CHAPTER 1

INTRODUCTION

Contents

1.1 Catalyst

Catalysis is a process where the rate of a chemical reaction is influenced due to the participation of an external entity, called a catalyst.

A catalyst accelerates a chemical reaction. It does so by forming bonds with the participating molecules, and by allowing these to react to produce the product, which detaches from the catalyst, such that it is available for the next cycle of the reaction. In fact, we can describe the catalytic reaction as a cyclic event in which the catalyst participates and is recovered at the end of the cycle.

Let us consider the catalytic reaction between two molecules A and B to give a product P. The cycle starts with the bonding of molecules A and/or B to the catalyst. A and/or B then react within this complex to give a product P, which is also bound to the catalyst. In the final step, P separates from the catalyst, thus leaving the reaction cycle in its original state as shown in Figure 1.[1]

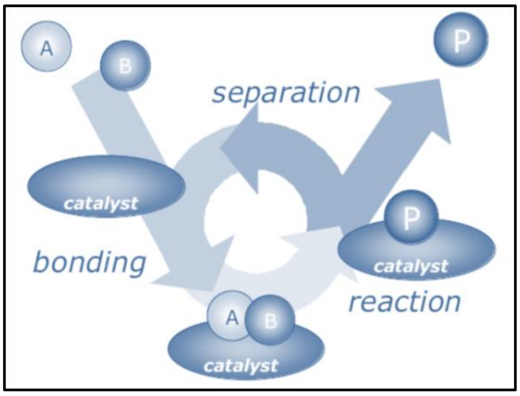


Figure 1: Catalytic cycle

The role of catalysts in organic transformations is extremely vital and much of the efforts of research in last several decades have been focused on various aspects of this area. A considerable portion of any literature on modern organic chemistry deals with some or other aspect of catalysis. The areas which involves catalytic processes are described in the Figure 2. Advent of green chemistry and emergence of stereoselective reactions has also fuelled the interest in the research on new catalysts and efficient ligands.

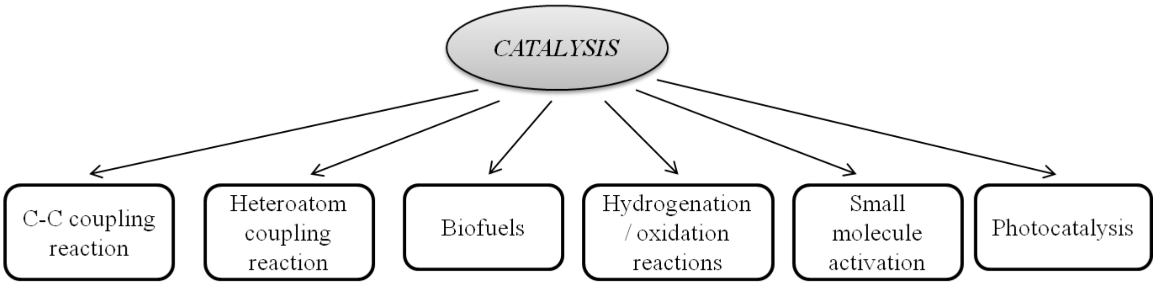


Figure 2: Areas involving Catalytic processes

1.2 Types of Catalyst

The catalytic reactions are mainly divided into two main types

1. Homogeneous
2. Heterogeneous

In a homogeneous catalytic reaction, the catalyst is in the same phase as the reactants. Typically, all the reactants and catalysts are either in one single liquid phase or gas phase. Although, the former version is considered as more effective and more controllable, the limitations are observed for their extrapolation in large scale industrial applications. This is particularly evident when costly, toxic and rare transition metal based catalytic systems are used for homogeneous reactions.

On the other hand, in second type the catalyst and the reactants are in different phases. Reactions of liquid or gases in the presence of solid catalysts are the typical examples. Some advantages of heterogeneous catalyst are mentioned below.

Advantages of Heterogeneous Catalyst

- ✓ Easy immobilization
- ✓ Convenient to recover and reuse
- ✓ Effortless Extraction
- ✓ High Activity
- ✓ Solvent Compatibility
- ✓ Economy when costly metals are used
- ✓ Possibility to control the contamination of toxic metal ions in products

1.3 Heterogeneous catalyst and its applications

In heterogeneous catalyst, the metal catalysts or metal ions are anchored on heterogeneous support. The mode of attaching a metal ion, which generally acts as the center for catalytic activity, to the solid support is a critical aspect of this approach. The mode of attaching a metal ion can be achieved by two ways.

In the first approach generally the solid material (inert or reactive) is attached with a device, which can be a ligand having affinity for metal ions. Thus the ligand is first anchored with solid material and then this supported ligand is treated with the metal salts for the metal ions to bind and produce a heterogeneous catalyst.[1,2] Schematic diagram is shown in Figure 3.

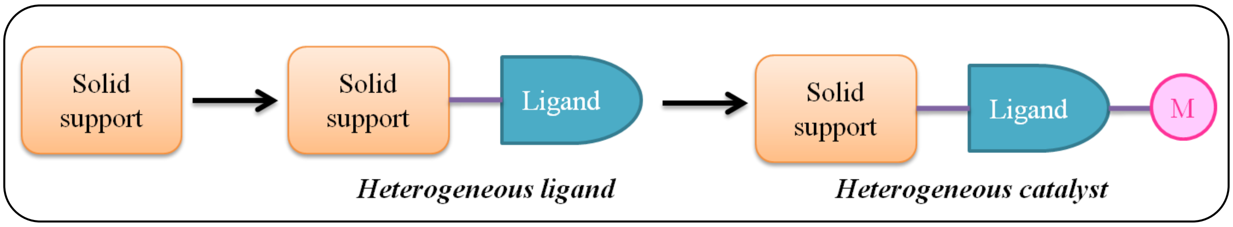


Figure 3

The method is also quite successful in terms of anchoring different metal ions for the catalytic applications and the heterogeneous systems are found to be effective, recoverable and reusable to a great extent. The development in the field of polymer chemistry has led to the easy use of polymeric materials which are insoluble in many organic solvents, moreover they can be easily functionalized and its porosity can be tuned to alter permeability. The area of polymer-anchored metal complexes and their applications as heterogeneous catalysts for many useful organic transformations is widely investigated.[3,4] Various supports includes the use of polysiloxanes[5], nano-particles[6], metal ions anchored on clays and zeolites[7], metal oxides and mesoporous materials[8] etc. are extensively used for several transformations. Several Pd anchored heterogenous system were reported and such system were used for different C-C cross-coupling reactins. Few of the examples include mesoporous silica-supported Pd catalyst[9], Pd(II)-Schiff base complex supported on multi-walled carbon nanotubes[10], Pd catalyst supported on amine-functionalized glycidylmethacrylate gel type terpolymers[11], Pd–pyridine complex immobilized on hydrotalcite[12], Pd-grafted porous metal–organic framework material[13] and polymer-supported Pd–NHC complex[14].

Most commonly used polymer support was cross-linking polymer/resin of styrene and divinylbenzene, which is easily available and is well-studied support for easy functionalization. This concept was introduced by Merrifield in his pioneering use of heterogeneous chloromethylated polystyrene with cross-linking by divinylbenzene. These materials were known as Merrifield resin and has been used in various ways for synthesis and product purification in large number of processes.[15] Phan *et al.* have reported immobilisation of salen-type palladium (II) complex onto Merrifield resin[16] [Figure 4].

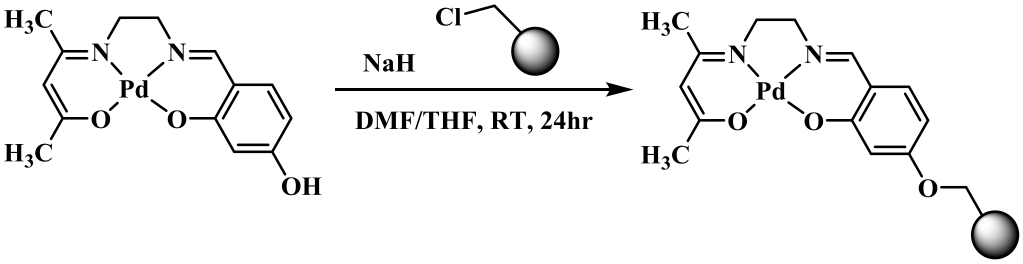


Figure 4

Our group has also studied this material by attaching Schiff base ligands and then studied its role in palladium catalyzed Mizoroki–Heck reaction, Suzuki reaction and one-pot *O*-Alkylation-Suzuki reaction. Chloromethylated poly(styrene-divinyl benzene) copolymer spherical beads with suitable crosslink were attached with two sets of diamines, 1,3-diaminopropane or 4,4’-diaminobiphenyl to afford polymer supported primary amines. These were then treated with salicylaldehyde to get appropriate polymer anchored palladium catalyst as shown in Figure 5.[17]

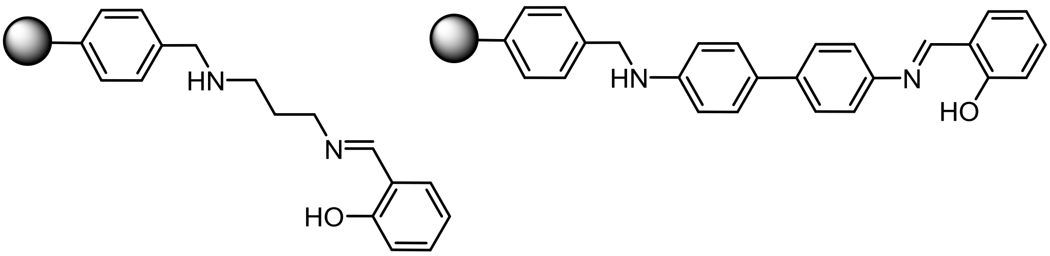


Figure 5

Lee *et al.* prepared a novel polymer-supported N-heterocyclic carbene (NHC) system from chloromethyl polystyrene resin using a simple procedure and used as the ligand for palladium catalyst as shown in Figure 6. The polymer-supported Pd-NHC complexes were shown to be efficient for the catalytic Suzuki cross-coupling reaction.[18]

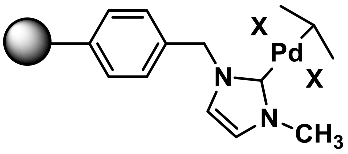


Figure 6

Another well explored solid support is modified silica. Wang *et al.* reported palladium nanoparticles supported on mesoporous silica with phosphine complex, which was used for coupling reactions.[19] Mukherjee *et al.* synthesized gold particles and supported into mesoporous silica by direct interaction between colloidal gold and the solid silica, by *in situ* reduction of chloroaurate in its presence, and also by chemical modification of the silica surface with thiol moieties, and finally incorporation of gold particles.[20] Shimizu *et al.*[21], Bedford *et al.*[22] and Crudden *et al.*[23] reported mesoporous silica as support and employed for the cross-coupling reactions, such as the Suzuki–Miyaura and Heck reactions. Some of the examples where silica has been used as support are discussed below.

Nandi *et al.* reported metal-grafted mesoporous silica with highly ordered 2D-hexagonal structure. Silica has been functionalized with 3-aminopropyltriethoxysilane (3-APTES) followed by condensation with a dialdehyde, 4-methyl-2,6-diformylphenol to produce an immobilized Schiff-base ligand. This material is separately treated with solution of copper(II) chloride and nickel(II) chloride to obtain copper and nickel anchored mesoporous materials as shown in Figure 7. The catalyst was used for selective epoxidation of alkenes.[24]

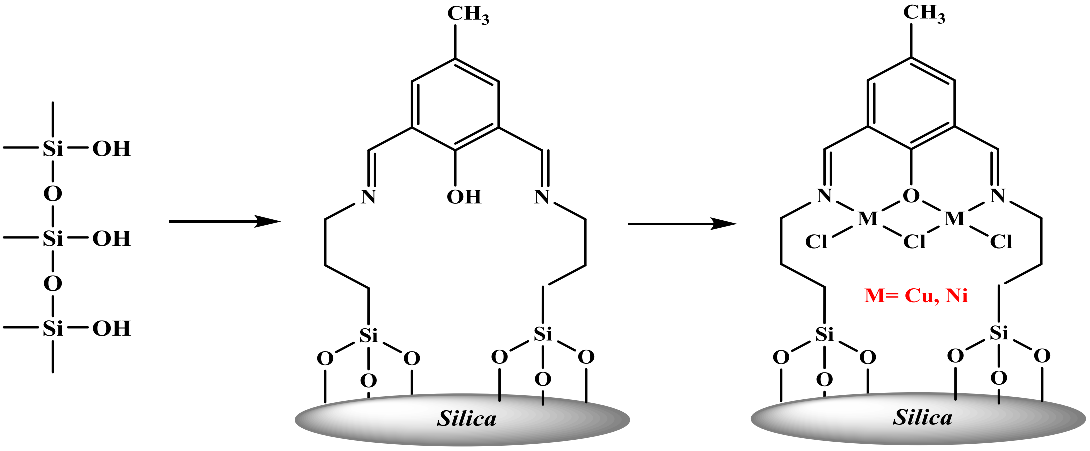


Figure 7

Gruber, Woelfler *et al.* reported novel catalytic system where $Pd(OAc)_2$ was attached to a bis(oxazoline) ligand that is covalently bonded to 3-mercaptopropyl-functionalized silica gel. The material shows excellent catalytic activity for Suzuki-Miyaura reaction as shown in Figure 8.[25]

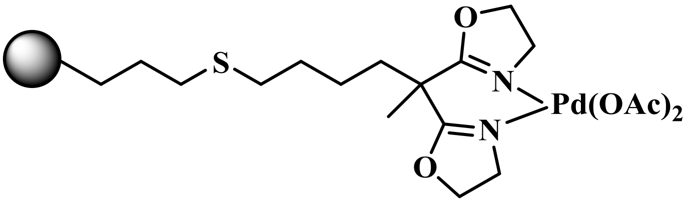


Figure 8

Ghiaci *et al.* have reported the synthesis of an efficient heterogeneous Pd catalytic system based on immobilization of Pd nanoparticles (PNPs) on silica-bonded propylamine–cyanuric–cysteine (SiO_2–pA–Cyan–Cys) substrate as shown in figure 9.[26] To synthesize this, Silica was refluxed with 3-aminopropyl-trimethoxysilane to give SiO_2–pA, which was treated with diisopropylaminecyanuric chloride to yield SiO_2–pA–Cyan which was further treated with cysteinemethyl ester and N-ethyldiisopropylamine to give silicapropylamine–cyanuric–cysteine (SiO_2–pA–Cyan–Cys) which was then refluxed with palladium acetate to give final catalyst. The catalyst was applied for Suzuki and Sonogashira reactions.

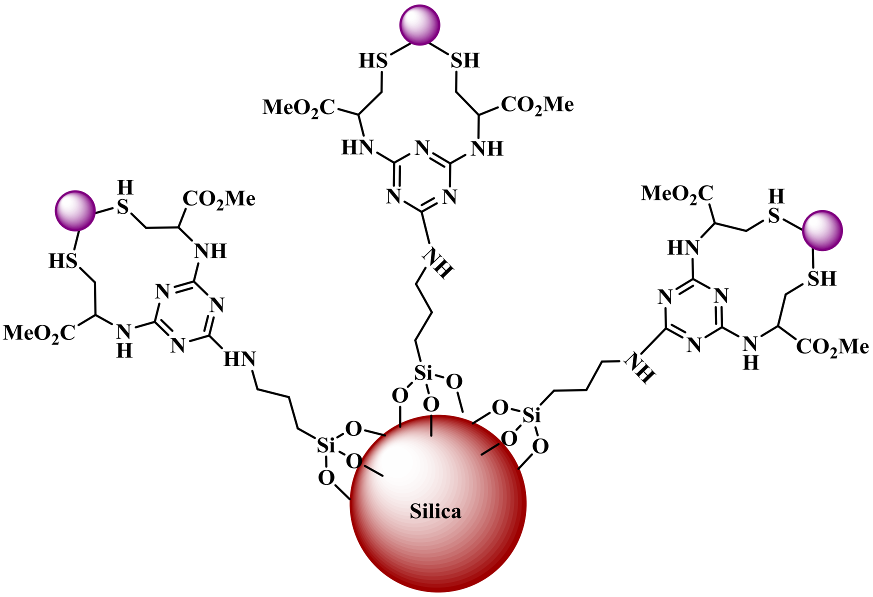


Figure 9

A palladium-Schiff base complex immobilized covalently on magnetic nanoparticles (Pd-imino-Py-γ-Fe_2O_3) was synthesized *via* the reaction of chloro-functionalized γ-Fe_2O_3 with imino pyridine followed by the reaction with palladium acetate.[27]

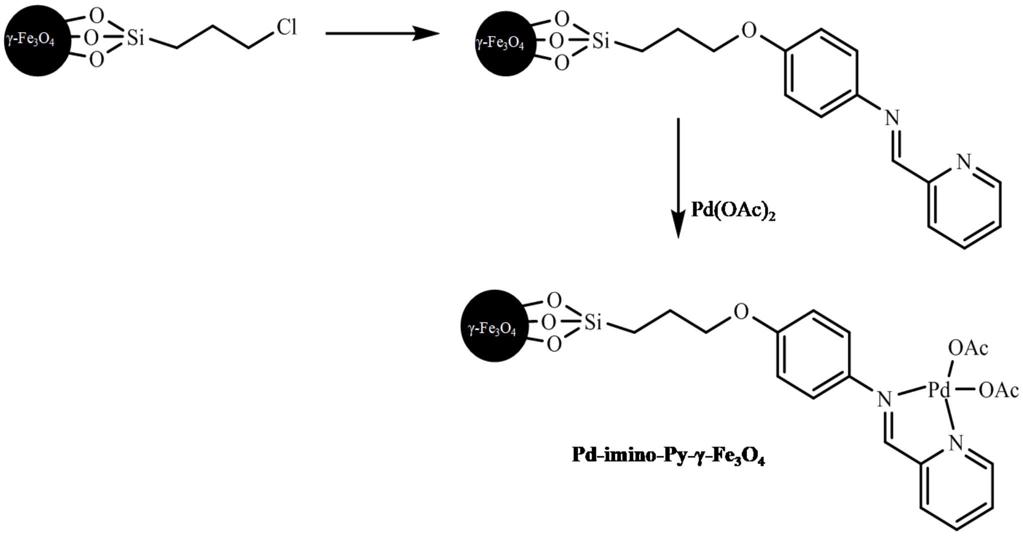


Figure 10

Similarly copper and cobalt metal complexes of novel ligands, immobilized on 3-aminopropyl functionalized silica, were used as catalysts for the oxidation of cyclohexane and cyclooctane by H_2O_2 under moderate reaction conditions.[28]

Sayed *et al.* reported silica nanoparticles which were functionalized with thiol units and bulky polar polyamines. They used this system with squaraine dye which was used for the selective colorimetric detection of formaldehyde as shown in Figure 11. The reaction of thiols groups on surface with a squaraine dye resulted in loss of the π-conjugation of the chromophores, and the subsequent bleaching of the solution. On the other hand, when formaldehyde was present in the solution, the thiol-squaraine reaction was inhibited and a chromogenic response was observed.[29]

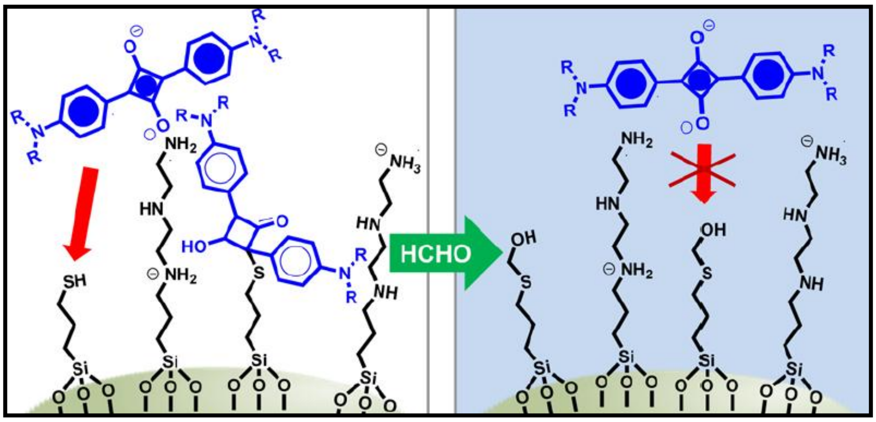


Figure 11

Recently silica and MCM-41 attached M(II) complexes as a part of the bidentate Schiff base were synthesized as shown in Figure 12. The catalyst were scanned for oxidation of secondary alcohols.[30]

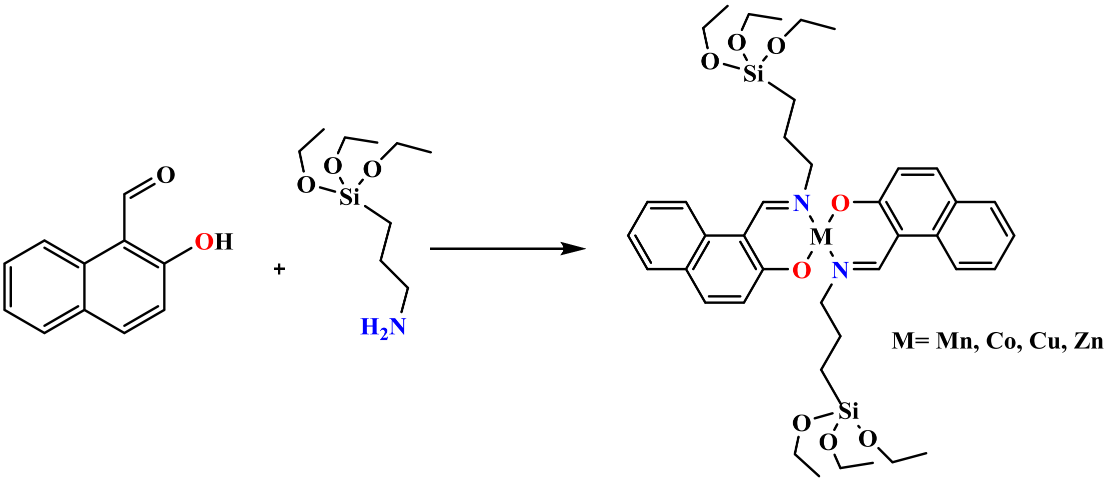


Figure 12

In yet another approach, the solid support can be designed or chosen in such a way that the metal ion can be directly bound or anchored on its surface, thus making a type of heterogeneous catalyst system.

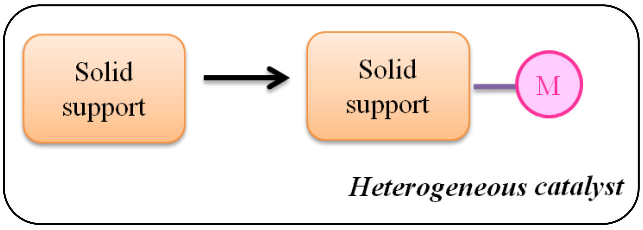


Figure 13

The second approach eliminates the need to attach ligand since the solid support can itself link with the metal ion. The polymers with imines or amines links can be used as solid support as they can easily linked with metal ions. Organic polymers are frequently used as supports to anchor metal ions to prepare heterogeneous catalysts. Various supports includes the use of soluble polymer support,[31] dendrimers,[32] self-supported polymeric catalysis.[33]Some natural biopolymers, such as chitosan[34], cellulose[35], wool[36], etc. have also been used as efficient polymer supports in several important palladium-catalyzed transformations. Silk fibroin-supported palladium catalyst was reported and used for chemoselective hydrogenation. The fibroin would be an appropriate catalyst support due to the coordination ability of its abundant nitrogen atoms to the Pd metal, as composition of silk fibroin is a protein produced by silkworms, and consists of 90 mol% of the amino acid like glycine, alanine, serine, tyrosine and very few residues of sulfur amino acids, which can be a catalyst poison to achieve chemoselectivity.[37]

Ganesan *et al.* synthesized hyperbranched polyethylenimine derivative as shown in Figure 14. The catalyst was effectively used as catalyst in Henry reaction. The nitroalcohol products were obtained in excellent yield within short reaction times. Moreover polyethylenimines along with zinc chloride were used in one-pot synthesis of β-nitrostyrenes.[38]

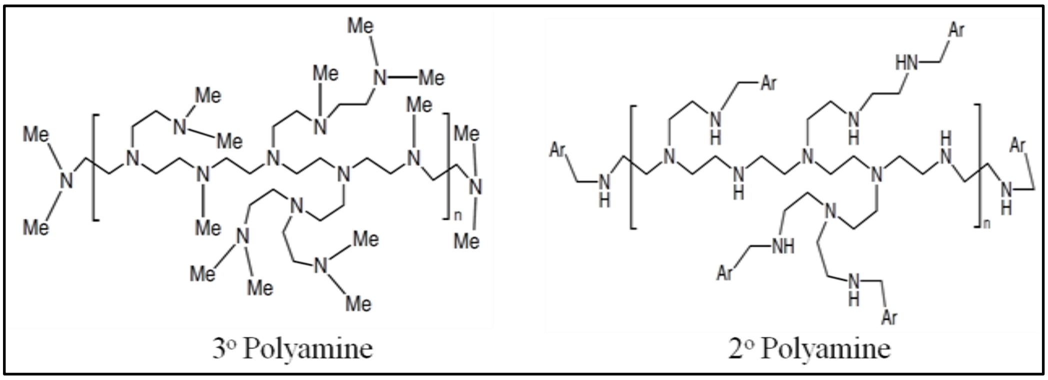


Figure 14

1.4 Polyaniline anchored metal catalysts and its applications

One of such solid supports capable of directly attaching with metal ions is polyaniline [PANI], mainly known for its electrical properties.[39]The sample of polyaniline is capable of undergoing easy ion exchange reaction when treated with metal salts under the appropriate conditions to furnish heterogeneous metal catalyst.

Polyaniline can be found in one of three oxidation states:[40] leucoemeraldine, emeraldine, (per)nigraniline out of which leucoemeraldine is fully reduced state with amine linkage as shown in Figure 15 (blue color portion). Pernigraniline is the fully oxidized state with imine links instead of amine links (red color portion in Figure15). The emeraldine form of polyaniline, often referred to as emeraldine base (EB), is neutral, most stable and useful form at room temperature. Out of all the forms of polyaniline emeraldine salt is only electrically conducting.

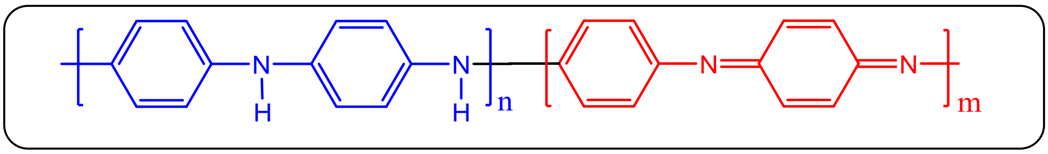


Figure 15

The polymer prepared from polymerization of aniline has the following generally accepted structure which is emaraldine base as shown in Figure 16.

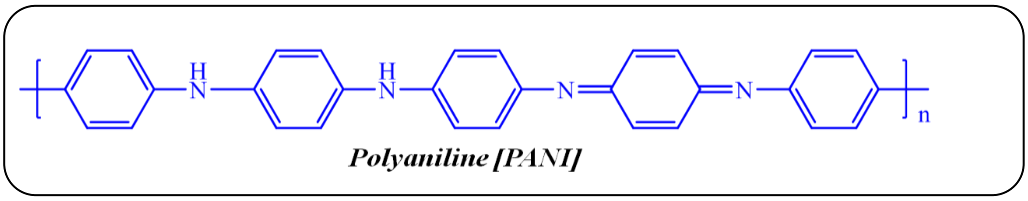


Figure 16

The metal ion is believed to be possibly link with amino group of the ligand by accepting the lone pair of electrons from the –NH- or –N= group(s) of PANI as shown in Figure 17.

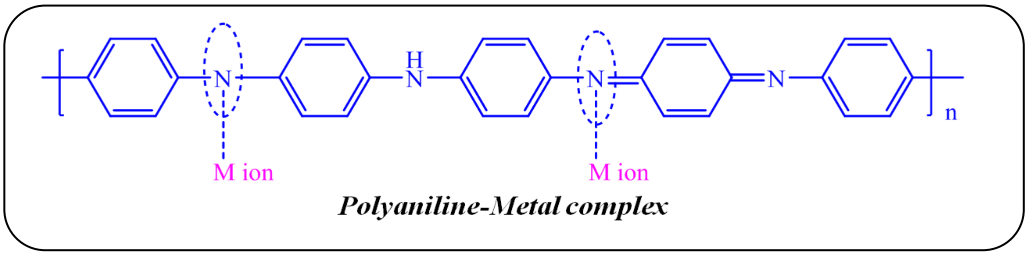


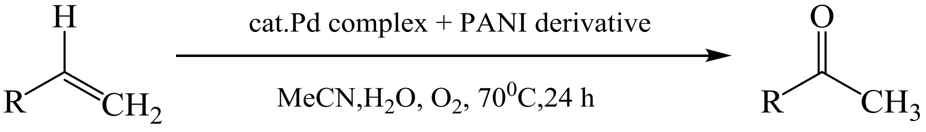
Figure 17

This type of polyaniline-metal complexes have been prepared by some researchers and scanned as catalysts for organic transformations. Some of the applications of polyaniline supported,metal catalysts for different applications are presented below.

A] Oxidation Reactions:

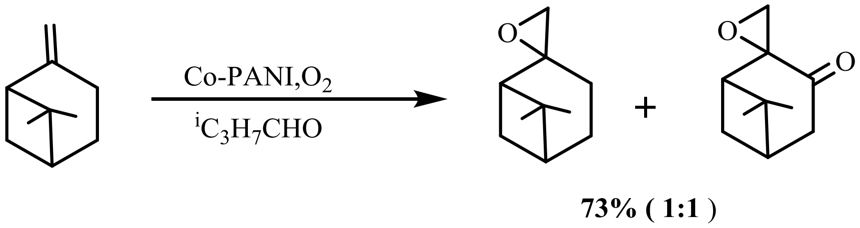
Oxidation reactions are very important methods of preparing functionalized organic molecules from simple compounds. Most of the oxidation reactions involve redox processes involving metal catalysts. Polyaniline supported Co, Cu and Mo complexes are used by researchers for specific oxidations.

Hirao *et al.* reported complex system consisting of palladium(II) acetate and polyaniline derivatives which allowed the catalytic Wacker oxidation[41], as shown in Scheme 1. They proposed novel redox system for the palladium(II)-catalyzed oxidation, in which polyaniline serve as a ligand with redox function under oxygen atmosphere.



Scheme 1

In another reaction the Polyaniline supported Co(II) acetate catalyst was used for oxidation of different alkenes in the presence of 2-methylpropanal as solvent under the oxygen atmosphere at ambient temperature.β-pinene underwent oxidation to afford a 1:1 mixture of the corresponding epoxide and epoxy ketone as shown in Scheme 2.[42] This catalyst can be reused for epoxidation without compromising its catalytic efficiency.



Scheme 2

Based on the above results the authors further extended the synthesis for polyaniline supported cobalt (II) salen as shown in Figure 18. Activity of this catalyst is further extended to the synthesis of more complex molecules.

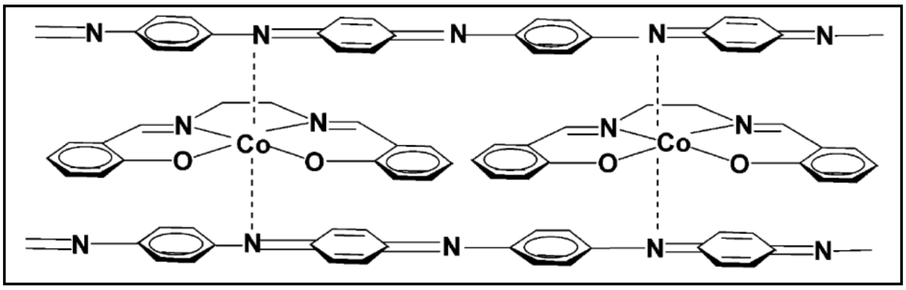


Figure 18

A novel synthesis of pyrrolidine containing α-hydroxyamide core structures as inhibitors for HIV protease is developed by employing polyaniline supported cobalt(II)salen which can performs a dual role, first catalyzes the epoxidation of cinnamoyl amide of L-proline and subsequently promotes the opening of the epoxide with aniline and its derivatives.[43]

S.R. Reddy *et al* prepared polyaniline supported vanadium complex as shown in Figure 19.This catalyst was used for oxidation reaction of alcohols to aldehydes and ketones in high yields under molecular oxygen in toluene at 100°C as shown in Scheme 3. The catalyst complex can be recycled without much loss of activity.[44]

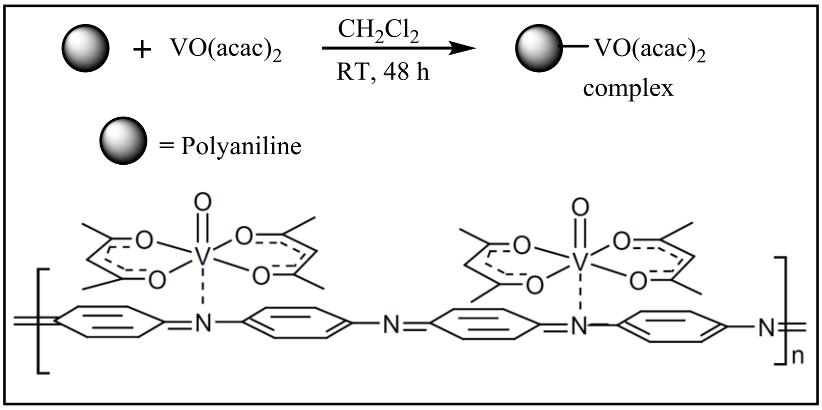
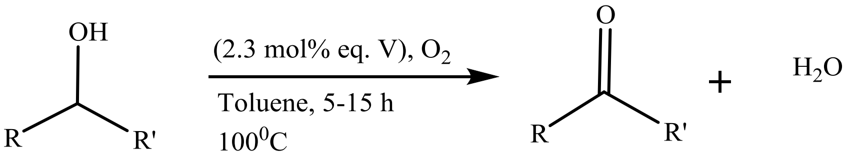


Figure 19



Scheme 3

Similarly, the oxidation of alcohols to aldehydes and ketones has been studied with molecular oxygen in presence of polyaniline-supported Molybdenum-catalyst as shown in Figure 20. The reactions of primary alcohols are faster compared to secondary alcohols and the catalyst can be recycled without loss of activity.[45]

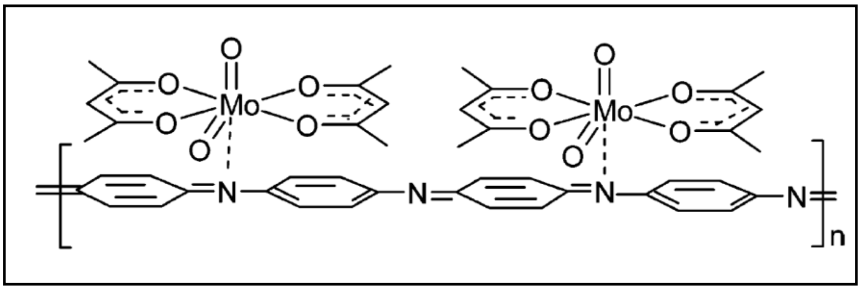


Figure 20

Haberthe *et al.* reported synthesis of Fe, Co and Mn porphyrins, supported on polyaniline (PANI) as shown in Figure 21. They also studied this catalyst in liquid phase or gaseous phase and used it as catalysts for oxidation of styrene and *iso*-butyraldehyde. The reaction proceeds along two parallel reaction pathways leading to the formation of benzaldehyde and epoxystyrene with products of its tautomeric isomerisation. The catalytic activity decreases in the order Co- >Fe- >MnT(*p*-SO_3H)PP in the case of both porphyrins in the liquid phase and supported on polyaniline. Supporting metalloporphyrins on polyaniline modifies their catalytic properties. Catalytic activity of Co-porphyrin decreases after supporting and the reaction pathway to epoxystyrene becomes more favoured, whereas the catalytic activity of Fe- and Mn-porphyrin increases and the reaction towards benzaldehyde becomes more favorable.[46]

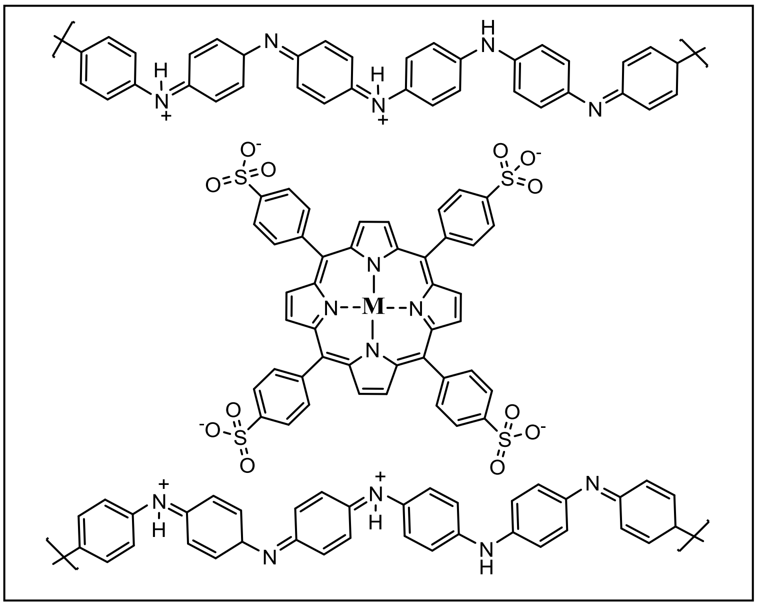


Figure 21

In another quite different application, the C.W. Lee *et al.* [47] described the efficient and convenient catalytic oxidation of hydroquinone and primary/secondary alcohol compounds into benzoquinone and aldehyde/ketone using various oxidation states of polyaniline as shown in Figure 22. As seen before the structure of PANI consists of a repeating unit of benzenoid and quinoid, which is similar to the structure of quinone derivatives. When the quinoid moiety of PANI was introduced into a hydroquinone or alcohol system, it is expected that HQ and primary/secondary alcohol compounds would be readily oxidized by suitable attractions such as a hydrogen bond and π–π interaction between the PANI and these compounds. It was found that the oxidation capacity of the pernigraniline base polymer can be increased by designing a tailor-made catalyst to be used as a powerful oxidant and it was easily recovered and regenerated for recycling.

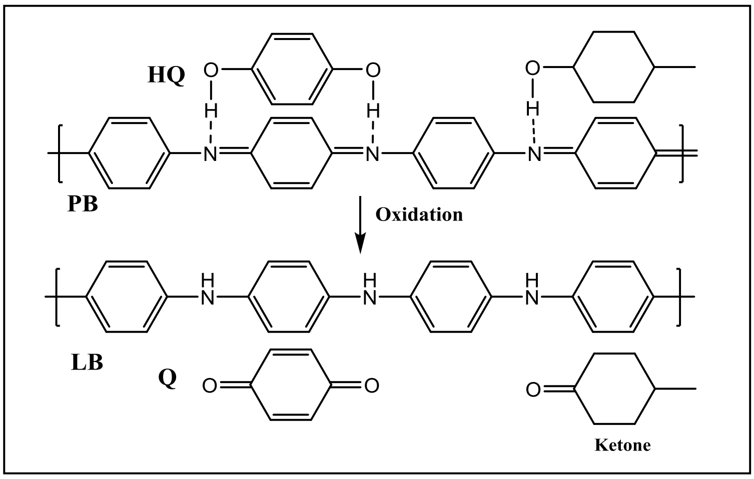
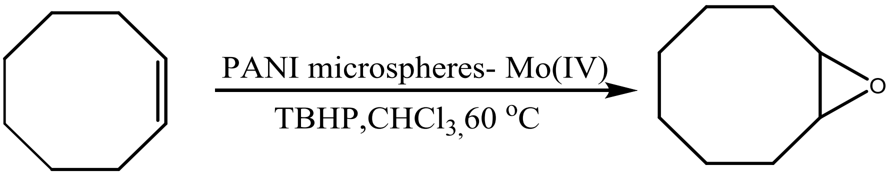


Figure 22

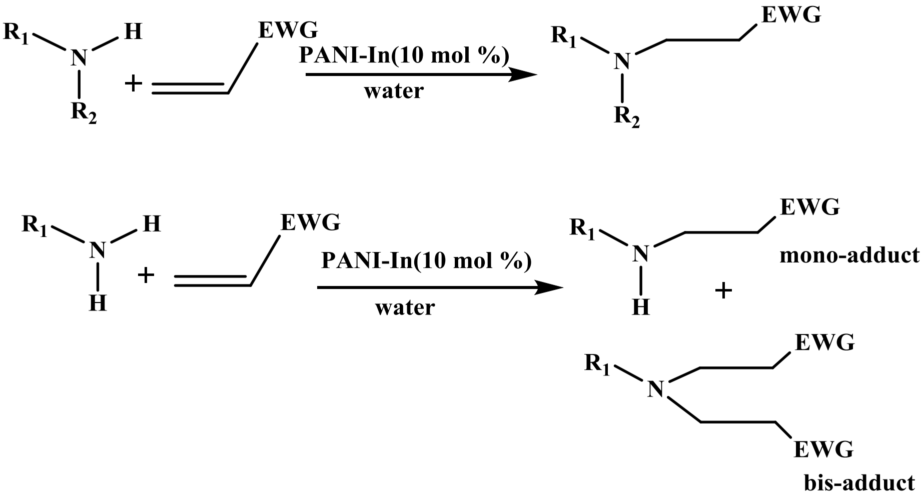
Ding *et al.* reported novel sea urchin-like polyaniline microspheres-supported molybdenum catalyst.The sea urchin like PANI hollow microspheres are synthesized by a self-assembly process using commercial polystyrene (PS) hollow spheres template. Mo catalyst was prepared by stirring a mixture of the sea urchin like PANI hollow microspheres and homogenous $MoO(O_2)_2(DMF)_2$ in acetonitrile at room temperature for 48 h.These catalysts were successfully applied for efficient epoxidation of olefins using *tert*-butylhydroperoxide (TBHP) as oxidant as shown in Scheme 4. The catalytic activity of the PANI microspheres-supported catalysts (95%) was found to be higher than that observed for its corresponding homogenous catalyst. The immobilized catalyst showed a stable catalytic activity in manifold reuses.[48]



Scheme 4

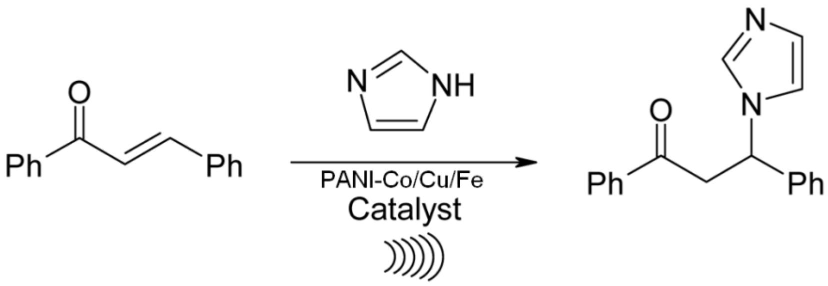
B] Michael reaction:

Polyaniline supported indium(III) trichloride (PANI-In) catalyst was synthesized and the catalyst was efficiently used in the aza-Michael reaction of amines with electron-deficient olefins as shown in Scheme 5 and in aza-Diels-Alder reaction of cyclic enol ethers with aromatic amines in water. The authors reported the preparation, characterization and catalytic properties of polyaniline supported indium chloride in two important organic reactions namely aza-Michael reactions of amines with electron-deficient olefins.[49] The simple procedure of catalyst preparation, easy recovery and reusability of the catalyst is expected to contribute to the development of benign chemical processes and products.



Scheme 5

Our group has also contributed in the area of PANI-Metal catalyst work and have studied the carbo- and aza-Michael reaction.[50] Complex of polyaniline with Co, Cu and Fe salts were screened for reaction as shown in Scheme 6 and found that the Cu works better under typical conditions.



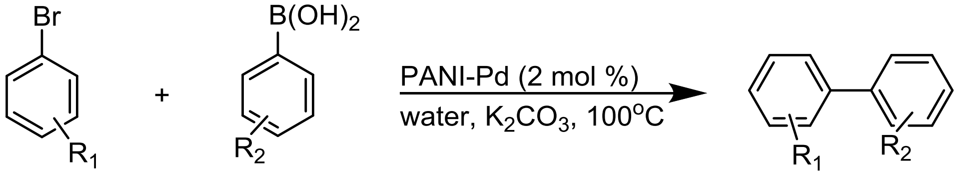
Scheme 6

C] Coupling reactions:

Palladium catalyzed coupling reactions such as Heck, Suzuki, Sonogashira etc. are important reactions in the repertoire of organic chemists. This is also evident with the award of the Chemistry Nobel Prize (2010) to the scientists who discovered these reactions. The expensive catalyst system of palladium is an ideal case for modifying in to a heterogeneous system. The polyaniline based hetrogenization of Pd catalyst has been investigated by some researchers.

The Suzuki reaction is one of the most versatile methods for the formation of C-C bonds. In general, the known methods for cross-coupling of aryl halides with hydrophilic functional groups are not well developed in organic solvents due to their insolubility. Gallon *et al.* reported polyaniline nanofibers stabilized palladium nanoparticles. This system is stable in water, and shows good activity in Suzuki reaction.[51]

Polyaniline supported palladium catalysts were prepared from different palladium precursors. All the catalysts were tested for Suzuki- Miyaura as shown in Scheme 7 and the catalyst prepared from $PdCl_2$ precursors was found to be the most effective. The catalyst can be easily recovered by simple filtration and reused for several cycles.[52]



Scheme 7

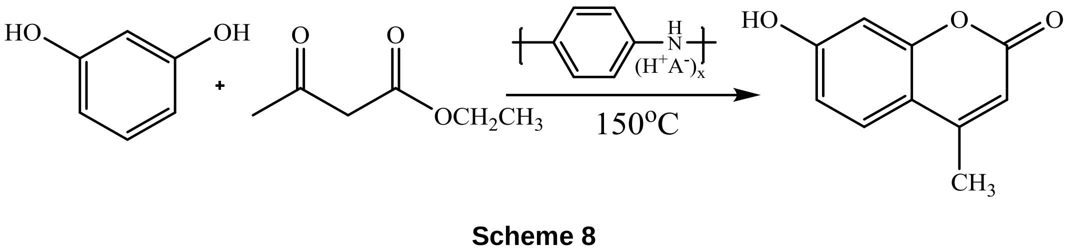
Palladium-polyaniline nanocomposite material was synthesized using an *in-situ* technique in which palladium acetate and aniline hydrochloride were used as the precursors of the composite. The metal-polymer composite material was used as a catalyst for the coupling of phenyl boronic acid with aryl halides. They found that the hybrid material was very active as a catalyst for the Suzuki reaction and the reaction could be carried out in the absence of phosphine ligand.[53]

Recently Fe_3O_4/Polyaniline as reactive magnetic supporters have been firstly synthesized, followed by the addition of $PdCl_2$ to initial redox reaction between PANI and Pd ions to form Pd nanoparticles on surfaces of Fe_3O_4/PANI cores. Suzuki cross-coupling reactions of aryl bromides with phenylboronic acids have been investigated using this catalyst.[54]

D] Polyaniline supported acid as catalyst:

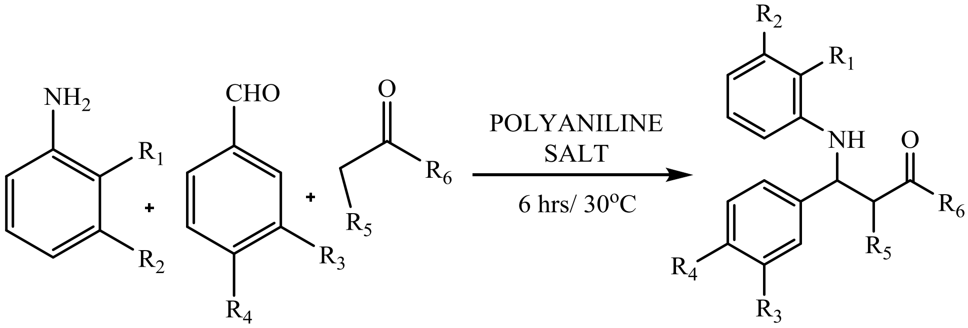
In these class of catalysts the polyaniline is treated with a protic acid, either during its synthesis or after it is purified. The acid forms a salt with amino units of the polyaniline and the salt behaves as a Brønsted acid catalyst. Many proton mediated chemical conversions are assisted by this catalyst system.

Polyaniline-sulfate salts were prepared using four different oxidizing agents such as benzoyl peroxide, ammonium persulfate, sodium persulfate and potassium dichromate. Polyaniline base was redoped to different polyaniline salts using various acids. Polyaniline salts are used as polymer supported acid catalysts for the preparation of 7 hydroxy-4-methyl coumarin as shown in Scheme 8. The efficiency of the catalyst depend upon the amount of acid present on the polymer chain and also the strength of the acid used. The catalytic use of polyaniline salts is feasible because of their easy preparation, high stability, easy handling, recovery, reusability and its eco-friendly nature.[55] Furthermore polyaniline supported acids are used for conversion of alcohols to the corresponding acetates. [56]



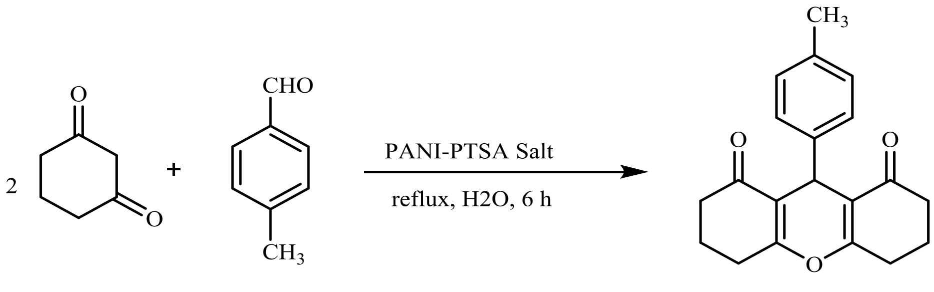
Scheme 8

Polyaniline salts and polyaniline complexes were prepared by post-doping process of Emeraldine base using Bronsted, organic and Lewis acids. The amount of acid group, acid group per aniline unit present in the polyaniline chain, pellet density and conductivity of the polyaniline system were reported. Three component Mannich-type reaction of aniline, benzaldehyde and cyclohexanone are effectively catalyzed by polyaniline salt under solvent free condition at 30°C as shown in Scheme 9. This method has several advantages; the catalytic use of polyaniline salt is quite feasible because of its easy preparation, easy handling, stability, easy recovery, reusability and eco-friendly nature.[57]



Scheme 9

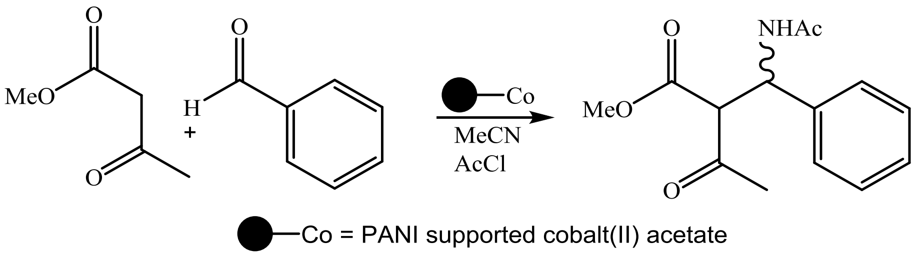
An efficient and straightforward procedure for the synthesis of 1,8-dioxo-dodecahydroxanthene was achieved through one-pot condensation of aryl aldehyde and 1,3-cyclohexanedione in the presence of polyaniline-*p*-tolulenesulfonate salt as polymeric solid acid, shown in Scheme 10.[58]It is demonstrated that polyaniline salt could be used as catalyst in aqueous medium also. This method provides several advantages such as easy synthesis, simple work up, versatility, reusability of the catalyst.



Scheme 10

E] Miscellaneous Reactions:

Polyaniline supported cobalt-catalyzed three-component coupling protocol for the synthesis of *α*-amino acid derivatives that can be manipulated to useful building blocks required for the synthesis of the peptidomimetic compounds. Polyaniline-supported cobalt(II) acetate catalyzes the coupling between methyl acetoacetate, an aldehyde, and acetonitrile to provide a general synthetic route to *α*-amino acid derivatives as shown in Scheme 11.[59]



Scheme 11

Polyaniline nanofiber supported $FeCl_3$ was used in the selective acylation of alcohols and amines employing acetic acid as an acylating agent to obtain the corresponding acetates and acetamides in good to excellent yields as shown in Scheme 12.[60]

$$\text{R-OH} + \text{AcOH} \xrightarrow[100^{o}\ \text{C/ 2-3 hr}]{\text{PANI}_n\text{-Fe}} \text{R-OAc} + \text{H}_2\text{O}$$

$$\text{R-NH}_2 + \text{AcOH} \xrightarrow[\text{0.5 - 4hr}]{\text{PANI}_n\text{-Fe}} \text{R-NHAc} + \text{H}_2\text{O}$$

Scheme 12

Choudary *et al.* prepared different Polyaniline-supported Sc, In, Pd, Os and Re catalysts by using a simple protocol and these catalysts were well characterized using different techniques. All the catalysts were successfully employed in a wide range of organic transformations PANI-Sc was first used in two fundamental Lewis acid-catalyzed carbon-carbon bond forming reactions, namely cyanation and allylation of carbonyl compounds. Suzuki cross-coupling of aryl halides and arylboronic acids was chosen as the model reaction to examine the catalytic efficacy of PANI-Pd catalyst. PANI-Os catalyst or PANI-Os-Re bifunctional catalyst was used in the dihydroxylation of olefins of *trans*-stilbene using *N*-methylmorpholine *N*-oxide (NMO) as the cooxidant.[61]

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1.6 Objective of work

Although the above summary indicates substantial work is reportedly done by the polyaniline supported catalysts, there is more scope for using this type of system of heterogeneous catalysis for newer applications. The main objectives of the present work are as follows:

- Study newer applications of PANI bound metal catalysts in one-pot methodologies.
- Explore the method of loading polyaniline on other heterogeneous solid supports, rather than using neat PANI for loading metal catalysts.
- Synthesis of π-conjugated molecules which shows applications in electrical and optical devices using PANI bound metal catalysts.
- Preparation of chiral analogue of PANI to be used as catalysts for asymmetric reactions.