CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Significant developments in the area of catalysis has made an impact on the rapid growth of chemical industries in all sectors- petroleum, petrochemicals, fine chemicals, pharmaceuticals, pollution control, automobiles etc. In the modern world, catalysis forms the basis of most of the industrial processes and more than 90% of the newly developed processes are catalyst based.

From a commercial point of view, a catalyst is supposed to lower the raw material consumption or the energy requirement of a chemical reaction. The former can be achieved, by increasing the yield or the selectivity towards a particular product, whereas for the latter, a catalyst must bring down the activation energy and thereby reaction temperature. In general, a major target of the catalyst is to obtain chemical products in high purity and high yields with excellent selectivity at a considerably lower temperature. Further, the catalyst also plays a significant role in pharmaceutical and fine chemicals by reducing the number of steps involved in producing a desired chemical. It thereby reduces potential environmental hazards by reducing the large amount of waste in each individual step.

Some popular terminologies used in the current scenario, to define process environmental compatibility [1] include,

E-factor: Indicates the amount of waste produced per kilogram of the product. E-factor for various segments of chemical industry can be given as.

Industry	***Product tonnage***	***kg byproduct/kg product (E-factor)***
Petroleum	10^6–10^8	<0.1
Bulk chemicals	10^4–10^6	<1–5
Fine chemicals	10^2–10^4	5–>50
Pharmaceuticals	10–10^3	25–>100

Environmental Quotient (EQ): Indicates the environmental impact of the waste produced, during a particular process.

Environmental Quotient (EQ) = (E-factor x Unfriendliness quotient, Q)

where, Q =1 for NaCl and 100–1000 for heavy metal salts

Atom efficiency: Refers to the effectiveness with which a desired product is obtained in a particular process.

Atom Efficiency = Weight of desired product / ∑weight of all products

Zero Emission Technology is the emission of waste products that do not pollute the environment or disrupt the climate. It is focused towards achieving high selectivity towards desired product and recycle/reuse of reactants.

A lot of attention is focused on development of zero emission technologies for major industrial processes. To meet these challenges, the industry requires innovative catalytic technologies, that offer high space-time yield, improved selectivity, higher atom efficiency, as well as low solvent requirement.

Catalysis makes use of all the three classical branches of chemistry (organic, physical and inorganic) as well as the fundamental concepts of chemical engineering. The catalyst used is mostly inorganic or organo-metallic compounds and the reactions carried out using the developed catalyst are organic transformations. Hence a catalyst chemist must be familiar with inorganic and organic chemistry. The overall performance of a catalyst depends on various factors such as turn over number, turn over frequency, conversion, selectivity and rate of reaction linked to the kinetics of the reactions. Therefore a sound knowledge of physical chemistry is required to understand the kinetics of reaction and hence reaction mechanism, reactor design and its effect on the performance of a catalyst. In most industrial applications, it is a requirement to predict the overall rate of a chemical process with respect to entire reactor, which depends on several factors such as interface mass transfer, mixing of the reactants, temperature profile and intrinsic kinetics of the reaction. Therefore, the large scale application of a developed process requires the skills and knowledge of a chemical engineer.

Catalysis is a kinetic phenomenon which occurs due to a catalyst in action. Catalyst is a substance that aids in the attainment of chemical equilibrium by reducing the potential energy barriers in the reaction path. The catalyst can neither force a reaction to occur, nor can it alter the equilibrium concentration of various species present in the reaction mixture. It can be said to alter the rate of a reaction, without itself being consumed in the process. Catalyzed reactions usually involve a reaction intermediate formed by the reaction of a catalyst with one or more of the reactants. This transitory intermediate then leads to product formation. Thus, it is clear that it participates in the reaction at some stage and is regenerated at the end of the reaction, may be in a different physical form but the mass essentially remains the same. In some cases, an additional substance is added to the active catalyst, termed as "Promoter" or a "Co-catalyst". It not only enhances the activity of the catalyst but in some cases also helps in combating catalyst sintering and poisoning [2].

1.2 CONCEPTS IN CATALYSIS

The overall performance of a catalyst in a particular reaction is determined by the rate of conversion of a particular reactant, selectivity and life. The common terminologies used to describe the efficiency of a catalyst for a particular process are as described below.

Turn Over Rate (TOR): The speed of a catalyzed reaction is often described in terms of TOR, defined as the conversion of the number of reactant molecules to products, per unit surface area of the catalyst at a given temperature, pressure and concentration.

Active Site: These are the specific sites of importance, present on the catalyst surface which induces a catalytic action. The rate of a catalytic reaction is site dependant and hence can be increased by increasing the surface area of a catalyst. It is generally believed that higher the surface area of a catalyst, higher will be the activity. It is notable, that only a fraction of the whole catalyst surface (active site) is active during the reaction. However, the nature of activity of a catalyst differs under different reaction conditions. Hence it is important to distinguish the active behavior of a catalyst under different conditions.

Specific Rate: It indicates the number of reactant molecules reacting or product molecules produced per unit catalyst area per second at a given temperature, pressure and concentration. Its value can be used to judge a suitable catalyst by comparing the activity of different catalysts for the same reaction under similar conditions.

Turn Over Number (TON): The effectiveness of a catalyst can be expressed in terms of its "turn over number" – which is the number of molecules of the substrate, reacting per minute due to the intervention of one molecule of the catalyst. This depends on temperature, concentration of substrate and the number of active sites on the catalyst. TON can also be defined as the number of moles of substrate converted to product by a mole of catalyst (metal or active compound in case of supported catalysts). TON can also be defined as, mass/volume of substrate converted to the product per unit mass/volume of the catalyst.

Selectivity: A chemical reaction leads to the formation of several different thermodynamically feasible products. A selective catalyst will facilitate the formation of one product molecule, while inhibiting the formation of other molecules, even though formation of other products is thermodynamically feasible.

Reaction Probability (R_P): It is defined as the number of product molecules formed per number of reactant molecules, incident on the catalytic surface. It is readily obtained by dividing the specific rate of product formation by the rate of incident reactants(on catalytic surface) in a flow reactor. R_p reveals the overall efficiency of the catalyst and it is often quoted in place of turn over rate.

Regenerability: It indicates the effectiveness with which a deactivated catalyst can be brought back to its original state of activity and selectivity.

Recyclability: It indicates the number of cycles upto which the catalyst can be effectively regenerated and efficiently reused, for optimum yields, in particular process conditions.

Catalyst Deactivation: The deactivation of a catalyst occurs in every reaction which is attributed to side reactions or parallel reactions or poisoning. At least four main reasons [2] are recognized for catalyst deactivation.

Poisoning – It is a chemical effect and occurs on the catalyst surface due to the chemisorption of impurities, reactants, products or byproducts. Catalyst activity is affected due to blocking of the active centres. This blocking occurs either due to the permanent chemisorption of species at the active centre or due to the blockage of the pathway of adsorbed reactive species towards the active centres.

Fouling – It occurs when a carbonaceous material is deposited on the catalyst. Carbonaceous materials, either coke or carbon is the major cause of deactivation in most cases. Coke or carbon affects catalyst activity by adsorbing strongly on the active centers or by plugging the micro and meso pores of the catalyst.

Thermal degradation – It is common in case of supported metal catalyst systems or with oxides of higher surface area. It comes into effect either due to loss of metal surface area due to crystallite growth (Metal Sintering) or due to loss of support surface area due to pore collapse (Support Sintering).

Attrition – It is due to the inherent low mechanical strength of the catalyst. The catalyst when subjected to shear and stress, collapses, thereby losing its activity.

For successful application of a catalytic process, the role of a catalyst is the most important. Hence, catalyst selection for any process is crucial, the most important factors to be considered being

Activity – rate at which the catalyst causes the reaction to proceed to equilibrium.

Selectivity – efficiency with which the catalyst causes the reaction to proceed in a direction to give the desired product.

Stability – catalyst life including regenerability and reusability.

Environmental compatibility – should produce zero or minimum emission with potential environmental hazards.

1.3 CATALYST CHARACTERIZATION

Catalyst characterization is an important aspect in catalysis as it gives an idea about the physico-chemical properties associated with a material. Generally used characterization techniques are

Elemental analysis

Elemental analysis gives us an idea about the composition of the catalyst. It is important to know the composition of a catalyst before use, during use and after being used for a number of cycles. Conventional methods involve gravimetric/volumetric analysis. Instrumental methods used for elemental analysis are Flame photometry, Atomic absorption spectroscopy (AAS) and Inductively coupled plasma-Atomic emission spectroscopy (ICP-AES) which are both popular as well as accurate.

Chemical resistivity

The chemical resistivity of the catalyst in various media (e.g. acids, bases and organic solvents etc) or in the media/environment where catalyst would operate, gives us an idea about the stability/resistivity of the material in these environments.

Thermal analysis (TGA/DSC)

It gives an idea about the thermal stability of the catalyst and the possible phase changes that occur during the thermal treatment of the catalyst. An understanding of the thermal behavior is of basic importance for utilizing the catalyst in various temperature ranges where it is thermally stable.

FTIR spectroscopy

It is routinely used to derive information regarding the various chemical bonds, functional groups and the interactions among them. In case of solid acid catalyst, the catalyst material is adsorbed with ammonia or pyridine. The IR spectrum provides a direct evidence for the existence of Bronsted and Lewis acid sites on the surface of catalysts, a technique very useful for solid acid catalysts.

X-ray Diffraction

It indicates the amorphous or crystalline nature of the material. In case of crystalline materials, distinct peaks at characteristic 2θ values are obtained, whereas absence of peaks indicates amorphous nature of material. Besides, if any impurity is present, can be detected by the characteristic 2θ value of the peak in the X-ray diffractogram.

Microscopy

Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) are used to study the morphology of the material. Besides it also gives an idea about the changes in shape, size and surface that occur in a used catalyst.

Surface area(BET method)

BET surface area can be obtained by N_2 adsorption under liquid nitrogen atmosphere. The activity of any catalyst is linked to its surface area and hence the number of active sites present. Further, pore size can also be determined from the adsorption desorption curve obtained, during the measurement process.

Temperature programmed desorption

It involves Temperature programmed desorption of ammonia (NH_3TPD), Temperature programmed reduction (TPR) and Temperature programmed oxidation (TPO). NH_3TPD gives an idea about the nature of acid sites present in the material through an adsorption desorption programme. TPR and TPO give an idea about the active metal surface area of the material.

Electron spin resonance (ESR) spectroscopy

ESR provides information about the symmetry of the catalyst sites, the oxidation state of the metal and the interaction of the adsorbed species with the active sites.

X-ray photoelectron spectroscopy (XPS)

XPS is a quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS is also known as ESCA, an abbreviation for Electron Spectroscopy for Chemical Analysis. XPS is a surface chemical analysis technique that can be used to analyze the surface chemistry of a catalyst in its as synthesized state, or after catalytic run.

Mechanical properties

Mechanical properties of a catalyst is important, as it gives an idea about the utility of the catalyst in a reactor. The properties to be monitored are abrasion and attrition resistance, crushing strength etc.

The field of catalyst characterization is so widespread and important that ASTM has developed few standard test procedures of catalyst characterization which is practiced universally. A list of such procedures is summarized in table 1.1.

Table 1.1 ASTM procedures for catalyst characterization [3]

Properties	**ASTM NO.**
Surface area of catalyst	D3663
Pore volume distribution by mercury intrusion porosimetry	D 4284
Pore distribution of catalysts from N_2 desorption isotherms	D 4641
Hydrogen chemisorption for platinum on alumina catalyst	D 3908
Catalyst acidity by ammonia chemisorption	D 4824
Particle size determination by laser light scattering	D 4464
Attrition and abrasion of catalysts and catalyst carriers	D 4058

1.4 CLASSIFICATION OF CATALYSTS

Catalysts can be used in any physical form-solid, liquid or a gas, depending on the process conditions and requirements. However, based on the reaction system being monophasic or biphasic (with respect to the catalyst, reactant and product) catalytic systems can be classified into two distinct categories:

i) Homogeneous catalysts.
ii) Heterogeneous catalysts.

Homogeneous Catalysts:

When the catalyst is in the same phase as that of the reactants and the products i.e. no phase boundary exists, then the catalyst is said to be homogeneous catalyst and the phenomenon as homogeneous catalysis. Homogeneous catalysis generally occurs in liquid phase, hence homogeneous catalytic reactions essentially involve the use of liquid phase catalysts or soluble catalysts. They mainly constitute mineral acids, alkyl metal salts or metal complexes [4,5]. The active species are well distributed throughout the system and accessible to the reactant molecules. They thus exhibit high activity and selectivity even under mild operating conditions. In spite of this, the application of homogeneous catalysis has been limited, due to the difficulties in separation of the catalysts from products and the lack of thermal stability [4]. Homogeneous catalysis by soluble metal complexes has wide-ranging applications in chemical industry. Important examples include hydrogenation, oxidation, carbonylation, hydroformylation, polymerization, isomerization etc [6].

Heterogeneous Catalysts:

When the catalyst used is in a different phase than that of the reactants/products, then the catalyst is said to be Heterogeneous catalyst and the phenomenon as Heterogeneous catalysis. Herein solid catalysts are often used in liquid-solid, gas-liquid-solid or gas-solid reactions.

The overall catalytic reaction in case of heterogeneous reactions can be divided into several steps [7]:

i) Diffusion of reactants to the surface
ii) Adsorption of reactants at the surface

iii) Chemical reaction on the surface (molecular rearrangements at active sites)
iv) Desorption of products from the surface; and
v) Diffusion of products away from the surface

These are consecutive steps and the slowest step, therefore, determines the rate of the reaction. In most reactions, the chemical reaction on the surface is the rate limiting step.

The whole range of catalysts used in various reactions can be divided into different types, based on the nature of the catalytic sites, on which the reaction takes place. They can either act as acid or base catalysts or as hydrogenation or oxidation catalysts when supported with metals [7]. These could be termed as mono-functional catalysts. By a suitable combination of the acid and metal functions, bifunctional catalysts can be prepared, which are industrially more important. In general, solid catalysts can be divided into metals and oxides, based on the specificity of their catalytic action. Table 1.2 presents the general classes of heterogeneous catalysts and their applications.

In heterogeneously catalyzed reactions, the yield generally increases with a rise in temperature. Their major advantage is easy separation of catalyst from the reaction mixture and hence can be easily separated, reactivated and reused. They possess excellent thermal and chemical stability [8,9]. The activity is mainly due to the surface active sites and hence non uniform distribution of active sites may lead to side reactions and hence lower selectivity. In table 1.3 is presented a comparison of homogeneous and heterogeneous catalysts.

Table 1.2 General classes of heterogeneous catalysts and their applications [7]

Class of catalyst	Examples	Applications
Metals (supported – mono, bi-, multi-metallic), alloys etc.	Pt, Pd, Rh, Ru, Ni, Fe, Co, Cu, Ag etc. on SiO_2, Al_2O_3, activated carbon and others	Hydrogenation-dehydrogenation, Aromatization, Oxidation
Metal oxides (amorphous & crystalline) and Mixed metal oxides	Mgo, Cuo, SiO_2-Al_2O_3, Zeolites, AlPOs, SAPOs, oxides of Bi-MO, Fe-Mo, V-Mo, Perovskites, Spinels, Fluorites	Alkylation, Cracking, isomerization, Disproportionation Selective oxidation, Dehydration-hydration, Ammoxidation, Amination
Metal sulfides (supported)	Co-Mo, Ni-Mo, Ni-W on SiO_2, Al_2O_3or other supports	Hydrodesulpharization, Hydrotreating, Hydrogenation
Metal salts	$Zr_3(PO_4)_4$, ZnS,$LaPO_4$, sulfates, carbonates	Etherification, Amination
Ion-exchange resins	Nafion – H, or Br forms	Acid catalyzed reactions
Heteropoly acids (supported)	$H_3PMo_{12}O_{40}$, $H_4SiW_{12}O_{40}$	Acid catalyzed reactions, Oxidation, Condensation
Clays and Pillared clays(PILCs),	Kaolinite, Montmorillonite	Acid catalyzed reactions
Immobilized enzymes	Asparatase, Nitrilase, Amylase	Hydration, Amination
Metal complexes (Supported/encapsulated)	Metal porphyrines, salens and phthallocyanins	Selective oxidation

Table 1.3 Comparison of Homogeneous v/s Heterogeneous catalysts[4]

Property	Homogeneous	Heterogeneous
Activity (relative to metal content)	High	Variable
Selectivity	High	Variable
Reaction conditions	Mild	Harsh
Service life	Variable	Long
Product separation	Catalyst contamination	Easy seperation
Catalyst recycling	Expensive	Easy
Catalyst poisoning	Low	Highly susceptible
Health and safety concern	Toxic & corrosive	Nontoxic, non corrosive

1.5 PRESENT TRENDS IN CATALYSIS

Over the past few years, there has been an increasing concern for pollution prevention and the approach to solve this problem has been towards the development of processes and technologies that produce minimum or zero wastes. This new approach is popularly known as GREEN CHEMISTRY and involves the synthesis, processing and use of chemicals in order to reduce the potential risks for human health and the environment. This new approach is also popular by the names like Environmentally benign chemistry, Clean chemistry, Sustainable chemistry, Atom economy and Benign by design chemistry.

Green Chemistry

It can be defined as the design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances.

The basic idea of green chemistry is to increase production efficiency through atom economy, while at the same time eliminate or at least minimize wastes and emissions at their source, rather than treat them at the end of the pipe, after they have been generated.

It involves the use of chemical techniques and methodologies that reduce or eliminate the use or generation of feed stocks, products, by products, solvents, reagents etc. that are hazardous to human health or environment.

It is a fundamental and important tool, in accomplishing pollution prevention. Pollution prevention is an approach to addressing environmental issues that involves preventing waste from being generated, so that it does not have to be dealt with later by treatment and disposal.

It provides the best opportunity for manufacturers, processors and users of chemicals to carry out their work, most economically and under environmentally safe conditions.

The principles of green chemistry can be applied to all areas of chemistry including synthesis, catalysis, reaction conditions, separations, analysis and monitoring.

The principles of green chemistry [10] provide a significant guideline in dealing with the concept of betterment of the environment. The principles indicate

I. It is better to prevent waste than to treat or clean up waste after it is formed.
II. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
III. Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
IV. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
V. The use of auxiliary substances (solvents, separation agents etc.) should be made unnecessary whenever possible and when used, innocuous.
VI. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
VII. A raw material or feedstock should be renewable, rather than depleting whenever technically and economically practical.
VIII. Unnecessary derivatization (blocking groups, protection/deprotection, and temporary modification of physical/chemical processes) should be avoided whenever possible.
IX. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
X. Chemical products should be designed, so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.
XI. Analytical methodologies need to be further developed, to allow for real time in-process monitoring and control prior to the formation of hazardous substances.
XII. Substances and the form of a substance, used in a chemical process should be chosen such, so as to minimize the potential for chemical accidents, including releases, explosions and fires.

In evaluation of alternative pathways for the environmentally benign synthesis of chemicals to meet pollution prevention goals, one finds that catalysis can meet all aspects of an effective strategy. In catalysed reactions, less energy is often required for production and higher efficiency is frequently observed in conversion, resulting in generation of fewer by products, co-products and other potential wastes. In addition, catalysts can be and often are designed to be environmentally safe. Catalysis has played a significant role in reducing pollution. This area is well documented by the many applications of catalysts in improving air quality by NOx removal and emission control, reducing the use of volatile organic compounds, developing alternative catalytic technology to replace the use of chlorine or chlorine based intermediate in chemical synthesis and processing and waste minimization. A continuing role for catalysis in pollution prevention programs is in new synthetic pathways that do not pollute. With catalysis the reaction can be more efficient and selective thus eliminating large amounts of by products and other waste components. The challenge for the field of industrial catalysis in the 21st century is to create innovations in catalyst design that will be environmentally responsible, economical, and applicable to industrial syntheses.

Fundamental area of investigation that can effectively accomplish the goals of green chemistry is that of catalysis. This includes the recent advances such as heterogenised homogeneous catalysis, phase transfer catalysis, biocatalysis, environmental catalysis, shape selective catalysis and solid acid catalysis.

The present thesis involves practicing and achieving green chemistry goals in the area of solid acid catalysis and heterogenised homogeneous catalysis, therefore these two aspects are being discussed in detail.

Heterogenised Homogeneous Catalysis:

In recent times a new type of catalysis has emerged having advantages of both homogeneous and heterogeneous catalysis. This is temed as "Heterogenised homogeneous catalysis" This may be achieved by supporting the homogeneous catalyst onto a solid support (inorganic or organic) in such a way that the environment of the catalyst is essentially unchanged.

The catalyst molecule gets dispersed on the surface of the support and thus available for combination with reactants as in homogeneous catalyst. The resulting heterogenised homogeneous catalyst can function mechanistically as if it were in solution but it would operate as a separate immobile phase. Thus, the advantages of both, homogeneous catalyst (activity, specificity) are retained and at the same time the advantages of heterogeneous catalyst (easy separation and reuse) is obtained.

Major advantages of heterogenised homogeneous catalysis is the unique microenvironment created within the support/matrix, improved catalyst stability and enhanced selectivity for reactants/intramolecular reactions. Selectivity for the substrate is also altered, compared to the unbound catalyst. Further, supports enhance coordination unsaturation of the metal ion, due to steric effects, giving high activity, and prevents dimerisation, retaining the active species.

Supporting the homogeneous catalyst onto the matrix is based on physical and chemical methods.

Physical methods include physical adsorption [11], ion pair formation, entrapment within the matrix [12] or entrapment within micro capsules (zeolites) [13]. The metal/metal complex can be encapsulated within the pore of a zeolite or embedded into a mesoporous silicate. Chemical methods involve functionalisation of the matrix (organic supports) with functional groups/ligands, followed by addition of metal ion, leading to complex formation.

Organic (polymers) supports

The generally used polymeric support includes polystyrene, polyvinyl pyridine, polyvinyl alcohol and polyacrylamide based compounds [8,9]. They have certain advantages:

(i) They can be easily prepared with a wide range of properties.

(ii) They can be easily functionalized.

(iii) Their porosity, surface area and solution characteristics can be altered, varying the degree of cross linking.

(iv) They are chemically inert, as a result of which they do not interfere with the catalytic group.

(v) They can control the diffusion of the reactants within the polymeric matrices thereby introducing extra selectivity to the catalyst.

Though a wide range of organic materials have been used for immobilization, their main disadvantages are:

(i) They are subject to chemical degradation by organic solvents.
(ii) Substrate diffusion in many cases becomes the limiting factor in reaction velocity thereby decreasing activity of the supported metal.
(iii) When employed in chromatographic columns, the pH and solvent conditions give rise to swelling, which affects the flow rates of the substrates through the column.
(iv) Poor heat transfer ability.
(v) They are not very well defined and often contain unknown impurities.

Inorganic supports

A variety of inorganic materials used in catalysis as supports include silica, alumina, clays, zeolites etc. The major advantages of these materials over organic supports are –

(i) Rigidness of matrix surfaces – this prevents the possibility of surface molecules entering the coordination sphere of the metal on the support. If coordinated, they deactivate the catalyst.
(ii) The materials possess high thermal stability and hence can be used at even higher temperatures.
(iii) Availability of methods for large scale production of supports.

Though there are many advantages there are disadvantages too. They do not possess proper sites for anchoring (only weak hydroxyl groups are present on the surface) and hence leaching of precious metals can occur.

As discussed above, organic (polymers) and inorganic supports have their own advantages and disadvantages, the main one being that though the method of anchoring(ion exchange) is both easy and leads to a stable interaction in organic polymers as compared to the inorganic supports, their major disadvantage is poor heat transfer ability leading to degradation at comparatively low temperatures. It would be ideal to search for a new material which combines the advantages of both types of supports.

Solid Acid Catalysis

Among all the catalysts in use, acid catalysts account for the majority of applications. One of the recent developments in this field is the use of solid acids [14]. They have their acidities held internally.Their major advantages include ease of handling and separation, enhanced activity and selectivity, regenerability, nonvolatile, nontoxic and noncorrosive nature. In case of solid acids, it is possible to introduce desired acidity by modification of synthetic and post synthetic treatment steps. The major class of materials used as solid acids include zeolites, heteropoly acids, clays, solid superacids, tma salts etc. They catalyze a variety of industrially important reactions including esterification, isomerization, cracking, hydration, dehydration, polymerization etc.

Use of liquid acids such as H_2SO_4, HF, H_3PO_4 as catalysts have been a conventionally established method for a variety of organic transformations. Even as of today sulphuric acid is the most widely used catalyst in petroleum refining industry, mainly as an alkylation catalyst, for the production of isooctane. Though they are very effective, they are normally associated with operational difficulties such as toxicity, corrosiveness, effluent disposal, product separation, storage and handling etc. Owing to the increasing environmental awareness and a quest for zero emission technologies much attention is focused on developing an alternative to these existing acids.

Solid Acids

A drive for clean technology associated with the problems encountered while using the liquid acids has resulted in the development of a variety of solid acids. Though environmental benefits have been the major reasons for the introduction of solid acids in many chemical processes, these catalysts have proved to be more economical and often produce better quality products.

In general terms, solid acids can be described as a solid on which the color of a basic indicator changes, or as a solid on which a base is chemically adsorbed. More strictly, following both the Bronsted and Lewis definitions, a solid acid shows a tendency to donate a proton or to accept an electron pair. Solid acid catalysts are appealing since the nature of the acid sites are known and it is possible to modify the acidic properties of these materials by adopting various synthetic and post synthetic treatments. Being stronger acids, they have a significantly higher catalytic activity compared to conventional acid catalysts and above all they provide clean environment. Although they differ in structure from liquid acids they work on the same principles. Solid acids can be used to advantage.

(i) Reaction products can be easily harvested.
(ii) They can allay concerns about safety and environmentally hazardous emissions as they are nontoxic and nonvolatile.
(iii) They hold their acidity internally and are thus easy to handle
(iv) They are very effective and some of them are known to exceed the acidity of concentrated H_2SO_4.
(v) They possess high catalytic activity and selectivity.
(vi) They do not corrode reaction vessels or reactors.
(vii) Separation from the reaction mixture is easily achieved through filtration or centrifugation (heterogeneous medium).
(viii) Easy regeneration and reuse of catalyst is possible.
(ix) There is no problem associated with the disposal of used solid acids, though the disposal of liquid acids require much money and efforts for post use treatment and effluent neutralization.

The ability to lend protons makes solid acids valuable as catalysts. Protons are often released as ionisable hydroxyl groups in which the bond between hydrogen and oxygen is severed to give H^+ and O^-. Protons may also be released in the form of hydrated ions such as H_3O^+. When a reactant receives and incorporates a proton from an acid, it forms a reactive intermediate. This positively charged intermediate may change shape and configuration. It may then undergo either isomerization or rearrangement by shedding the proton or may undergo some organic transformation leading to the formation of a new molecule. In any case the proton is returned to the catalyst [15].

Several review articles have been published dealing with the use of solid acid catalysts as heterogeneous catalysts for the preparation of speciality and fine chemicals. The main characteristic of solid acids, as compared to liquid acids, is that solid acid encompasses different population of sites, differing in their nature and strength [16]. The effectiveness of a particular solid acid catalyst for a given reaction, depends on various factors including surface area, porosity, acidity, crystallinity and nature of acid sites. A particular acid comprises of more than one type of acid sites (weak acid and strong acid sites) and hence depending on the reaction conditions, same catalyst can be active in one reaction and inactive in another.

In the present endeavour, tetravalent metal acid (TMA) salts are used as solid acid catalysts and as supports in heterogenised homogeneous catalysis.

1.6 ABOUT TETRAVALENT METAL ACID SALTS

Though well known and researched since the last 50 years, of late, ***"Tetravalent Metal Acid (TMA) Salts"*** have emerged as promising advanced materials as they possess robust properties.

An extensive literature on tma salts, exists today, which have been reviewed and detailed in four books.

1. Varshney K G and Khan A M 1991 *Inorganic Ion Exchangers in Chemical Analysis* (Eds.) Qureshi M and Varshney K G. CRC Press Inc, Boca Raton, Florida
2. Clearfield A 1982 *Inorganic Ion Exchange Materials* CRC Press, Boca Raton, Florida
3. Clearfield A, Nancollas G H and Blessing R H 1973 *Ion Exchange and Solvent Extraction* (Eds.) Marinsky J H and Marcus Y. Marcel Dekker, New York **Vol 5**
4. Amphlett C B 1964 *Inorganic Ion Exchangers,* Elsevier, Amsterdam

Systematic studies on their synthesis, structure elucidation and applications in the area of separation science, catalysis and solid electrolytes have been carried out by various groups – Dr. A. Clearfield (USA), Dr. G. Alberti, Dr. U. Costantino (Italy), Dr. D. Whittaker (UK), late Dr. M. Qureshi and Dr. K. G. Varshney (Aligarh Muslim University, India) and Dr. U. V. Chudasama (The M S University of Baroda, India).

Salient Features of TMA salts

(i) Tma salts are cation exchangers, possessing the general formula M(IV) $(HXO_4)_2.nH_2O$, where M(IV) = Zr, Ti, Sn, Ce, Th etc. and X = P, Mo, As, Sb, W etc.

(ii) The materials possess structural hydroxyl groups, the H of the –OH being the exchangeable sites, due to which the material possesses cation exchange properties.

(iii) Tma salts can be prepared both in amorphous and crystalline forms that exhibit selectivity for certain metal ions.

(iv) The materials possess granular nature and can be obtained in a range of mesh sizes, very suitable for column operations.

(v) The materials are generally hard and range in physical appearance from totally opaque to transparent.

(vi) These materials have shown a great promise in preparative reproducibility, ion exchange behaviour and stability towards thermal, chemical and ionizing radiations.

Structural Aspects of TMA salts

Almost all the possible combinations of tetravalent metals with polybasic acids have been examined and properties of the obtained materials investigated. This has led to an extensive literature on their synthesis, structure and properties. Earlier work was carried out with amorphous materials. The first crystalline α-zirconium phosphate was prepared by Clearfield and Stynes [17]. Structure elucidation was first carried out in 1969 [18]. Based on that structure, a large variety of layered compounds has since been developed all over the world [19]. Extensive work has been carried out on the structure property relationship and their applications as ion exchangers, catalysts and solid electrolytes, explored.

Much of the earlier work was focused on zirconium phosphate [20]. De Boers [21] reported a gel with P:Zr ratio equal to 2 as zirconium mohydrogen phosphate $Zr(HPO_4)_2$, but other workers [22,23] argued that under the preparation conditions the formation of a zirconyl salt $[ZrO(H_2PO_4)_2]$ was more likely. Bluementhal [20,23] proposed the structural formula for the precipitated product (figure 1.a). Paterson [24] has described the structure of zirconium phosphate as presented in figure 1.b

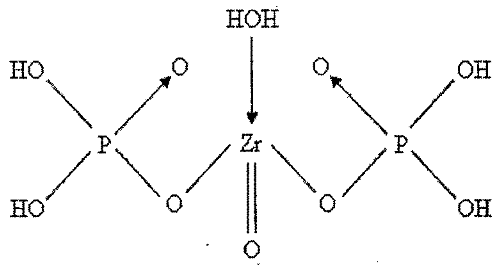


Figure. 1.a

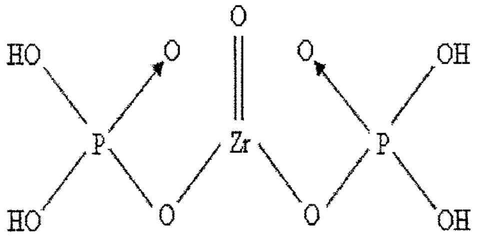


Figure. 1.b

According to these structures the H of the –OH groups are the exchangeable protons. Baestle and Pelsemakers [24] suggested the following structure (figure 1.c)

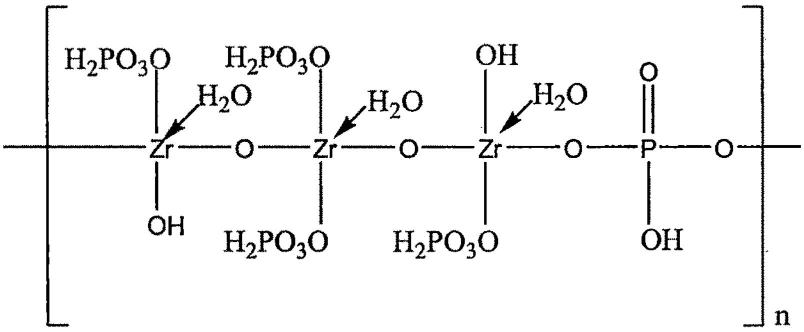


Figure 1.c

In this case also, the exchange can take place through the hydroxyl groups. Nancollas and Pekarek [24] proposed the following formula for crystalline zirconium phosphate (figure 1.d).They represented the semicrystalline zirconium phosphate by the formula shown in figure 1.e

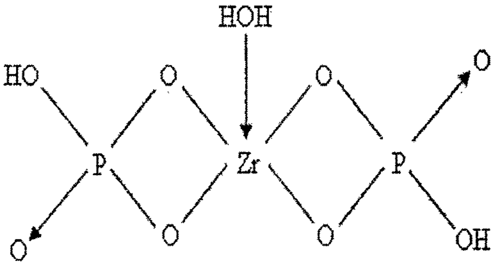


Figure 1.d

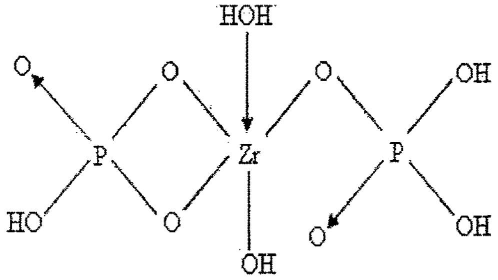


Figure 1.e

Much of the pioneering work in this area was done by the research group at the Oak Ridge National Laboratory led by K A Kraus [25] and in the United Kingdom by C B Amphlett [24].

The structure of crystalline α-ZrP [18] was solved by Clearfield and Smith in 1969. Zirconium phosphate has a layered structure. The structure of α-ZrP is monoclinic: a = 9.06 Å, b = 5.30 Å, c = 16.19 Å, β = 111.42° and space group $P2_1/c$. Zirconium atoms lie slightly above and below the *ab* plane as shown in figure 1.f and are bridged by the phosphate groups. These are situated alternatively above and below the metal atom plane. Three oxygen atoms of each phosphate, are bonded to three adjacent metal atoms, forming a distorted equilateral triangle. Each zirconium atom is thus octahedrally coordinated by oxygens. Lamellar macroanions $[Zr_n(PO_4)_{2n}]^{2n-}$ (figure 1.g) have charge balancing protons (H^+) bonded to oxygens adjacent to the interlayer region. These protons are responsible for the ion exchange, surface acidity and proton conductivity of α-ZrP. Crystal water molecules are located close to the centre of the interlayer cavities, held by hydrogen bonds with phosphates of both adjacent layers. An idealized picture of a portion of the layer is given in figure 1.g

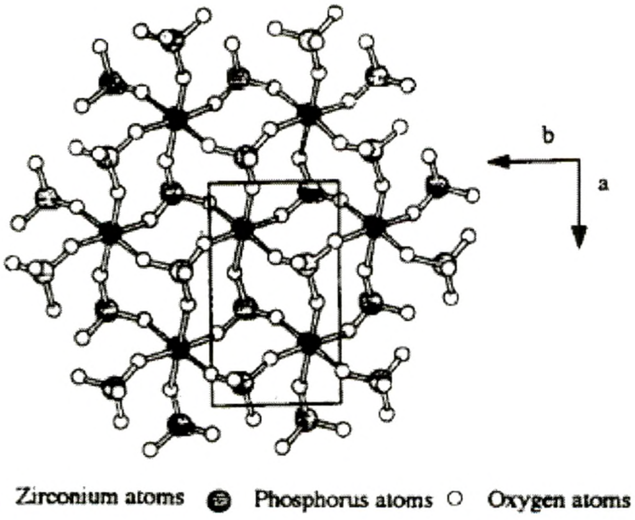


Figure 1.f ab layer of α-ZrP structure, showing the approximate position of the monoclinic cell [26].

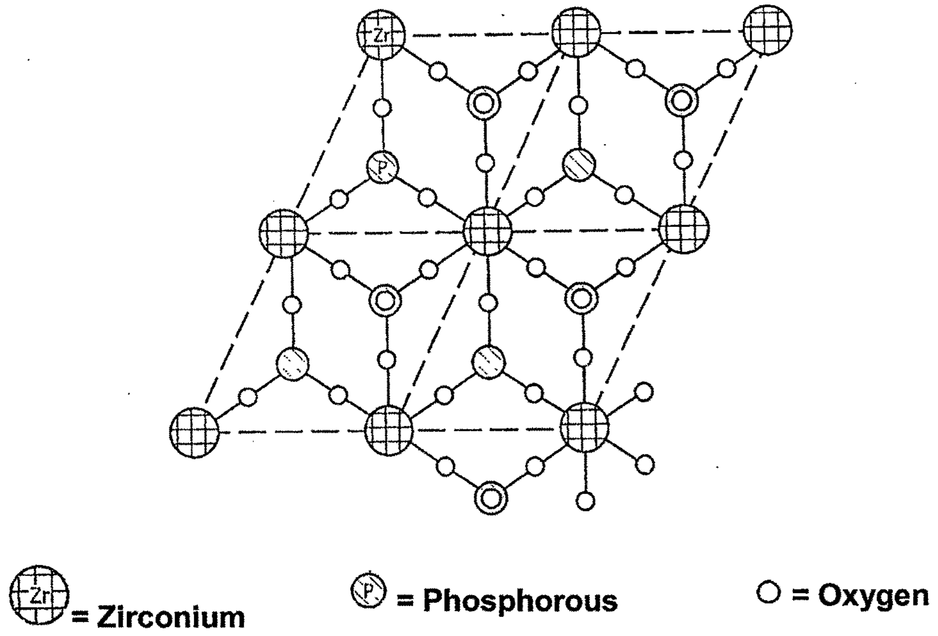


Figure 1.g Idealized diagram showing arrangement of Zr and P

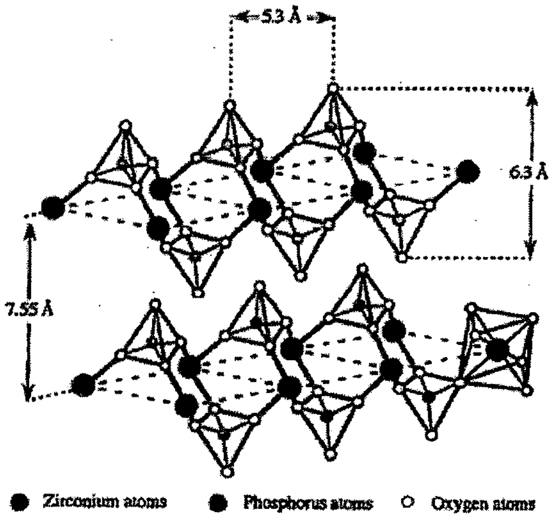


Figure1.h Schematic diagram of the arrangement of two adjacent macroanions in α-ZrP[26].

Zirconium phosphate, the most extensively studied tma salt of the crystalline type can be prepared as fibrous, layered or as three-dimensional structures [17]. The layered acid salts, in turn, may be obtained in at least two different modifications, usually known as α-ZrP and γ-ZrP having the formula $Zr(HPO_4)_2.\ H_2O$ and $Zr(PO_4)(H_2PO_4).2H_2O$ respectively [27]. The structure of the α-ZrP (figure 1.i) arises from the ABAB stacking of layers, each of which is formed by zirconium atoms lying in a nearly ideal plane and sandwiched between O_3POH groups, with the exchangeable proton pointing into the interlayer region as P–OH [28]. The interlayer distance is 0.76 nm, the free area surrounding each P–OH group is ~0.24 nm^2 and there are 6.64 mmol of exchangeable proton per gram. The layers of the γ-ZrP are made up of zirconium atoms lying in two parallel ideal planes and bridged by PO_4 groups, while $O_2P(OH)_2$ groups are directed towards the interlayer region [29,30]. The layers in the γ-ZrP are thus thicker (0.92 nm) than those in α-ZrP (0.64 nm), and the OH groups bound to the same phosphorous atoms have different acidities. The interlayer distance is 1.22 nm and the free area surrounding each $P(OH)_2$ group is ~0.33 nm^2, with an ion exchange capacity of 6.27 mmol/g. A new phase of zirconium phosphate known as τ-ZrP has been reported, having composition identical to α-ZrP [31].

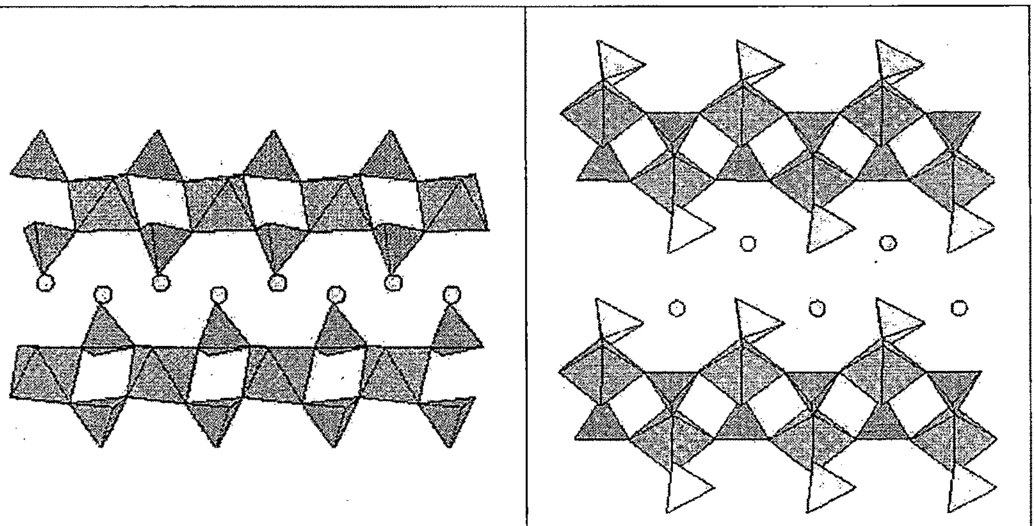
After α-ZrP, α-TiP is the most widely investigated α material. It has been obtained independently in various laboratories and structural aspects investigated [19, 32]. Since the length of the Ti – O bond is shorter than that of the Zr – O bond, the distance between fixed charges in the planar macroanion $[Ti(PO_4)_2]_n^{2n-}$ is shorter than in $[Zr(PO_4)_2]_n^{2n-}$. The unit cell dimensions are, $a = 8.631 \pm 0.001$ Å; $b = 5.002 \pm 0.001$ Å; $c = 16.176 \pm 0.002$ Å; and $\beta = 110.20 \pm 0.01°$.

Owing to its smaller unit cell, the dimensions of the windows connecting the cavities in α-TiP are correspondingly smaller and the density of the fixed charges higher, than in α-ZrP. Owing to its high density of fixed charges, α-TiP tends to behave as a rigid layered exchanger and therefore it possesses more marked ion sieve properties than does α-ZrP [33].

The insoluble acid salts of tetravalent metals can be obtained with different layered structures, usually known as γ-structure. After γ-$Zr(HPO_4)_2 \cdot 2H_2O$, first obtained by Clearfield [34], another compound with formula $Ti(HPO_4)_2 \cdot 2H_2O$ and showing marked analogies with γ-ZrP, was prepared by Alluli et al [35].

Although the γ structure is as yet unknown, some indirect information has been obtained [36] as follows: both γ-ZrP and γ-TiP are able to take up stoichiometric amount of several polar organic molecules and the first d –

values of these γ materials increase with increase in the length of these molecules. Furthermore, there is a discontinuous change of the first d-value during the dehydration of γ-$Zr(HPO_4)_2 \cdot 2H_2O$.(from 12.2 to 9.4 Å) and of γ-$Ti(HPO_4)_2 \cdot 2H_2O$ from (from 11.6 to 9.2 Å). These properties provide strong evidence that the γ structure, like that of α materials, is built up of polymeric macro anion $[M(IV)(XO_4)_2]_n^{2n-}$, with negative charges neutralized by protons, while the hydration water, or other polar molecules can be accommodated between adjacent layers. It can probably be assumed that γ-$Ti(PO_4)(H_2PO_4) \cdot 2H_2O$ is isostructural to γ-$Zr(PO_4)(H_2PO_4) \cdot 2H_2O$. Figure 2 presents the polyhedral representations of layered phosphates in the *a-b* plane.



α -$Ti(HPO_4)_2 \cdot H_2O$
[d_{002}=7.6Å]

γ-$Zr(PO_4)(H_2PO_4)_2 \cdot 2H_2O$
[d_{002}=12.2Å]

Figure 2. Polyhedra representations of layered phosphates in the a-b plane [30]

α-$Ti(HPO_4)_2 \cdot H_2O$: Octahedra represent TiO_6, dark grey tetrahedra represent HPO_4 and spheres represent water molecules.

γ-$Zr(PO_4)(H_2PO_4)_2 \cdot 2H_2O$: Octahedra represent ZrO_6, dark grey tetrahedra represent PO_4 and light grey tetrahedra represent H_2PO_4 and spheres represent water molecules.

References pertaining to the structural aspects of the TMA salts discussed above has been described in literature [19,24,37-40] and references therein.

1.7 PRESENT OBJECTIVES

TMA salts possessing structural hydroxyl groups (the H of the –OH being the exchangeable sites) indicates good potential for application in solid acid catalysis due to presence of surface protons/ acidity. TMA salts with varying water content, composition and crystallinity [24] can be obtained depending on various factors viz. mole ratio of reactants M:X (M= tetravalent metal, X=polyvalent anion), temperature of mixing, mode of mixing (metal salt solution to anion salt solution or vice versa), rate of mixing and pH. Variation in any of these parameters, yields materials with different characteristics. TMA salts can be obtained in both amorphous and crystalline forms. It is observed that both surface area and surface acidity decreases with increasing crystallinity of the material. Hence their acidity can be tailored for a specific application by controlling the crystallinity of the material. The preparation procedure thus affects the structural hydroxyl groups, which is reflected in the performance of TMA salts as solid acid catalysts. The area of study of TMA salts is thus evergreen and much remains to be investigated.

As already indicated earlier in the text, the supports used in heterogenised homogeneous catalysis are either organic or inorganic supports. Both kind of supports (organic/inorganic) have their own advantages and disadvantages, the main one being that though the method of anchoring(ion exchange) is both easy and leads to a stable interaction in organic (polymers) supports as compared to the inorganic (oxides) supports, their major disadvantage is poor heat transfer ability leading to degradation at comparatively low temperatures. It would be ideal to search for a new material which combines the advantages of both types of supports. The answer to this is inorganic ion exchangers of the class of TMA salts, that can be used to advantage. TMA salts being cation exchangers, homogeneous catalysts (metal ion or metal complexes) can be supported by ion exchange method, besides TMA salts being thermally and chemically stable.

The present thesis deals with synthesis and characterization of advanced materials of the class of "TMA salts" and exploring their possible use in the area of solid acid catalysis and as supports in heterogenised homogeneous catalysis.

1.8 LITERATURE SURVEY ON CATALYTIC ASPECTS OF TMA SALTS

TMA salts in both amorphous and crystalline forms have been extensively explored since early days as ion exchangers and in separation science, due to the high selectivity for certain metal ions [19,24,39-43]. As mentioned earlier in the text, various groups all over the world have been working on these materials. The work carried out in the area of ion exchange and sorption has been on alkali metal ions and other cations [19,24,41], in nuclear technology [19], development of quantitative separation procedures [19], detection and estimation of metal ions in ayurvedic and antacid drugs, multivitamin formulations [34,35,44] and sorption and recovery of metal ions [36,38].

From our laboratory extensive work on the applications of TMA salts as solid acid catalysts in a variety of organic transformations have been reported. These include esterification [45-51], dehydration of alcohols [52,53], hydrolysis of nitriles [54], ketalization of ketones [55] and as supports in heterogenised homogeneous catalysis [56-58].

A wide variety of other reactions such as Friedel Crafts reaction [59] , reverse Prins reaction [60], hydration [61] and oxidative dehydrogenation [62] are also reported.

David Whittaker [63] studied the mechanism of cyclohexanol dehydration through deuterium labeling over amorphous zirconium phosphate and showed it to proceed through a carbocation mechanism. Whittaker [64,65] further continued his studies on other substrates to understand the mechanism of dehydration. Balandin et al [66] were the first to report zirconium phosphate for the dehydration of C_2-C_4 olefins. Malendberg found zirconium phosphate to be a better catalyst for propanol dehydration showing a conversion efficiency of 97% [67].

Alberti et al have reported the use of γ-zirconium phosphate-silica composite for conversion of ethylbenzene to styrene and found that catalytic activity is strongly influenced by the total amount of surface acidic groups present [68]. Zirconium and titanium phosphates in α and γ form have been used as catalyst in the dehydration of fructose and insulin. Complete selectivity and comparable activity on recycling was obtained in their study [69]. Holderich has studied tma salts for applications in amination reactions and reported 100% selectivity to a mixture of 1-octylamine and octane nitrile mixture [70]. He has also reported the effect of synthesis parameters on the formation of dimethyl ethyl amine from ethyl amine and methanol over a zirconium phosphate catalyst [71]. Isomerization of hexane with a initial high isomerization activity on crystalline zirconium phosphate is reported by Roy et al [72]. The gas phase hydration of ethane was studied over various metal phosphates including zirconium phosphate and high activity and selectivity are reported with tin phosphate [73].

Potassium exchanged zirconium phosphate and sulfophenyl phosphonates have also been investigated in condensation reactions for the preparation of pyrroles under solvent free conditions [74].

Cheng et al [75] have reported the catalytic properties of the layered compounds-zirconium phosphate, titanium phosphate, mixed zirconium titanium phosphate, and their organically pillared derivatives-toward methanol conversion. TMA salts have also been explored as supports in heterogenised homogeneous catalysis [76-83].

1.9 AIM AND SCOPE OF THE PRESENT WORK

In the present endeavour, TMA salts, the phosphates and tungstates of tetravalent Zirconium, Titanium and Tin abbreviated as ZrP, TiP, SnP, ZrW, TiW and SnW respectively have been synthesized, characterized and their applications explored as,

(1) **Solid acid catalysts** by studying esterification, Pechmann condensation, Friedel Crafts acylation and Friedel Crafts alkylation as model reactions. Crystalline materials have also been synthesized and characterized in order to see the effect of crystallinity on catalytic performance.

(2) **Supports in heterogenised homogeneous catalysis,** where Ru(III) has been exchanged onto M(IV) Phosphates and tungstates by ion exchange technique to give Ru(III)ZrP, Ru(III)TiP, Ru(III)SnP, Ru(III)ZrW, Ru(III)TiW,

Ru(III)SnW and catalytic activity investigated for oxidation of benzyl alcohol and styrene. Further, Ru(III) has been converted to Ru by treating with hydrogen at 200 °C to give RuZrP, RuTiP, RuSnP, RuZrW, RuTiW, RuSnW. The catalytic activity has been explored for hydrogenation of 1-octene, nitro benzene and cyclohexanone.

Chapter II of the thesis deals with synthesis of M(IV) phosphates(amorphous and crystalline) and tungstates(amorphous) of the class of TMA salts[M(IV)=Zr,Sn,Ti]. The materials have been characterized for elemental analysis(ICP AES), FTIR, X-ray diffraction, surface area(BET method), surface acidity(NH_3 TPD), pore volume and pore size distribution(Hg porosimetry), thermogravimetric analysis (TGA) and scanning electron microscopy(SEM). Since the materials are to be used for catalytic applications in varied environments, chemical resistivity of the materials have been assessed in acids, bases and organic solvent media. Ion exchange capacity also has been determined to assess the protonating ability of the materials.

Chapter III of the thesis deals with the study of catalytic aspects of TMA salts, M(IV) phosphates and M(IV) tungstates, using esterification as a model reaction wherein monoesters ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA) and benzyl acetate (BzA) and diesters dioctylphthalate (DOP), dibutyl phthalate(DBP) and diethyl malonate(DEM) have been synthesized. The catalytic activity of amorphous and crystalline materials as well as M(IV)phosphates and tungstates have been compared and correlated with surface properties of the materials.

Chapter IV of the thesis deals with the study of catalytic aspects of TMA salts, M(IV) phosphates and M(IV) tungstates, using Pechmann condensation as a model reaction wherein coumarin derivatives 4-methyl 7-hydroxycoumarin, 4-methyl 7,8-dihydroxy coumarin and 4-methyl 5,7-dihydroxycoumarin involving condensation of resorcinol, pyrogallol and phloroglucinol respectively with methyl aceto acetate have been synthesized under solvent free conditions. The catalytic activity of amorphous and crystalline materials as well as M(IV)phosphates and tungstates have been compared and correlated with surface properties of the materials.

Chapter V of the thesis deals with the study of catalytic aspects of TMA salts, M(IV) phosphates and M(IV) tungstates, using Friedel Crafts acylation and alkylation as model reactions to synthesise 4-methoxy acetophenone (4 MA),3,4-dimethoxy acetophenone (3,4DMA) and p-benzyl toluene (PBT) involving anisole and veratrole with acetyl chloride (acylating agent) and toluene with benzyl chloride (alkylating agent) respectively under solvent free conditions. The catalytic activity of amorphous and crystalline materials as well as M(IV)phosphates and tungstates have been compared and correlated with surface properties of the materials.

Chapter VI of the thesis deals with the study of application of TMA salts, M(IV) phosphates and M(IV) tungstates, as supports in heterogenised homogeneous catalysis wherein Ru(III) has been supported onto TMA salts by ion exchange method. Ru(III) supported materials have been explored for catalytic oxidation of benzyl alcohol and styrene. Further, Ru(III) has been converted to Ru(0) by reduction with hydrogen and the catalytic activity explored for hydrogenation of 1-octene, nitrobenzene and cyclohexanone.

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