole-9,10-diones and 1$H$-pyrazolo[1,2-b]phthalazine-5,10-diones in aqueous media.


4. Fe$_3$O$_4$@SiO$_2$/EDAC–Pd(0) as a novel and efficient inorganic/organic magnetic composite: sustainable catalyst for the benzylic C–H bond oxidation and reductive amination under mild conditions.


5. Magnetically recoverable graphene oxide supported Co@Fe$_3$O$_4$/L-dopa for C-C cross-coupling and oxidation reactions in aqueous medium.