1.1 General Introduction to Catalyst

In recent years the need to reduce production costs and the increasing regulations in pollution prevention prompted industries and academia to revise old processes in order to obtain safer and cleaner procedures for fine chemical and pharmaceutical synthesis. This trend popularly what has become known as "Green Chemistry" [1, 2, 3] or "Sustainable Technology" necessitates a paradigm shift from traditional concepts of process efficiency, that are mostly based on chemical yield, to one that assigns economic value to eliminating waste at source and avoiding the use of toxic and/or hazardous substances. Application of catalyst in synthesis is preferred on economic ground to minimize the energy consumption. Catalyst retard the reaction duration and also make the reaction selective in some cases.

The term ‘catalysis’ was introduced in 1835, and since then the concept of catalysis has evolved greatly [4]. Catalysis can be defined as “the change of the rate of chemical reactions under the action of certain substances” [5]. A catalyst is the substance that increases the rate of a reaction by lowering the activation energy, without being used up in the reaction [4]. They preserve their composition throughout the chemical reaction and are not wasted in the course of the catalysis. Furthermore, catalysts can speed up the reaction in a more selective manner which allows chemical processes to work more efficiently and with less byproduct [4]. This makes catalysts of great importance in industrial applications [5].

1.2 Role of Catalyst and their Properties

The energy profile (Figure 1.1) shows that the catalyst decreases the activation energy of the catalytic reaction compared to the uncatalyzed reaction. It shows that the catalyst does not affect the equilibrium of the reaction. The rates of forward and reverse reaction are same with the catalyst [6]. Important properties of the compound to be employed as the catalyst are summarized below. The physical properties and specificity of the action play very important role in proper selection of the catalyst for a chemical reaction. Ideally just a small amount of the catalyst should be needed to achieve big increase in the rate of reaction. Catalyst may undergo physical changes during the course of a reaction.
Physical properties:

- Pore size
- Surface area
- Morphology of the carrier
- Geometry and strength of the support

These properties affect the effectiveness and applicability of the catalyst.

Chemical properties:

- Chemically the catalyst should remain unchanged during a reaction (chemical stability)
- Catalyst does not change the quantity of products
- Activity, selectivity and specificity of the catalyst.

The most important property of catalysts is specificity of action; that is, each chemical reaction or group of uniform reactions can be accelerated only by very specific catalysts. Catalyst specificity is most clearly manifested in cases where catalysts can determine the course of the reaction. Various products are formed from the same original substances depending on the type of catalyst used. For example, from a mixture of carbon monoxide and hydrogen, using different catalysts it is possible to obtain methane, a mixture of liquid hydrocarbons, high-molecular weight solid hydrocarbons, mixtures of oxygen
containing compounds of various composition, and methyl or isobutyl alcohols. Selectivity serves as the measure of specificity of catalysts and is estimated by the ratio of the specific reaction rate to the general transformation rate of the initial substances in the presence of a given catalyst. In addition to activity and selectivity, another operational characteristic of catalysts is stability, which often determines the advisability of using catalysts for one or another industrial process.

Specific chemical compounds or their mixtures serve as catalysts in homogeneous catalytic processes. In this case, the catalytic properties of the catalysts are wholly determined by their chemical composition and structure. Heterogeneous catalytic processes using solid catalysts in the form of porous grains with a highly developed inner surface are primarily used in industry. The catalytic properties of solid catalysts are dependent on the size of their inner surface and the porous structure as well as on composition and structure. The essential stages of catalytic processes with solid catalysts are the transfer of reactants, products, and heat between the reaction mixture and the external surface of the catalyst grains (external transfer) and the transfer of substances and heat within the porous catalyst grains (internal transfer). The influence of internal mass transfer by diffusion is most frequent in the use of industrial catalysts. When this rate is insufficient, the efficiency of the catalyst decreases and the overall intensity of the process drops. Furthermore, this can lead to a reduction in the yield of unstable intermediate products capable of further transformation on the surface of the catalysts, which in many cases are specific. Activity relative to 1 m² of catalyst surface is known as specific catalytic activity.

1.3 Types of Catalysis

1.3.1 Homogeneous Catalysis

Homogeneous catalysis involves process in which product and reactant are in the same phase with the phase of catalyst. The phase commonly is either in gaseous or liquid [4] e.g. The chlorine atom is the catalyst in the decomposition of the ozone layer in the atmosphere [6]. The decomposition of ozone will occur spontaneously under the sun light. However, the presence of chlorine atom will accelerate the reaction tremendously. Both reactant and catalyst are in the same
gas phase. Another example of homogeneous catalysis is the industrial oxo process for manufacturing of isobutyl aldehyde. The reactants and the catalyst are both in the liquid phase. The reaction in liquid phase has been found to accelerate the reaction rate greatly due to the inter phase mass transfer limitations are eliminated [4].

1.3.2 Heterogeneous Catalysis

Heterogeneous catalysis involves more than one phase. The catalyst used usually is in solid phase. However, the reactants and products are in liquid or gaseous form. The solid phase catalysts are porous and impenetrable to let the catalytic reactions occur at the surface. This is to save the expensive materials such as platinum. Heterogeneous catalysis usually used in the chemical and petrochemical industry [7]. Furthermore, heterogeneous catalysis allows a few more improvements over the homogeneous one that can contribute to develop cleaner, safer and more economically feasible processes. However, heterogeneous catalysts, in order to be practical, have to meet numerous requisites as:

- The catalyst preparation should be simple, efficient and of general applicability.
- The performance of the immobilized catalyst should be comparable to (or better than) its homogeneous counterpart.
- The separation of the heterogeneous catalyst from the reaction mixture after completion of reaction should be possible via simple filtration in which more than the 95% of the catalyst should be recovered.
- The leaching of the active species from the heterogenized catalyst should be minimal.
- The recycling of the catalyst for several successive cycles should be possible without loss of activity.
- The supports carrying the catalyst should be mechanically, thermally and chemically stable; they should be compatible with the solvent and commercially available in a good quality.
From environmental (increasing disposal costs) and economical (cost of raw materials and of downstream separation) viewpoints, the catalyst selectivity might sometimes become more important than its activity or lifetime.

In recent years two preferential tendencies have been developed for the catalysis, viz. polymer supported catalysts and inorganic oxides heterogenized catalysts \[8, 9\]. Inorganic oxides show several advantages, such as more mechanical stability, easier handling and a wider range of solvents that can be used. In particular the general area of cross-linked polymer supports has shown an explosive growth connected with the development of new macro porous materials that are characterized by a rigid porous matrix that persists even in the dry state. These polymers are typically produced as spherical beads by suspension polymerization process, which is based on the mixture of cross-linking monomer, inert diluents and the porogen. Cross-linked polymer supports have been used in the preparation of “molded” porous materials with high characteristics for catalysis and asymmetric catalysis \[10\].

1.3.3 Supported Catalyst

The ideal supported catalyst should thus satisfy many requirements in order to combine both advantages of homogeneous and heterogeneous catalysis. However, the creation of the ideal supported catalyst is far to be accomplished and indeed many problems related to this technology have to be overcome. First of all the heterogenization procedure usually causes a decrease in both selectivity and activity of the homogeneous catalyst. In fact, the solid support allows limited diffusion of reactants to the active sites and these results in lower reaction rates. The lower selectivity has to be ascribed to the matrix effect. With its chemical and physical properties the support surface in close proximity of the anchored catalytic site can influence the extent of the reaction and determine a lower selectivity. As an example, when using silica as support, the polar surface can easily form hydrogen bonds with many organic polar functional groups or interact with metal atoms. This effect can change the spatial orientation of reactants towards catalysts. On the other hand, organic polymeric supports have usually little porosity; therefore there is a spatial constriction of catalysts which are not completely free to assume the best orientation. Moreover, the
recyclability of solid catalysts has not yet reached a good level of efficiency to be of practical interest. In this respect there are many problems related to the catalyst and support characteristics. The catalyst can be damaged during the reaction or can undergo partial leaching of the active species in the reaction medium that determines a partial deactivation of the catalyst itself. In some cases, however, the supporting procedure can improve the catalyst stability by eliminating, dimerization, and/or aggregation effects, which are the main causes of deactivation under homogeneous conditions. In fact “site isolation”, i.e. attaching the catalyst to a support in such a way that the active sites can no longer interact with each other, is a key concept that might lead to better performing heterogeneous catalysts [11]. With a careful catalyst design and an appropriate support choice based on reaction conditions (e.g. solvent, temperature, reactant etc.) it is possible to overcome these drawbacks.

1.3.3.1 Alumina Supported Catalyst

In many industrial processes (steam reforming, oxidation, selective hydrogenation), $\alpha$-M$_2$O$_3$ is used as catalytic support. $\alpha$-Al$_2$O$_3$ is thermally stable, chemically inert, and mechanically strong, it is very advantageous to select this material for a catalyst support, especially when the catalyst is subjected to high temperature due to the presence of reactor hot spots or because the reaction is carried out at a high temperature. However, relatively low specific surface area and pore volume are unfavorable characteristics of this type of supports [12]. The active exchange sites are the surface hydroxyl groups, which have a more basic character and will also exchange or react with anions. These surface hydroxyl groups can be removed by thermal dehydroxylation or be ‘deactivated’ by anionic replacement by anions of both minerals and organic acids. The dehydroxylated surface is more readily rehydrated and is fairly readily hydrolysed by mineral acids; Aluminas have a weak cationic exchange capacity above pH 7.

1.3.3.2 Silica Supported Catalyst

The active exchange sites on a silica surface are the silanol groups, which are weakly acidic. Cationic exchange takes place at pH values greater than 5. The surface concentration of silanol groups appears to depend upon the pH of the
solution from which the silica is formed. These groups get decreased as the pH increases. Acid precipitation (pH 2) gives an almost fully hydroxylated surface (a high surface-area, low pore-volume gel), whereas base precipitation (pH 6) gives a surface perhaps only 40% hydroxylated (a medium surface-area, high pore-volume gel) [13]. Crystalline silica (silicalite) prepared at a very high pH is reported to be hydrophobic and devoid of surface hydroxyls [14]. The concentration of active silanol groups can be reduced by thermal dehydroxylation above 400 K, being virtually complete at 900 K [15]. Silicas made by flame hydrolysis of SiCl₄ will have low exchange capacity because of the high temperature of formation. Similarly diatomaceous earths will have low capacity because of calcinations during preparation in addition to their inherently low surface areas. The siloxanes resulting from thermal dehydroxylation are resistant to subsequent hydrolysis. The silanol groups can also be deactivated chemically, although this would not be normal commercial catalyst-preparation practice. Possibilities would be ligand replacement by fluoride or esterification by benzyl alcohol and silanation. These silanol groups can also interact very weakly with complex anions either by ion pairing or hydrogen bonding.

1.3.3.3 Magnesia Supported

Magnesia is not a particularly useful support since it hydrates and dehydrates too readily leading to a loss in physical integrity of the catalyst granule. It is, however, a frequent component of mixed catalyst where because of its greater basicity it can confer a useful anionic exchange capacity.

1.3.3.4 Polymer Supported Catalyst

Polymer-supported (PS) organic reactions, i.e., reactions where at least one of the reactants is bound to a polymer, have many attractive features. The most important of which stem from the easy separation of the supported and non supported species at the end of the reaction. The separation is especially easy if the polymer is in the form of cross-linked, and therefore totally insoluble, polymer beads. At the end of the reaction period, separation can be achieved simply by filtering off the beads and washing them with proper solvent. Clearly such a separation procedure can easily be automated. This concept has led to PS organic reactions being of interest for more than 60 years [16-20]. They started
to be studied seriously in the 1940s and early 1950s by following the commercial introduction of various organic ion-exchange resins [16]. The ion exchange resins were usually sulfonated cross-linked polystyrene beads (strong acid cation exchange resins), cross-linked beads prepared using acrylic or methacrylic acids (weak acid cation-exchange resins), or cross-linked polymer beads containing quaternary ammonium salt residues (anion-exchange resins). Typical early studies using resin beads bearing sulfonic acid groups as catalysts for reactions involve sucrose inversion, alcohol dehydration, ester hydrolysis, acetalization, and acetal hydrolysis [16]. Ion exchange resins were also used in an appropriate form to achieve organic separations; for example, the bicarbonate form of an anion-exchange resin could be used to separate acids from aldehydes and ketones [21]. The study of PS reactions received an enormous boost in 1963 when Merrifield [22], and Letsinger and Kornet [23], reported the first examples of “solid phase” peptide synthesis. About the same time Letsinger and Mahadevan reported the first studies of “solid phase” oligonucleotide synthesis [24]. In these methods the first residue of an oligopeptide or oligonucleotide was attached to insoluble polymer beads and more appropriate residues were added one by one until the required oligomer was been assembled. The oligomer was then cleaved from the beads. These methods were the first important examples of reactions involving PS substrates. The major advantage of these methods was recovery of PS oligomer at each stage simply by filtering off and washing the beads. When carrying out such syntheses it is, however, crucial that there are no side reactions and the required reactions proceed in 100% yield because the various products bound to the beads cannot be separated unless they are first cleaved from the support. As a consequence, for every reaction the conditions need to be very carefully tuned. This is a challenging and time-consuming task. It is not helped by the fact that monitoring the transformations of PS species is not as easy as monitoring transformations in solution. This makes such syntheses, so-called “solid phase syntheses”, quite demanding. More recently, the solid phase approach has been successfully extended to oligosaccharide synthesis [25]. In the early 1970s several research groups sought to extend Merrifield’s and Letsinger’s methods to other areas of organic synthesis [15-19]. Sherrington [26] has recalled many of the developments at this time. The supported reactant
could be a substrate, a reagent, a catalyst, or a scavenger. Many examples of organic reactions using PS substrates, PS reagents, PS catalysts, or PS scavengers were investigated at this time and in 1980 approximately a thousand relevant references were to be found in the primary literature. A wide variety of supports were investigated [27]. The importance of the correct choice of reaction solvent, the ideas of site isolation, and examples of micro environmental effects were identified, studied, and substantially understood [17-19, 28]. Interest in the field of PS organic chemistry intensified essentially because at the time it was an excellent technique in search of an application. In the late 1980s combinatorial chemistry was introduced by Furka et al. [29], Hruby et al. [30] and Houghten [31]. Combinatorial synthesis involved to carrying out reactions with PS substrates and manipulating the beads to make large numbers of organic compounds [32]. Closely related is high-throughput synthesis achieved by carrying out many reactions in parallel. Reactions using PS substrates were the ones studied most extensively in the 1990s. “Linkers”, i.e., the functionalities that attach the substrate to the support, that are stable to the various reagents used in the synthesis, but can be cleaved easily and efficiently at the end of the synthesis, so releasing the desired product from the support, received much attention [33].

1.3.3.5 Polymer Supported Sulfonic Acid Derivatives as Catalyst

Modern organic polymeric resins are made by addition polymerization or vinyl polymerization. Sulfonic groups are introduced onto the surface by way of sulfonation reactions. A silica surface can also be sulfonated. Catalyst structure may be made up of a two-dimensional polymer sheet with the ‘pendant’ catalytic centres (such as –SO$_3$H groups) either on one side of the polymeric sheet or on both side of the sheet. The polymeric sheet can then be rolled and joined at the ends with the pendant catalytic centers outward, as in Figure 1.2a or inward as in Figure 1.2b, or on both sides as in Figure 1.3 [34]. Leena rao [34] reported synthesis of copolymer of styrene-divinyl benzene and introduced SO$_3$H groups by sulphonation (Scheme 1.1).
**Figure 1.2 (a)** Polymeric bead without pore with acid sites on its surface. **(b)** Polymeric bead with pore and acid catalyst embedded within it.

**Figure 1.3** Polymeric beads with acid catalyst sites on surface as well as inside pore.
Congming Li et al. [35] synthesized PSS/SBA-15 via atom transfer radical polymerization (ATRP) method. SBA-15 material was first grafted with 4-(chloromethyl) phenyltrimethoxysilane. The surface-initiated polymerization of sodium salt of p-styrenesulfonate inside the pore wall of functionalized SBA-15 results in p-styrenesulfonic acid functionalized SBA-15 (PSS-SBA-15) (Scheme 1.2).
1.4 Use of Polymer Supported Sulfonic Acid Catalyst in Organic Reaction

Some of the recent reports are cited in the selection describing application of polymer supported sulfonic acid derivatives as catalyst in heterocyclic preparation.

Piscopo et al. [36] have carried out chemoselective oxidation of unsaturated cis-bicyclo-[3.2.0]-hept-2-en-6-one 1 by using SiO$_2$-(CH$_2$)$_3$-SO$_3$H as a catalyst at room temperature in 45 min. The compound 1 underwent selective conversion to lactone 2 (94% yield, 100% selectivity) without formation of epoxides 3 and 4 (Scheme 1.3).

Bentolhoda et al. [37] synthesized polystyrene immobilized acidic IL ([PS-IM(CH$_2$)$_4$SO$_3$H][HSO$_4$]) by copolymerization of 3-vinyl-1-(4-sulfonic acid) butylimidazolium hydrogen sulfate with styrene in the presence of benzoyl peroxide. It was used as catalyst in the Hantzsch synthesis of 1,4-dihydropyridines 8 via one-pot three-component reaction of aromatic aldehydes 5, ethyl acetoacetate 6 and ammonium acetate 7 (Scheme 1.4).

Maggi R et al. [38] carried out oxidation of methylhydroquinone 9 with 30% aqueous hydrogen peroxide to methylbenzoquinone 10 by using silica supported sulfonic acids catalyst at room temperature using methanol as the solvent (Scheme 1.5).
Jasmin et al. [39] synthesized 4,5-dihydropyrano[3,2-c]chromenes 14, 4-hydroxycoumarin 11, benzaldehyde 12 and Malononitrile/Ethyl cyanoacetate 3 by using polystyrene divinylbenzene supported sulphanilic acid as the catalyst under microwave irradiation and solvent free condition (Scheme 1.6).

Wang et al. [40] developed an efficient and environmentally friendly process for the synthesis of 3,4-dihydropyrimidones 17 via the Biginelli type condensation reaction of aromatic aldehyde 5, ethylacetooacetate 15 and urea/thiourea 16 using poly(ethylene glycol)-bound sulfonic acid as catalyst under microwave irradiation (Scheme 1.7).

![Scheme 1.6 Synthesis of 4,5-dihydropyrano[3,2-c]chromenes](image)
1.5 Introduction to Heterocyclic Compounds Covered Under the Study

Heterocyclic compounds consist of cyclic structures in which one or more of the ring atoms are of elements other than carbon. The common hetero atoms are nitrogen, oxygen and sulphur. About a third of known organic compounds are heterocycles. They can be divided into alicyclic and aromatic compounds, which possess five or six member rings. The chemistry of heterocyclic compounds is one of the most complex branches of organic chemistry. It has seen unparalleled progress owing to their wide natural occurrence, specific chemical reactivity and widespread utility in the field of therapeutics. It is equally interesting for its theoretical implications, for the diversity of its synthetic procedures and for the physiological and industrial significance of heterocyclic compounds. Heterocyclic compounds provide convenient building blocks to which biologically active substitutes can be attached. The interesting biological activities of heterocycles have stimulated considerable research work in recent years including their synthetic utility. Most of the natural products obtained from plants and animal origin contain heterocyclic compounds such as alkaloids-nitrogenous bases and glycosides. They have been used since old age as remedial agents. Reserpine alkaloid from Indian Rouwolfia, febrifuge from ancient Chinese drug changshan, curar alkaloid from arrow poison, codeine, Ψ-tropine and strychnine are all well known examples of heterocyclic compounds.
1.5.1 Benzimidazole and Benzoxazole

Structures containing benzimidazole are well-known to have a wide range of biological properties. They have commercial applications in various realms of therapy, including antiulcerative, antihypertensive, antiviral, antifungal, anti-tumor and antihistaminic agents, and antihelminthic agents in veterinary medicine [41, 42]. These heterocycles are considered to be privileged structures by medicinal chemists. Compounds with imidazole ring systems have many pharmaceutical activities and play important roles in biochemical processes [43, 44]. Benzimidazoles and substituted imidazoles have been widely used in the medical field [45]. Some of them belong to highly stable fluorescent derivatives [46, 47]. A number of methods are available for synthesis of these compounds. A traditional method for synthesis of benzimidazoles is the reaction between o-phenylenediamine and carboxylic acid under harsh dehydrating reaction conditions, for example, in the presence of HCl, PPA (polyphosphoricacid), H3BO3, or p-toluenesulfonic acid. Some new methods are reported under microwave irradiation using PPA as catalyst [47, 48] or Montmorillonite KSF or SiO2 as solid support [49].

The benzoxazole derivatives are a well known kind of heterocycles that have considerable importance in the field of materials chemistry, in particular due to their fluorescence properties. These electronic states and behavior are mainly attributed to the reached planarity and rigidity of the delocalized electronic system. Taking advantage of this distinctive attribute, several groups have used these types of compounds in a number of different applications, such as electronic devices [50], sensors for metals [51], as well as their use as photoluminescent dyes [52]. Moreover, the family of benzoxazoles is a frequent motif in nature and have potential uses in medicinal chemistry as anticancer [53], antimicrobial and antiinflammatory agents [54]. The most traditional method for the synthesis of the benzoxazole moiety is the reaction of o-aminophenols with carboxylic acid derivatives in the presence of strong acids at high temperature [55]. Nevertheless, these harsh conditions do not allow the presence of several acid sensitive groups such as nitro or t-butyl; furthermore the yields are low due to the side reactions. The other most often used methodology is the oxidative cyclization of the phenolic Schiff bases obtained...
from the condensation of aldehydes and \( \omega \)-aminophenols using different oxidant agents, including DDQ \[56\], \( O_2/\text{TEMPO} \) \[57\], \( O_2/Pd(\text{II}) \) \[58\] and Dess Martin reagent \[59\]. Some other synthetic protocols have been reported, for example, the reaction of \( \omega \)-aminophenol with 1, 1-dibromoethenes \[60\], or the reaction of \( \omega \)-nitrophenols with orthoesters in the presence of In(III) as catalyst \[61\].

### 1.5.2 Quinoxaline

Heterocyclic quinines containing nitrogen atom are known to possess antibacterial \[62,63\], antifungal \[64-66\] and cytotoxic activities \[67-70\]. The clinical significance of this class of compounds has stimulated the synthesis of new lead compounds retaining the ‘core’ quinone chromophore \[71-73\]. Quinoxaline derivatives are nitrogen containing heterocyclic compounds and their importance has been reported in the literature \[74-76\]. They possess well known biological activities including anti-viral, anti-bacterial, anti-inflammatory, antiprotozoal, anthelmintic, anticancer and as kinase inhibitors. Quinoxaline derivatives constitute the basis of many insecticides, fungicides, herbicides, as well as being important in human health and as receptor antagonists. Although rarely described in nature, synthetic quinoxaline moiety is a part of number of antibiotics such as echinomycin, levomycin and actinomycin which are known to inhibit the growth of gram positive bacteria and also active against various transplantable tumours. In addition, quinoxaline derivatives are reported for their application in dyes, efficient electroluminescent materials, organic semiconductors and DNA cleaving agents. These are useful as intermediates for many target molecules in organic synthesis and also as synthons.

### 1.5.3 Quinazoline

Nitrogen containing heterocycles have always played a major role in the pharmaceutical and agrochemical industries because of their often potent physiological properties, which have resulted in numerous applications \[77\]. Diseases of the arterial tree cause more premature deaths than all other diseases such as cancer. Among the major risk factors for arterial diseases, high blood pressure is the most important one \[78\]. Quinazolines and condensed quinazolines are reported to possess interesting pharmacological activities such as antihypertensive \[79\], antihistaminic \[80\], analgesic and anti-inflammatory
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[81], anticancer [82], and anti-HIV [83] activities. Quinazolinone possess benzimidazole and triazole unit which are important structural motif in medicinal chemistry and can be found in a number of biologically active molecules [84-85].

1.6 Objective of the Present Work

Objective of the work are as follow.

- To synthesize novel polymer supported sulphanilic acid (ENPFSA) as the heterogeneous catalyst and characterize it by TGA and IR techniques.
- To find out new synthetic pathway to well-known condensation reactions for the synthesis of benzimidazoles, benzoazoles, quinoxalines and benzimidazolo quinazolinones by employing polymer supported sulphonic acid (ENPFSA) as the heterogeneous catalyst under different energy source such as conventional method, ultrasound irradiation and microwave irradiation as applicable in particular reactions.
- To characterized the synthesized compounds by spectroscopic techniques.
- To determine antioxidant activity of all synthesized compounds.

1.7 Outline of the Present Work

This thesis comprises of six chapters dealing with the study of new synthetic routs to well known heterocyclic compounds by using heterogeneous ENPFSA as catalyst.

CHAPTER-1: deals with introduction to the catalyst, types of catalyst and their applications.

CHAPTER-2: deals with the objective of synthesizing Polymer supported catalyst ENPFSA. The synthesized ENPFSA was characterized by IR-Spectroscopy. It was also characterized by thermogravimetric analysis (TGA) for its internal stability on the basis of decomposition temperature and degradation pattern.

CHAPTER-3: deals with ENPFSA catalyzed one pot synthesis and characterization of various benzimidazoles and benzoazoles. This chapter is divided in following two sections.
Section-I: deals with ENPFSA catalyzed one pot synthesis of 2-substituted benzimidazole derivatives from aromatic 1, 2-diamines and various aromatic aldehydes using ethanol as the solvent under microwave irradiation as well as conventional energy source. All the synthesized compounds are characterized by $^1$H NMR, $^{13}$C NMR, APT, IR spectroscopy and MASS spectrometry. Synthesized compounds are also characterized by their melting point and Elemental analysis.

Section-II: deals with ENPFSA catalyzed one pot synthesis of 2-substituted benzoxazole derivatives from aromatic 2-aminophenol and various aromatic aldehydes using ethanol as the solvent under microwave irradiation as well as conventional energy source. All the synthesized compounds are characterized by $^1$H NMR, $^{13}$C NMR, APT, IR spectroscopy and MASS spectrometry. Synthesized compounds are also characterized by their melting point and Elemental analysis.

CHAPTER-4: deals with ENPFSA catalyzed one pot synthesis of quinoxaline derivatives from aromatic 1, 2-diamines and 1, 2-diketones under ethanol as the solvent under ultrasound irradiation, conventional routs as well as at room temperature. All the synthesized compounds are characterized by $^1$H NMR, $^{13}$C NMR, APT, IR spectroscopy and MASS spectrometry. Synthesized compounds are also characterized by their melting point and Elemental analysis.

CHAPTER-5: deals with ENPFSA catalyzed one pot synthesis of benzimidazoquinazolinone derivatives by multi component condensation reaction of 2-amino benzimidazole, dimedone/cyclohexane-1,3-dione and various aromatic aldehydes using DMF as the solvent by using microwave irradiation and conventional energy source. All the synthesized compounds are characterized by $^1$H NMR, $^{13}$C NMR, APT, IR spectroscopy and MASS spectrometry. Synthesized compounds are also characterized by their melting point and Elemental analysis.

CHAPTER-6: deals with anti-oxidant activity of all the synthesized compounds by FRAP assay method.
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