1.1 TOWARDS A WORKABLE DEFINITION

Several substances have the ability to exercise a force on other substances and are able to bring about a transformation in the reactants giving rise to new products without themselves undergoing a chemical change. This force was termed as catalytic force and the transformation brought about by this force was termed “Catalysis” which was introduced by Berzelius as early as 1836.

Ostwald in 1895 applied the principles of thermodynamics to show that a catalyst just modifies the rate at which the chemical transformation takes place (provided it is thermodynamically feasible). A catalyst does not alter the equilibrium concentration of the various species present in a chemical transformation. Catalysis therefore emerges as a kinetic phenomenon, and one can define a catalyst as a substance that alters the rate of a reaction without itself being consumed in it and also without modifying its equilibrium constant.

While it was formerly assumed that the catalyst remained unchanged during the course of the reaction, it is now known that the catalyst is involved in chemical bonding with the reactants during the catalytic process, termed as intermediate which in most cases are highly reactive and difficult to detect.

The basic concept is that a catalyzed reaction involves the transitory adsorption of one or more of the reactants on the surface of the catalyst followed by rearrangement of bonding and desorption of the products. The catalyst does not remain as it is during the reaction. It participates in the reaction at some stage, but this occurs in a cycle and the catalyst is regenerated at the end of every cycle. Often the catalyst undergoes a structural change, or change in the stoichiometry in course of the reaction. But the total quantity of the catalyst remains more or less unchanged.

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 [1].

Apart from accelerating reactions, catalysts have another important property; they can influence the selectivity of chemical reactions. This means that completely different products can be obtained from a given starting material by using different catalyst systems. Industrially, this targeted reaction control is often even more important than the catalytic activity. A good catalyst is one which not only produces selective products but also does not undergo deactivation quickly. There are various reasons for deactivation, for example, the catalyst may restructure as a consequence of selective adsorption of impurities from the reactant stream, carbon may be deposited and thus suitable additives must be incorporated to resist these changes on the catalyst surface.

Studying catalysis is an academically valuable exercise and clearly demonstrates the essential unity of science and technology. An understanding of the phenomenon of catalysis requires some familiarity with all three classical branches of chemistry as well as the fundamental concepts of chemical engineering. The catalysts used are mostly inorganic or organometallic compounds while the reactions carried out using the developed catalyst are organic transformations. Hence a catalyst chemist must be familiar with inorganic chemistry, coordination chemistry, 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 [1].

1.2 CATALYST DEVELOPMENT AND COMMERCIALIZATION

Catalysis provides the chemist and the technologist with a valuable tool for developing existing industries on a more economic and sound footing, besides discovering new industrial processes. It is estimated that over 80% of the existing chemical processes are catalytic, and of the newly developed processes, 90% are catalytic based. Technological advances in chemical, petrochemical, oil processing, food and many other industries, involve the application of catalysts. Catalysts not only reduce the cost of production but are directed primarily at improving the quality of products. The answer to some problems of atmospheric pollution is also sought through catalysis. Catalysts play an important role in purifying waste gases and reducing pollution. Obviously, the importance of catalysis, both fundamental and applied, in the economic and industrial growth of a country cannot be overestimated [2].

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. Thus, 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 [3]**.**

Catalysts have been successfully used in the chemical industry for more than 100 years, examples being the synthesis of sulfuric acid, the conversion of ammonia to nitric acid, and catalytic hydrogenation. Later developments include new highly selective multi component oxide and metallic catalysts, zeolites, and the introduction of homogeneous transition metal complexes in the chemical industry. This was supplemented by new high-performance techniques for probing catalysts and elucidating the mechanisms of heterogeneous and homogenous catalysis [4]. A brief historical survey given in Table 1.1 shows the development of catalysis linked to the history of industrial chemistry.

Table 1.1 *History of Industrial catalytic processes [4]*

Catalytic reaction	Catalyst	Discoverer or company/ year
Sulphuric acid (lead- chamber process)	NO_x	Désormes, Clement, 1806
Chlorine production by HCl oxidation	$CuSO_4$	Deacon, 1867
Sulfuric acid (contact process)	Pt, V_2O_5	Winkler, 1875; Knietsch, 1888
Nitric acid by NH_3 oxidation	Pt/Rh nets	Ostwald, 1906
Fat hardening	Ni	Normann, 1907
Ammonia synthesis from N_2, H_2	Fe	Mittasch, Haber, Bosch, 1908
Hydrogenation of coal to hydrocarbons	Fe, Mo, Sn	Bergius, 1913; Pier, 1927
Oxidation of benzene, naphthalene to MSA or PSA	V_2O_5	Weiss, Downs, 1920
Methanol synthesis from CO/H_2	ZnO/Cr_2O_3	Mittasch, 1923
Hydrocarbons from CO/H_2	Fe, Co, Ni	Fischer, Tropsch, 1925
Oxidation of ethylene to ethylene oxide	Ag	Lefort, 1930
Alkylation of olefins with isobutene to gasoline	$AlCl_3$	Ipatieff, Pines, 1932
Cracking of hydrocarbons	Al_2O_3/SiO_2	Houdry, 1937
Hydroformylation of ethylene to Propanal	Co	Roelen, 1938 (Ruhrchemie)
Cracking in a fluidized bed	aluminosilicates	Lewis, Gilliland, 1939
Ethylene polymerization, low-pressure	Ti compounds	Ziegler, Natta, 1954
Oxidation of ethylene to acetaldehyde	Pd/Cu chlorides	Hafner, Smidt (Wacker)
Ammoxidation of propene to Acrylonitrile	Bi/Mo	Idol, 1959 (SOHIO process)
Olefin metathesis	Re, W, Mo	Banks, Bailey, 1964
Hydrogenation, isomerization, Hydroformylation	Rh-, Ru complexes	Wilkinson, 1964
Asymmetric hydrogenation	Rh/chiral phosphine	Knowles, 1974; l-Dopa (Monsanto)
Three-way catalyst	Pt, Rh/monolith	General Motors, Ford, 1974
Methanol conversion to Hydrocarbons	Zeolites	Mobil Chemical Co., 1975
α- olefines from ethylene	Ni/chelate Phosphine	Shell (SHOP process) 1977
Sharpless oxidation, epoxidation	Ti/ROOH/tartrate	May & Baker, Upjohn, ARCO, 1981
Selective oxidations with H_2O_2	titanium zeolite (TS-1)	Enichem, 1983
Hydroformylation	Rh/phosphine	Rhône-Poulenc/Ruhrchemie, 1984
Polymerization of olefins	zirconocene/MAO	Sinn, Kaminsky, 1985
Selective catalytic reduction SCR (power plants)	V, W, Ti oxides/ Monolith	1986
Acetic acid	Ir / I^- / Ru	“Cativa”-process, BP Chemicals, 1996

For the successful development of a practical catalyst, the following infrastructural facilities are essential:

Basic Research provides a thorough understanding of the catalyst science through modern scientific tools and techniques. Basic Research generates data leading to the understanding of the catalyst phenomena, kinetics and mechanism of catalytic reactions and other fundamental aspects. The literature available in the relevant fields provides the starting point, as also the guidelines for planning the working program. The data generated in the laboratory are used in identifying the catalyst for a particular reaction mechanism, studying the phenomena associated with its deactivation, which help to predict the performance, life and selectivity of the catalyst in actual use.

Applied Research leads to the development of the “real” catalyst and optimization of the production through pilot scale trial production and evaluation facilities. Applied research in catalysis is based on two distinct types of activities: the first, related to developmental research aimed at the formulation of practical catalysts, and the other related to operational research involving catalyst application techniques in the industry.

Developmental Research aims at the formulation of a practical catalyst on a bench scale level, and its commercial rationalization through pilot scale investigation and standardization. The developmental research is carried out with close interaction and cooperation of various disciplines of science, technology and engineering. The first step in this direction is catalyst preparation after ascertaining the probable combination of active components, carriers, promoters etc. Catalyst preparation involves ways and means of compounding the formulation and its activation. There may be several possible routes to arrive at the desired chemical composition of the catalyst, but its physical and physico-chemical properties and hence the catalytic activities may differ widely. Judicious selection of the method of formulation of a catalyst through bench scale experimentation constitutes the major activity in the first step of developmental research.

Efficient functioning of modern chemical plants depends, to a great extent, on performance, life and stability of the catalyst used. High activity, selectivity, good mechanical strength, good thermal stability and resistance to poisons are the prime requisites of an industrial catalyst. In addition, it should withstand plant instabilities, and abnormal operating conditions. It is also essential to avoid a sudden failure of the catalyst in a plant which can cause a heavy loss of production. So, a commercial catalyst formulation should have the following essential features:

Optimum activity: to achieve a close approach to equilibrium with minimum catalyst volume and under economic operating conditions.

Sufficient mechanical strength and good thermal stability: to withstand handling and charging operations as well as the cycle of stress and strain involved in plant operation including shut-downs and start-ups.

Stable activity: to sustain satisfactory performance for a reasonable period of time.

Sufficient resistance: to normal level of poisons present in the feed.

The above qualities of a catalyst depend on certain essential factors like surface chemical composition, concentration and distribution of active sites, and structure and textural stability of the catalyst support or matrix. A catalyst cannot work in isolation in an industrial reactor as its efficiency depends, to a great extent, on the environment in which it is operating. This, in turn, is greatly influenced by reaction conditions, reactor design and mode of operation. Optimization of all these factors is essential for the efficient performance of a catalyst.

Commercial Production of a catalyst recipe is taken up on the basis of the procedures standardized during pilot trial production. During commercial production of a catalyst, the active involvement of the following disciplines is essential.

- Process design and engineering: to establish efficient facilities for catalyst production and catalyst improvements.
- Plant operation and maintenance: to ensure the regular production of catalyst.
- Quality control of catalyst at different stages of production.
- Commercial strategies to establish linkages with customers.

1.3 CATALYSIS CONCEPTS AND TERMINOLOGIES

The suitability of a catalyst for an industrial process depends mainly on the following properties such as Activity, Selectivity, Stability (deactivation behavior) and Environment compatibility [4].

Activity

It can be defined as the rate at which the catalyst causes the reaction to proceed to equilibrium. Active sites 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. Activity is a measure of how fast one or more reactions proceed in the presence of the catalyst. Activity can be defined in terms of kinetics or from a more practically oriented viewpoint. In a formal kinetic treatment, it is appropriate to measure reaction rates in the temperature and concentration ranges that will be present in the reactor. There are three ways of expressing catalyst activity: Reaction rate (r), Rate constant (k) and Activation energy (E_a).

Reaction rate (r)

The reaction rate (r) is calculated as the rate of change of the amount of reactant molecules n_A of reactant A with time relative to the reaction volume or the mass of catalyst:

$$r = \frac{Converted\ amount\ of\ substance\ of\ a\ reactant}{Volume\ or\ catalyst\ mass \times time} \left(mol\ L^{-1}\mathrm{h}^{-1}\ or\ mol\ kg^{-1}\mathrm{h}^{-1}\right) \qquad \textbf{(Eq. 1.1)}$$

Rate constant (k)

Kinetic activities are derived from the fundamental rate laws. For a simple irreversible reaction A ⟶ P:

$$\frac{dn_A}{dt} = kVf(c_A) \qquad \textbf{(Eq. 1.2)}$$

Where, k = rate constant, $f(c_A)$ = concentration term that can exhibit a first or higher order dependence on adsorption equilibria.

Activation energy (E_a)

The effect of a catalyst is always to reduce the activation energy (enthalpy) of a reaction. If the temperature dependence of rate constant (k) is given by the Arrhenius equation (1.3), then the implication is that Ea is always reduced and A remains more or less unchanged.

$$k = k_0 e^{-\left(\frac{Ea}{RT}\right)} \qquad \textbf{(Eq. 1.3)}$$

Where, k = rate constant, E_a = activation energy, k_0 = pre-exponential factor and R = gas constant.

Empirical rate equations are obtained by measuring reaction rates at various concentrations and temperatures. If, however, different catalysts are to be compared for a given reaction, the use of constant concentration and temperature conditions is often difficult because each catalyst requires its own optimal conditions. In this case it is appropriate to use the initial reaction rates r_o obtained by extrapolation to the start of the reaction.

For comparative measurements following activity measures are used:

A given constant conversion is expressed by space velocity.

$$Space\ velocity = \frac{V_0}{m_{cat}}\ (m^3\ kg^{-1}\ s^{-1}) \qquad \textbf{(Eq. 1.4)}$$

Where V_0 = volume flow rate and m_{cat} = relative to the catalyst mass. If we replace the catalyst mass in equation 1.4 with the catalyst volume, then we see that the space velocity is proportional to the reciprocal of the residence time. For conversion under constant reaction conditions, since catalysts are often investigated in continuously operated test reactors, in which the conversions attained at constant space velocity are compared, the conversion X_A is the ratio of the amount of reactant $A(n_1A_0)$ that has reacted to the amount that was introduced into the reactor. For a batch reactor:

$$X_A\ =\ [(n_{A,0}\ -\ n_A)\ /\ n_{A,O}]\ (mol/mol\ or\ \%) \qquad \textbf{(Eq. 1.5)}$$

Often the performance of a reactor is given relative to the catalyst mass or volume, so that reactors of different size or construction can be compared with one another. This quantity is known as the space time yield (STY):

$$STY = \frac{Desired\ product\ quantity}{Catalyst\ volume\ \times time}\ (mol\ L^{-1}h^{-1}) \qquad \textbf{(Eq. 1.6)}$$

Temperature required for a given conversion is another method of comparing catalysts. The best catalyst is the one that gives the desired conversion at a lower temperature. This method cannot however, be recommended since the kinetics are often different at higher temperature, making misinterpretations likely. This method is better suited for carrying out deactivation measurements on catalysts in pilot plants.

Catalysis is a kinetic phenomenon. The speed of a catalyzed reaction is often designated by the parameter called “turn over number” which denotes the number of reactant molecules that are converted on an active site or on a unit catalyst surface area per second at a given temperature, pressure and concentration of reactants and products. Since the catalytic reaction occurs at specific sites on solid surfaces, the rate of catalytic reaction can be increased by using catalysts with very high surface area. This could be achieved by dispersing the active species and therefore a parameter termed **‘catalyst dispersion’** defined as the number of surface atoms per total number of atoms is important which can assume any value from 1 (entire surface area active sites) to approximately 0.01. The catalyst particle sizes may vary between 10-500Å. This dispersed system must maintain structural and chemical stability for thousands of hours under the conditions of high temperature (400-900K) and high pressure (1-10^2 atm). The design of new and stable, catalysts which resist chemical attrition and sintering of the small particles is a constant concern of the catalyst scientist.

The common terminologies used to describe the efficiency of a catalyst in terms of rate of conversion are described as follows:

- **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.
- **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.
- **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 turnover rate.

Selectivity

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

The selectivity S_p of a reaction is the fraction of the starting material that is converted to the desired product P. It is expressed by the ratio of the amount of desired product to the reacted quantity of a reaction partner A and therefore gives information about the course of the reaction. In addition to the desired reaction, parallel and sequential reactions can also occur (Figure 1.1).

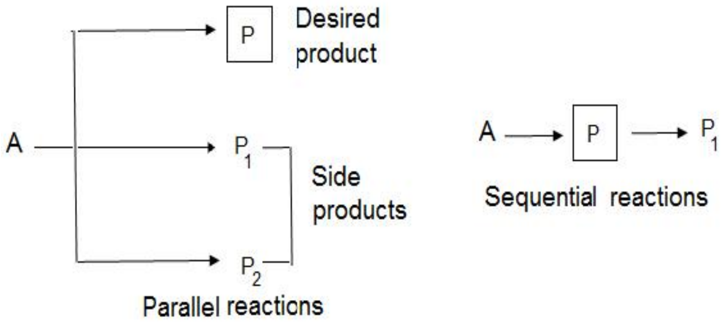


Figure 1.1 *Parallel and sequential reactions*

Since this quantity compares starting materials and products, the stoichiometric coefficients of the reactants must be taken into account, which gives rise to the following equation:

$$Sp = \frac{n_p/\upsilon_p}{(n_{A,0}-n_A)/|\upsilon_A|} = \frac{n_p|\upsilon_A|}{(n_{A,o}-n_A)\upsilon_p}\,(mol/mol\ or\ \%) \qquad \textbf{(Eq. 1.7)}$$

In comparative selectivity studies, the reaction conditions of temperature and conversion or space velocity must, of course, be kept constant. If the reaction is independent of the stoichiometry, then the selectivity $S_P = 1$. The selectivity is of great importance in industrial catalysis.

Stability

The chemical, thermal, and mechanical stability of a catalyst determines its lifetime in industrial reactors. Catalyst stability is influenced by numerous factors, including decomposition, coking, and poisoning. Catalyst deactivation can be followed by measuring activity or selectivity as a function of time. Catalysts that lose activity during a process can often be regenerated before they ultimately have to be replaced. The total catalyst lifetime is of crucial importance for the economics of a process. Today the efficient use of raw materials and energy is of major importance, and it is preferable to optimize existing processes than to develop new ones. For various reasons, the target quantities should be given the following order of priority: Selectivity >Stability > Activity

The following are the terminologies recognized for catalyst deactivation [1].

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 centers. 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 centers.

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 mesopores of the catalyst.

Thermal degradation – It is common in case of supported metal catalyst systems or with oxides of high 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.

Environmental compatibility

Catalytic processes should produce zero or minimum emission with potential environmental hazards. Some popular terminologies used in the current scenario, to define process environmental compatibility [3] include:

E-factor: Indicates the amount of waste produced per kilogram of the product. E-factor for various segments of chemical industry is presented in Table 1.2.

Table 1.2 *E-factor for various segments of chemical industry.*

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.

$Environmental\ Quotient\ (EQ) = (E\_factor \times Unfriendliness\ QQuotient, Q)$ ***(Eq. 1.8)***

(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.

$Atom\ Efficieny = Weight\ of\ desired\ product/\sum weight\ of\ all\ products$ ***(Eq. 1.9)***

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.

1.4 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 as follows.

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)

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.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is 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 catalyst.

Energy-dispersive X-ray spectroscopy (EDX)

This analytical technique is used for both identification of an element as well as to have a rough estimate of the composition of the materials. EDX is used in coordination with and as supportive analysis with ICP-AES which is more accurate compared to EDX.

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.

Mechanical properties

Mechanical properties of a catalyst are 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 1.3.

Table 1.3 *ASTM procedures for catalyst characterization [5].*

Properties	**ASTM No.**
Surface area of catalyst	D 3663
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

1.5 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 waste. This new approach is popularly known as Green Chemistry and involves the synthesis, processing and use of chemicals so as 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. Today, green chemistry is a frontier area of research and is receiving considerable attention.

Green chemistry

Green chemistry focuses on the design, manufacture, and use of chemicals and chemical processes that have little or no pollution potential or environmental risk, and processes that are economically and technologically feasible, thus providing the best opportunity for chemists, manufacturers, and processors to use chemicals safely and to carry out their work under safe conditions. The basic idea of green chemistry is to increase production efficiency through atom economy, and at the same time eliminate or at least minimize wastes and emissions at their source, rather than treat them at the end of the process, after they have been generated.

Green chemistry principles

Twelve principles [6] outlined below, provide a significant guideline in dealing with the concept of green chemistry.

I. It is better to prevent waste than to treat or clean up waste after it is generated.
II. Synthetic methods should be designed to maximize the utility of all materials used in the process, in the conversion of 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. Catalysts (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.

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

Green chemistry and catalysis

Catalysis provides an important opportunity to achieve the goals of green chemistry. Both, greener catalytic processes and catalytic processes for greener products, must play key roles in green chemistry. Asymmetric catalysis, biocatalysis, heterogeneous catalysis, environmental catalysis, shape selective catalysis, phase transfer catalysis and solid acid catalysis are just a few examples that have a direct and significant impact on accomplishing the goals of green chemistry. Amongst the various catalytic systems used, solid acid catalysts are making a huge impact.

1.6 SOLID ACID CATALYSTS - AN ALTERNATE APPROACH TO LIQUID ACID CATALYSTS

Liquid acids such as H_2SO_4, HF, and H_3PO_4 have been extensively used as catalysts in a variety of organic transformations for long. Though they are very effective, liquid acid catalysts are cited as potential environmentally hazardous chemicals and are becoming a major area of concern mainly due to operational difficulties such as toxicity, corrosiveness, effluent disposal, product separation, storage and handling. Owing to increasing environmental awareness and a quest for zero emission technologies, much attention is focused on developing alternatives to these existing acids. Solid acids are safe alternatives for conventional liquid acid catalysts, used in synthetic organic chemistry in petroleum refineries, fine chemical synthesis, pharmaceuticals etc [7].

In general terms, a solid acid 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. Though they differ in structure from liquid acids, solid acid catalysts work on the same principles.

The ability to lend protons makes solid acids valuable as catalysts. Protons are often released from 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 [8].

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. The main characteristic of solid acids, as compared to liquid acids, is that solid acids encompasses different population of sites, differing in their nature and strength (weak acid and strong acid sites) and hence depending on the reaction conditions, the same catalyst can be active for one reaction and inactive for another [9]. 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. Several review articles have been published, dealing with the use of solid acid catalysts for the preparation of speciality and fine chemicals [10-12].

Advantages of solid acid catalysts

- 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.
- They are very effective and some of them are known to exceed the acidity of concentrated H_2SO_4. Besides, they hold their acidity internally and thus easy to handle and also reaction vessels or reactors are not corroded.
- They can allay concerns about safety and environmentally hazardous emissions as they are nontoxic and nonvolatile.
- They possess high catalytic activity and selectivity.
- Being heterogeneous in nature, separation from reaction mixture is easy and the catalyst can be regenerated and reused.
- Problems associated with the disposal of used solid acids are less compared to the disposal of liquid acids that require much money and efforts, for post use treatment and effluent neutralization.

1.7 SOME IMPORTANT SOLID ACID CATALYSTS

A drive for clean technology associated with the problems encountered while using the liquid acids has led to the development of a variety of solid acids. Several inorganic materials tested as solid acid catalysts include silica-alumina gels, zeolites, oxides and hydrous oxides, heteropolyacids, clays, solid superacids and TMA salts.

Silica Alumina Gels

Silica-alumina gels have no well defined structures and contain many pores, which range in diameter from few to few hundred angstroms. Further, their amorphous nature makes them less than ideal catalysts. These compounds tend to lose their activity due to clogging of pores. In addition, because of their irregular structure, protons are unevenly distributed and are therefore difficult to control catalysis precisely. Silica gels were replaced by zeolites in mid 1960's.

Zeolites

Zeolites are crystalline solids with three dimensional frame work, containing micropores of uniform size throughout the structure. They are formed by the corner sharing of $(SiO_4)^{4-}$ and $(AlO_4)^{5-}$ tetrahedra. Due to the excess negative charge on the tetrahedron, a counter ion is required to neutralize the charge. When this counter ion used is a proton, the material behaves as a solid acid (Bronsted acidity). If the zeolite is heated, water may then be eliminated from the Bronsted sites leaving aluminum atoms coordinated to only three oxygen atoms. These will act as Lewis acids [13]. Zeolites have found widespread application as solid acid catalysts in petroleum industries [14]. The acid strength of the protons in some zeolites can be very high, quite often being 100 % stronger than H_2SO_4 and hence the H-zeolite makes excellent solid acid catalysts [15]. However, zeolites are unstable in acid media, have low aberration resistance and undergo rapid deactivation due to plugging of the pores.

Oxides and Hydrous Oxides

In oxide based solid acids, protons balance net negative charges produced by the replacement of a high valent cation with one of lower valence or by the attachment of an anion to the surface of a neutral oxide support. These protons are responsible for acidity. They include oxide and hydrous oxides of Zr^{4+}, Ti^{4+}, Fe^{3+}, Al^{3+}, Nb^{5+}, Cr^{3+}, Th^{4+}, etc. Of the hydrous oxides, zirconia has received much attention as a solid acid catalyst [16]. A mechanism for the generation of acid sites by mixing two oxides has been proposed by Tanabe [17]. They suggest that the acidity generation is caused by excess of a negative or positive charge in model structure of a binary oxide related to the coordination number of a positive and negative element. $Zr(OH)_4$ and $Ti(OH)_4$ is synthesized by traditional sol gel method. Obtaining high acid strength comparable to sulfuric acid, halides, or oxy halides in these catalysts remains a challenge due to the smaller electronegativity difference in metal-oxygen bond compared to the metal halide bonds [18].

Solid superacids

Solid acids with low surface acidity could be converted to solid acids with high surface acidity. Such catalysts are known as solid superacids. Solid super acids of oxides and hydrous oxides are prepared by introducing sulphate ion (sulphation). Sulphation is carried out by washing hydrous ZrO_2 at room temperature thoroughly with $H_2SO_4/(NH_4)_2SO_4$ or passing H_2SO_4 (SO_4^{2-}) through a packed column of ZrO_2 or immersing ZrO_2 into H_2SO_4, stirring and filtering. Though different methods are used, enough H_2SO_4 should be added to form a monolayer. These processes lead to adsorption of sulphate ions on ZrO_2. Finally, the resultant material is calcined at >500°C to remove excess H_2SO_4. Some get firmly grafted on surface- introducing acidity. The solids consist mainly of the metal dioxides with sulphate ions coordinated to the metal ions on the surface. They have the general formula $S0_4^{2-}/M_xO_y$ (M = Zr, Ti) exhibiting acidity higher than 100% H_2SO_4. They can be easily prepared, are stable at elevated temperatures and can be easily regenerated. They have been extensively used for a range of important organic transformations such as isomerization, alkylation, acylation, esterification, etherification, oligomerization, oxidation [19-25] etc. The main limitation of these catalysts is, they get easily deactivated by loosing the sulfate ions.

Heteropoly acids

Heteropoly acids (HPAs) offer appealing characteristics as solid acid catalysts in many acid-catalyzed reactions [26]. Various types of heteropoly compounds [27] are known, but the most popular is based on Keggin structure corresponding to the formula $[XM_{12}O_{40}]^{n-}$, M being a transition element (usually Mo or W) and X a hetero atom (P, Si, As, Ge etc.). It displays a tetrahedral symmetry based on a central XO_4 tetrahedron, surrounded by twelve MO_6 octahedra arranged in four groups of M_3O_{13} of three edge-bridged octahedra. The central atom is the important factor in determining the acid strength and the acidity is related to the total charge on the anion.

Heteropoly acids (HPAs) have proved to be the alternative for traditional acid catalysts due to both strong acidity and appropriate redox properties. The major disadvantage of HPAs, as catalyst lies in their low thermal stability, low surface area (1-10m^2/g) and separation problems from reaction mixture. HPAs can be made eco-friendly, insoluble solid acids, with high thermal stability and high surface area by supporting them onto suitable supports. The support provides an opportunity for HPAs to be dispersed over a large surface area which increases catalytic activity [28]. In recent years alternate to existing solid acid catalysts, development of metal oxide supported catalysts, such as, zirconia supported heteropoly acid catalysts have gained importance, since these provide advantages over others like higher thermal stability, cost effective and eco-friendly systems for applications in large-scale productions.

Clays

Clays are some of the most abundant, porous and benign materials on the earth. Clays are complex layered oxides essentially comprising of parallel tetrahedral silicate and octahedral aluminate sheets [29]. For charge compensation, various cations (especially Na^+ and Ca^{2+}), may occupy the interlayer gallery. When these cations are replaced by hydrated protons in the form of H_3O^+, acidity is introduced. They have been used in a variety of reactions including Friedel-Crafts alkylation, acylation and production of methyl tertiary butyl ether (MTBE).

1.8 TETRAVALENT METAL ACID SALTS AS SOLID ACID CATALYSTS

Introduction

"Tetravalent Metal Acid (TMA) Salts" have been researched since the last 50 years, and have emerged as promising advanced materials owing to their good thermal stability, chemical resistivity, resistance towards ionizing radiations, and found important applications in the area of ion exchange, catalysis and solid state proton conduction. An extensive literature on TMA salts exists today, which have been reviewed and detailed in four books.

- Varshney K G and Khan A M, 1991, *Inorganic Ion Exchangers in Chemical Analysis*, (Eds.) Qureshi M and Varshney K G, CRC Press, Boca Raton, Florida.

- Clearfield A, 1982, *Inorganic Ion Exchange Materials*, CRC Press, Boca Raton, Florida.
- Clearfield A, Nancollas G H and Blessing R H, 1973, *Ion Exchange and Solvent Extraction*, (Eds.) Marinsky J H and Marcus Y, Marcel Dekker, Vol 5, New York.
- 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), Dr. W. H. J. Hogarth (Australia), 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).

Structural aspects of TMA Salts

Almost all the possible combinations of tetravalent metals (such as Zr, Ti, Ce, Sn, Th etc) with polybasic acids (containing P, W, Mo, As, Sb etc) have been examined. Earlier work was carried out with amorphous materials. Much of the earlier work was focused on zirconium phosphate (ZP) [30]. Extensive information on the structure of ZP has been reviewed by C B Amphlett [31]. De Boers reported the structure of ZP as $Zr(HPO_4)_2$, but other workers suggested it to be $[ZrO(H_2PO_4)_2]$. Bluementhal (Figure 1.2a), Paterson (Figure 1.2b), Baestle and Pelsmaekers (Figure 1.2c), Nancollas and Pekarek (Figure 1.2d) and (Figure 1.2e) proposed the following structural formula for ZP [31]. According to these structures, the H^+ of the structural –OH groups are the exchangeable protons. 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 [32] and in the United Kingdom by C B Amphlett [31].

The first crystalline α-ZP was prepared by Clearfield and Stynes [33]. Structure elucidation was first carried out in 1969 [34]. ZP has a layered structure. Three oxygen atoms of each phosphate, are bonded to three adjacent metal atoms, forming a distorted equilateral triangle [35]. Each zirconium atom is thus octahedrally coordinated by oxygens. An idealized picture of a portion of the layer is given in Figure 1.3. Zirconium phosphate, the most extensively studied TMA salt of the crystalline type can be prepared as fibrous, layered or as three-dimensional structures [35]. The layered acid salts, in turn, may be obtained in at least two different modifications, usually known as α-ZP and γ-ZP having the formula $Zr(HPO_4)_2 . H_2O$ and $Zr(PO_4)(H_2PO_4).2H_2O$ respectively [36].

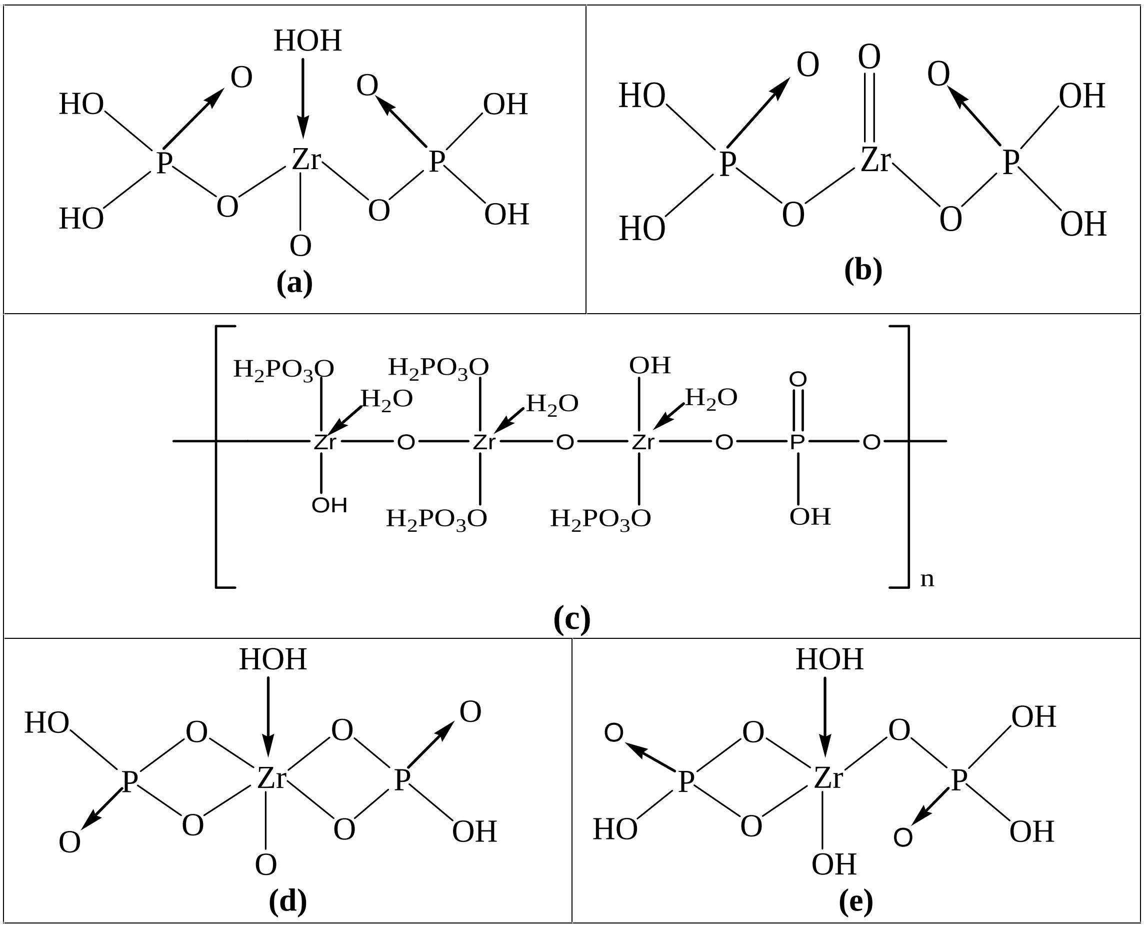


***Figure 1.2** Structures of zirconium phosphate* [31]

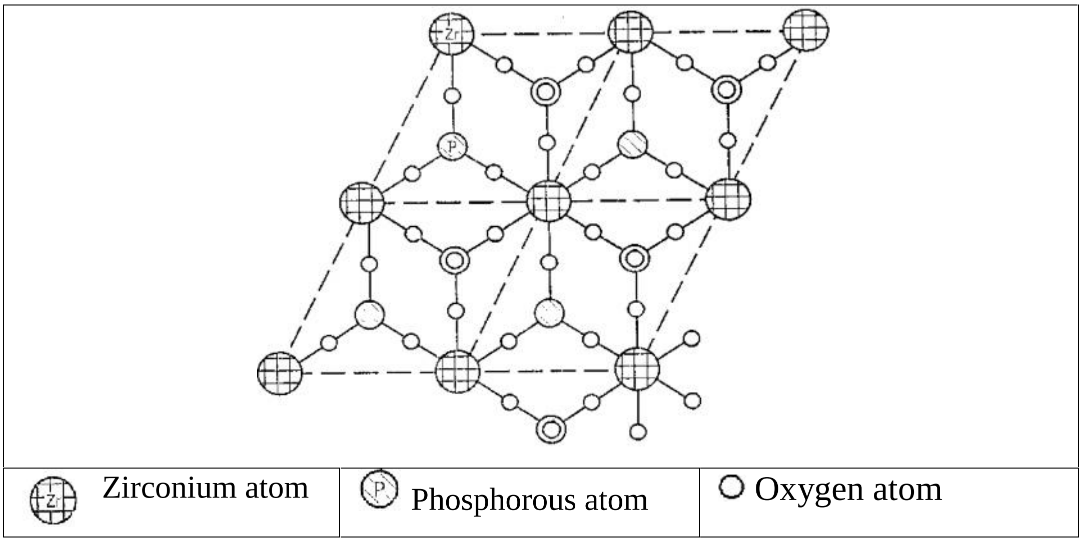
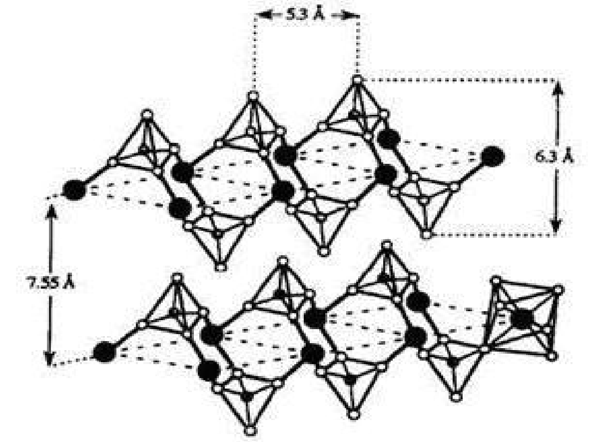


***Figure 1.3** Idealized portion of ZP layer [34]*



● Zirconium atom	◆ Phosphorous atom	○ Oxygen atom

Figure 1.4 *Schematic diagram of the arrangement of two adjacent macroanions in α-ZP [37]*

The structure of the α-ZP (Figure 1.4) 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 [36]. These protons are responsible for ion exchange [38]. The layers of the γ-ZP 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 [39,40]. The layers in the γ-ZP are thus thicker (0.92 nm) than those in α-ZP (0.64 nm), and the –OH groups bound to the same phosphorous atoms have different acidities.

After α-ZP, α-titanium phosphate (α-TP) is the most investigated material. It has been obtained independently in various laboratories and structural aspects investigated [41]. 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 $\beta = 110.20 \pm 0.01^o$.

Owing to its smaller unit cell, the dimensions of the windows connecting the cavities in α-TP are correspondingly smaller and the density of the fixed charges higher, compared to α-ZP. Thus, the steric hindrance to the diffusion of large cations is expected to be higher in α-TP than in α-ZP and the ion exchange rate is slower.

Owing to its high density of fixed charges, α-TP tends to behave as a rigid layered exchanger and therefore it possesses more marked ion sieve properties than does α-ZP. The ion sieve properties of α-TP have been used [42] to effect separations of Cs^+ and K^+ ions from Na^+. Ion exchange equilibrium between α-TP and NaCl-KCl aqueous solution has been investigated by Kobayashi [43] who also considered the possibility of separating of Na^+ and K^+ ions. The insoluble acid salts of tetravalent metals can be obtained with different layered structures, usually known as γ-structure. After γ-$Zr(HPO_4)_2.2H_2O$, first obtained by Clearfield [44], another compound with formula $Ti(HPO_4)_2.2H_2O$ and showing marked analogies with γ-ZP, was prepared by Alluli et al [45].

Although the γ structure is as yet unknown, some indirect information has been obtained [46]. Both γ-ZP and γ-TP 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-$Zr(HPO_4)_2.2H_2O$ (from 12.2 to 9.4 Å) and of γ-$Ti(HPO_4)_2.2H_2O$ (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-$Ti(PO_4)(H_2PO_4).2H_2O$ is isostructural to γ-$Zr(PO_4)(H_2PO_4).2H_2O$. Extensive information on the chemistry of group IV metal phosphates with α and γ type structures has been compiled in reviews and books [47]. Polyhedral layered phosphates in the *a-b* plane are presented in Figure 1.5.

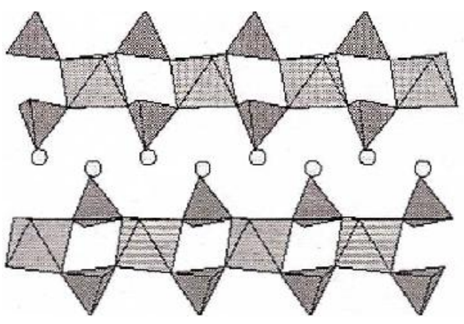
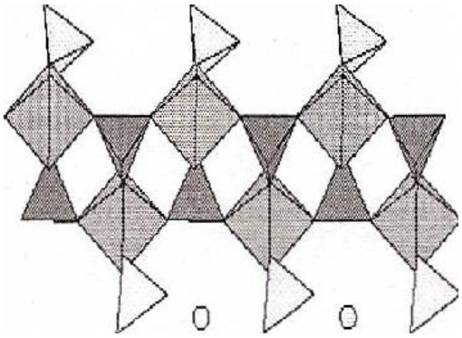
	

Figure 1.5 (a) *α-$Ti(HPO_4)_2.H_2O$ Octahedra represent TiO_6, dark grey tetrahedra represent HPO_4 and spheres represent water molecules.[d_{002}=7.6Å][47]*	***Figure 1.5 (b)*** *γ-$r(PO_4)(H_2PO_4)_2.2H_2O$ Octahedra represent ZrO_6, dark grey tetrahedra represent PO_4 and light grey tetrahedra represent H_2PO_4 and spheres represent water molecules. [d_{002}=12.2Å]*

Salient features of Tetravalent Metal Acid (TMA) salts

- 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.
- The materials possess structural hydroxyl groups, the H^+ of the –OH being the exchangeable sites, due to which the material possesses cation exchange properties.
- TMA salts can be prepared both in amorphous and crystalline forms that exhibit selectivity for certain metal ions.
- The materials possess granular nature and can be obtained in a range of mesh sizes, very suitable for column operations.
- The materials are generally hard and range in physical appearance from totally opaque to transparent.
- TMA salts have shown a great promise in preparative reproducibility and ion exchange behaviour.
- TMA salts exhibit both thermal and chemical stability.

When a tetravalent metal is treated with phosphoric acid/Na salts of phosphoric acid, M – O – P bonds are formed. In this process, a number of hydroxyl groups do not participate in the condensations which are referred to as pendant hydroxyl groups or defective P – OH, H^+ of the P – OH contributing to cation exchange [48]. Due to presence of structural hydroxyl protons in the TMA salts surface acidity is expected, giving rise to solid acid characteristics. Thus, TMA salts indicate good potential for application in solid acid catalysis.

TMA salts with varying water content, composition and crystallinity [38, 49-51] can be synthesized by sol-gel route by varying conditions of synthesis 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. 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.

Acidity in TMA salts is explained based on a synergic effect – to be due to mutual/cooperative interaction between cation and an anion in the TMA salt. Acidity of a cation is related to ion size and charge. Ionic sizes of tetravalent metals are Ti^{4+} (0.74Å), Zr^{4+} (0.86Å) and Sn^{4+} (0.83Å). Ti^{4+} with smallest ionic radius (0.74Å), the positive charge is concentrated in a smaller area compared to Zr^{4+} (0.86Å) and Sn^{4+} (0.83Å), due to which tendency to polarize or severe the –OH bond (structural –OH groups in anionic part of TMA salt) exhibits the order $Ti^{4+} > Sn^{4+} > Zr^{4+}$. The cation exchange capacity (CEC) and hence protonating ability/surface acidity also follows this order. Thus, the size and charge on the cation has an influence on the surface acidity of the materials.

The structural hydroxyl protons are provided from anionic part (PO_4^{3-} or WO_4^{2-}) of the TMA salt. Greater the number of H^+ provided/present in anionic part greater will be the number of H^+ that can be released or available. Thus acidity in TMA salt is a synergic effect.

TMA salts have been used as catalysts in various organic transformations by various groups - Dr. A. Clearfield (USA), Dr. G. Alberti (Italy), Dr. W. Holderich (Germany), Dr. D. Whittaker (UK) and Dr. U. V. Chudasama (The M. S. University of Baroda, India).

An excellent review on the catalytic aspects of TMA salts has been reported by Clearfield and Thakur [52]. Clearfield et al [53,54] investigated cyclohexanol dehydration to cyclohexene using α-zirconium phosphate, and found it to be an extremely selective catalyst with negligible isomerization and dehydrogenation activities (< 0.5%). Frianeza and Clearfield [55] examined catalytic activity of α-titanium phosphate in the above reaction and found it to be a more active catalyst compared to α-zirconium phosphate. Clearfield has also reported the oxidative dehydrogenation of cyclohexene to benzene using zirconium phosphate [56].

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 acid groups [57]. Holderich has reported zirconium phosphate as solid acid catalyst, in amination reactions that exhibit 100 % selectivity for 1-octylamine [58], formation of dimethyl ethyl amine from ethyl amine and methanol [59], and ethylene hydration [60]. David Whittaker [61,62] has studied the mechanism of cyclohexanol dehydration through deuterium labeling over amorphous zirconium phosphate and showed it to proceed through a carbocation mechanism. A wide variety of other organic transformations, such as hydrogenation of alkenes [63], reverse Prins reaction [64], dehydration of cyclohexanol and methylcyclohexanols [65], terpene rearrangements [66], ionic and radical rearrangements of α and β-pinene [67], alkylation of anisole with alcohols (Friedel-Crafts) [68] using TMA salts as catalyst have also been reported by David Whittaker.

Roy et al have reported isomerization of hexane with initial high isomerization activity using crystalline zirconium phosphate [69]. Cheng et al [38] have reported the catalytic properties of zirconium phosphate, titanium phosphate, and their organically pillared derivatives, towards methanol conversion. Sadykov et al have used zirconium phosphate for paraffin isomerization and selective oxidation [70]. The gas phase hydration of ethane was studied over various metal phosphates and high activity and selectivity were reported with tin phosphate [71]. Benvenuti et al [72] have reported use of zirconium and titanium phosphates as catalysts, in the dehydration of fructose and insulin.

A wide variety of organic transformations using TMA salts as solid acid catalysts have been reported from our laboratory. These include esterification [73-81 82], dehydration of alcohols [83,84], hydration of nitriles to amides [85], ketalization of ketones [86] and Pechmann condensation reactions [87].

1.9 AIM AND SCOPE OF THE PRESENT WORK

The current focus towards synthesis of solid acid catalysts (SACs) is that catalytic activity/surface acidity should be high which can be retained for long periods of time with good chemical and thermal stability upto elevated temperatures and which can be regenerated and reused. The answer to these requirements is TMA salts. TMA salts have been discussed in detail in the foregoing pages.

There is currently high interest in engineering mixed materials leading to the formation of new solid-state/lattice structures resulting from cooperative interactions between the two interacting components, where there is a promise of developing new materials with properties not seen in the pure compound giving rise to composite as well as wide range of interesting properties. In this context, materials of the class of TMA salts i.e. compounds containing two different cations and an anion [tetravalent bimetallic acid (TBMA) salts] or two different anions and a cation [tetravalent metal bianionic acid (TMBA) salts] are interesting since they could exhibit improved properties in comparison to their single salt counterparts (TMA salts).

From our laboratory, mixed material of the class of tetravalent bimetallic acid (TBMA) salt - zirconium titanium phosphate (ZTP) has been synthesized by sol gel route in amorphous and crystalline forms. The presence of protons contained in the structural hydroxyl groups of ZTP indicates good potential for application as solid acid catalysts. The potential use of ZTP as solid acid catalyst was explored by studying esterification as a model reaction wherein mono esters such as ethyl acetate, propyl acetate, butyl acetate and benzyl acetate and diesters such as dioctyl phthalate, diethyl malonate and dibutyl phthalate have been synthesized. The study shows, amorphous materials exhibit enhanced catalytic activity compared to crystalline materials and mixed material (ZTP) exhibited enhanced catalytic activity compared to their single salt counterparts [88].

Heteropoly acids (HPAs) are polyoxometallates made up of heteropoly anions having metal–oxygen octahedra as the basic structural unit. Heteropoly acids (HPAs) have proved to be the alternative for traditional acid catalysts due to both strong acidity and appropriate redox properties. The major disadvantage of HPAs, as catalyst lies in their low thermal stability, low surface area (1-10m^2/g) and separation problems from reaction mixture. HPAs can be made eco-friendly, insoluble solid acids, with high thermal stability and high surface area by supporting them onto suitable supports. The support provides an opportunity for HPAs to be dispersed over a large surface area which increases catalytic activity [28]. Acidic or neutral solids, which interact weakly with HPAs such as silica, active carbon and acidic ion-exchange resin, have been reported to be suitable as HPA supports. Recently, zirconia-supported heteropoly acids have attracted much attention as strong solid acid catalysts [89].

At this juncture, it is necessary to classify solid acid catalysts. In the present endeavour, solid acid catalysts are classified into two types.

Type – I: Solid acid catalysts possessing inherent acidity

The term “inherent” can be defined as, a property or character existing as natural or basic part in the constitution of the material. For e.g. TMA salts are solid acid catalysts possessing inherent acidity, since acidity is a natural or basic part in the material.

Type – II: Solid acid catalysts possessing induced acidity

The term “induced” is a process conducted/performed that leads to inducing a property. For e.g. Sulphated zirconia. ZrO_2 possesses negligible acidity. However, acidity can be induced into ZrO_2 by treating it with concentrated sulphuric acid to give sulphated zirconia.

Prompted by good surface acidity as well as thermal and chemical stability of materials of the class of TMA salts and enhanced catalytic activity observed in case of TBMA salts compared to single salts counter parts (TMA salts), it was thought of interest to explore the potential utility of mixed material of the class of Tetravalent Metal Bianionic Acid (TMBA) salts (containing two different anions and a cation) as solid acid catalyst with an aim to enhance surface acidity.

The present study is focused towards synthesis of M(IV) Phosphotungstates [M(IV)PWs], mixed materials of the class of TMBA salts possessing inherent acidity (Type-I catalysts), such as Zr(IV) Phosphotungstate (ZrPW), Ti(IV) Phosphotungstate (TiPW) and Sn(IV) Phosphotungstate (SnPW) by sol-gel routes. Looking to the potential utility of supported HPAs and for a comparative catalyst performance, 12-Tungstophosphoric acid (12-TPA) ($H_3PW_{12}O_{40}$) has been supported onto ZrO_2, TiO_2 and SnO_2 by process of anchoring and calcination, resulting in 12-TPA/ZrO_2, 12-TPA/TiO_2 and 12-TPA/SnO_2 which possess induced acidity (Type-II catalysts) and also possess similar elemental components (i.e. Zr, Ti, Sn, P and W) as the TMBA salts. The catalytic activity/performance of synthesized materials (Type – I and Type – II catalysts) has been compared and correlated with acid properties of the materials towards few organic transformations.

Chapter II of the thesis is entitled as “***Synthesis and characterization of solid acid catalysts possessing inherent and induced acidity***”.

Type – I catalysts possessing inherent acidity [M(IV)PWs of the class of TMBA salts] have been synthesized by sol-gel route.

- Zirconium (IV) Phosphotungstate (ZrPW)
- Titanium (IV) Phosphotungstate (TiPW)
- Tin (IV) Phosphotungstate (SnPW)

Type – II catalysts possessing induced acidity [12-TPA/M(IV)O_2 where, M(IV)=Zr,Sn,Ti] have been synthesized by process of anchoring and calcination.

- 12-TPA/ZrO_2
- 12-TPA/TiO_2
- 12-TPA/SnO_2

The synthesized materials have been subjected to **instrumental methods of characterization** [elemental analysis (ICP-AES), thermal analysis (TGA), spectral analysis (FTIR), X-ray diffraction studies (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)], and **catalyst characterization** [surface area measurements (BET method) and surface acidity (NH_3-TPD method)]. Chemical stability of all the synthesized materials has been assessed in various media (e.g. acids, bases and organic solvents etc) and in the media/environment where catalyst would operate. Further, the protonating ability [in terms of CEC] has been determined for M(IV)PWs (Type – I catalysts).

Chapter III of the thesis is entitled as "***Applicability of inherent and induced solid acid catalysts in the synthesis of monoesters and diesters***". The potential utility of M(IV)PWs (Type-I Inherent SACs) and 12-TPA/M(IV)O_2 (Type-II Induced SACs) has been explored by studying esterification as a model reaction, wherein monoesters ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA), benzyl acetate (BzA) and diesters diethyl malonate (DEM), diethyl succinate (DES), dioctyl phthalate (DOP) and dibutyl phthalate (DBP) have been synthesized. Reaction parameters, reaction time, catalyst amount and mole ratio of the reactants have been optimized. Catalytic performance of Type-I and Type-II catalysts have been compared at optimized condition and correlated with acid properties of the materials. The performance ability of the catalysts have also been assessed for regenerated/ reactivated catalysts. A reaction mechanism has been proposed for solid acid catalyzed esterification reaction.

Chapter IV of the thesis is entitled as "***Applicability of inherent and induced solid acid catalysts in the synthesis of coumarin derivatives via Pechmann condensation***". The potential utility of M(IV)PWs (Type-I Inherent SACs) and 12-TPA/M(IV)O_2 (Type-II Induced SACs) has been explored by studying Pechmann condensation as a model reaction, wherein phenols (resorcinol, pyrogallol, phloroglucinol, hydroquinone and p-nitrophenol) have been treated with methyl acetoacetate to give corresponding coumarin derivatives under solvent free conditions using conventional and MW heating. Reaction parameters, reaction time, reaction temperature, catalyst amount and mole ratio of the reactants have been optimized.

Catalytic performance of Type-I and Type-II catalysts have been compared at optimized condition and correlated with acid properties of the materials. The performance ability of the catalysts have also been assessed for regenerated/ reactivated catalysts. A reaction mechanism has been proposed for solid acid catalyzed synthesis of coumarins via Pechmann condensation.

Chapter V of the thesis is entitled as "***Applicability of inherent and induced solid acid catalysts in Friedel-Crafts reactions***". The potential utility of M(IV)PWs (Type-I Inherent SACs) and 12-TPA/M(IV)O_2 (Type-II Induced SACs) has been explored by studying following organic transformations:

(i) Friedel-Crafts alkylation and acylation wherein benzyl chloride is used as alkylating agent for toluene and acetyl chloride is used as acylating agent for anisole and veratrole.

(ii) Synthesis of anthraquinone derivatives *via* Friedel–Crafts reaction wherein substituted benzenes (toluene, resorcinol, hydroquinone and nitrobenzene) are treated with phthalic anhydride to give corresponding anthraquinone derivatives.

Friedel-Crafts alkylation and acylation and synthesis of anthraquinone derivatives have been carried out under solvent free conditions. For (i) and (ii), reaction parameters, reaction time, reaction temperature, catalyst amount and mole ratio of the reactants have been optimized. Catalytic performance of Type-I and Type-II catalysts have been compared at optimized condition and correlated with acid properties of the materials. The performance ability of the catalysts have also been assessed for regenerated/reactivated catalysts. A reaction mechanism has been proposed for solid acid catalyzed Friedel – Crafts alkylation, acylation and synthesis of anthraquinones.

Chapter VI of the thesis is entitled as "***Applicability of inherent and induced solid acid catalysts for acetalization of carbonyl compounds***". The potential utility of M(IV)PWs (Type-I Inherent SACs) and 12-TPA/M(IV)O_2 (Type-II Induced SACs) has been explored by studying acetal formation as a model reaction wherein, acetalization of carbonyl compounds (benzaldehyde, cyclohexanone, acetophenone and benzophenone) with pentaerythritol (PET) has been performed to yield the corresponding diacetal derivatives. Reaction parameters, reaction time, catalyst amount and mole ratio of the reactants have been optimized. Catalytic performance of

Type-I and Type-II catalysts have been compared at optimized condition and correlated with acid properties of the materials. The performance ability of the catalysts have also been assessed for regenerated/reactivated catalysts. A reaction mechanism has been proposed for solid acid catalyzed acetalization of carbonyl compound with PET.

Chapter VII of the thesis is entitled as "***Conclusions***". The chapter includes a conclusive outline of the work presented in the thesis and objectives achieved.

REFERENCES

1. Hagen J, *Industrial Catalysis: A Practical Approach*, Wiley-VCH, (IInd Edn.) **(2006)**.
2. Chudasama U, *Recent trends in Catalytic Aspects of Tetravalent Metal Acid Salts*, Bull. Cat. Soc. of India 9(2) **(1999)** 132-134.
3. Sivasanker S, Vishwanathan B, Ramaswamy A V, (Eds.) *Catalysis Principles and Applications*, Narosa Publishing House, New Delhi Ch. 17 **(2002)** 215.
4. Sheldon R A, *Atom efficiency and catalysis in organic synthesis*, Pure Appl. Chem. 72(7) **(2000)** 1233-1246.
5. Ramaswamy A V, Vishwanathan B, Sivasanker S, (Eds.) *Catalysis Principles and Applications*, Narosa Publishing House, New Delhi Ch. 4 **(2002)** 54.
6. Sanghi R, Srivastava M M, (Eds) *Green Chemistry Environment Friendly Alternatives*, Narosa Publishing House, New Delhi Ch. 3 **(2003)**.
7. Yadav G D, Murkute A D, *Kinetics of Synthesis of Perfumery Grade p-tert-Butylcyclohexyl acetate over Ion Exchange Resin Catalyst*, Int. J. Chem. React. Eng. 1(1) **(2003)** 1-4.
8. Mukherji S M, Singh S P, *Reaction Mechanism in Organic Chemistry*, McMillan India Ltd., New Delhi **(1976)**.
9. Tanabe K, Anderson J R, Boudart M, (Eds) *Catalysis - Science and Technology*, Springer-Verlag, Berlin **(1981)**.
10. Guido B, *Acid Catalysts in Industrial Hydrocarbon Chemistry*, Chem. Rev. 107 (**2007)** 5366-5410.
11. Klerk A, Nel R, *Phenol Alkylation with 1-Octene on Solid Acid Catalysts*, Ind. Eng. Chem. Res. 46(22) **(2007)** 7066-7072.
12. Giovanni S, Maggi R, *Use of Solid Catalysts in Friedel−Crafts Acylation Reactions*, Chem. Rev. 106(3) **(2006)** 1077-1104.
13. Huheey J E, Keiter E, Keiter R, *Inorganic Chemistry: Principles of Structure and Reactivity*, (4thEds.) Pearson Education (Singapore) Pvt. Ltd. India **(2006)**.
14. Horsley J A, *Producing bulk and fine chemicals using solid acids*, Chem. Tech. 45 **(1997)**.
15. Yoo K S, Srikant G, Panagiotis G, *Enhancement of n-Hexane Cracking Activity over Modified ZSM-12 Zeolites*, Ind. Eng. Chem. Res. 44(13) **(2005)** 4562-4568.

16. Liu X M, Lu G Q, Yan Z F, *Synthesis and Stabilization of Nanocrystalline Zirconia with MSU Mesostructure*, J. Phys. Chem. B. 108(40) **(2004)** 15523-15528.
17. Tanabe K, Misono M, Ono Y, Hattori H, *New Solid Acids and Bases*, Elsevier Science, Amsterdam **(1989)**.
18. Barton D G, Soled L S, Iglesia E, *Solid acid catalysts based on supported tungsten oxides*, Topics in catalysis, 6(1-4) **(1998)** 87-99.
19. Yadav G D, Pujari A A, *Friedel–Crafts acylation using sulfated zirconia catalyst*, Green Chem. 1 **(1999)** 69-74.
20. Thorat T S, Yadav V M, Yadav G D, *Esterification of phthalic anhydride with 2-ethylhexanol by solid superacidic catalysts*, Appl. Catal. A: Gen. 90(2) **(1992)** 73-96.
21. Wali A, Pillai S M, *Cyclodehydration of Some 1,n-Diols Catalysed by Sulfated Zirconia*, J. Chem. Res. (S) **(1999)** 326-327.
22. Yadav G D, Nair J J, *Sulfated zirconia and its modified versions as promising catalysts for industrial processes*, Micro. Meso. Mater. 33(1-3) **(1999)** 1-48.
23. Song X, Sayari A, *Sulfated Zirconia-Based Strong Solid-Acid Catalysts: Recent Progress*, Catal. Rev. Sci. Engg. 38(3) **(1996)** 329-412.
24. Arata K, *Preparation of superacids by metal oxides and their catalytic action*, Mater. Chem. Phys. 26(3-4) **(1990)** 213-237.
25. Yamaguchi T, *Recent progress in solid superacid*, Appl. Catal. 61(1) **(1990)** 1-25.
26. Hu C, Hashimoto T, Okuhara M, Misono M, *Catalysis by Heteropoly Compounds - XXII. Reactions of Esters and Esterification Catalyzed by Heteropolyacids in a Homogeneous Liquid-Phase Effects of the Central Atom of Heteropolyanions having Tungsten as the Addenda Atom*, J. Catal. 143(2) **(1993)** 437-448.
27. Mizuno N, Misomo M, *Heteropolyanions in catalysis*, J. Mol. Catal. 86(1-3) **(1994)** 319-342.
28. Khder A S, *Preparation, characterization and catalytic activity of tin oxide-supported 12-tungstophosphoric acid as a solid catalyst*, Appl. Catal. A: Gen. 343(1-2) **(2008)** 109-116.
29. Pinnavaia T J Interrante L V, Casper L A, Ellis A B, (Eds) *Materials Chemistry: An Emerging Discipline*, Ch.11 **(1995)**.

30. Clearfield A, *Layered Phosphates, Phosphites and Phosphonates of Groups 4 and 14 Metals*, Inorg. Chem. 10 **(1990)** 89-128.
31. Amphlett C B, *Inorganic Ion exchangers*, Elsevier, Amsterdam **(1964)**.
32. Kraus K A, Phillips H O, *Adsorption on Inorganic Materials. I. Cation Exchange Properties of Zirconium Phosphate*[1], J. Am. Chem. Soc. 78(3) **(1956)** 694.
33. Clearfield A, Stynes J, *The preparation of crystalline zirconium phosphate and some observations on its ion exchange behaviour*, J. Inorg. Nucl. Chem. 26(1) **(1964)** 117-129.
34. Clearfield A, Smith G D, *Crystallography and structure of .alpha.-zirconium bis(monohydrogen orthophosphate) monohydrate*, Inorg. Chem. 8(3) **(1969)** 431-436.
35. Clearfield A, *Layered and Three-dimensional phosphates of Tetravalent elements*, Eur. J. Solid State Inorg. Chem. 28 **(1991)** 37-42.
36. Alberti G, Casciola M, Constantino U, Vivani R, *Layered and pillared metal(IV) phosphates and phosphonates,* Adv. Mater. 8(4) **(1996)** 291-303.
37. Slade R C T, Knowels J A, Jones D J, Roziere J, *The isomorphous acid salts* α-$Zr(HPO_4)_2 \cdot H_2O$, α-$Ti(HPO_4)_2 \cdot H_2O$ *and* α-$Zr(HAsO_4)_2 \cdot H_2O$*: Comparative thermochemistry and vibrational spectroscopy*, Solid State Ionics 96(1-2) **(1997)** 9-19.
38. Cheng S, Peng G, Clearfield A, *Decomposition of alcohols over zirconium and titanium phosphates*, Ind. Eng. Chem. Prod. Res. Dev. 23 **(1984)** 219-225.
39. Christensen A N, Andersen E K, Andersen I G K, Alberti G, Nieben M, Lehmann M S, *X-ray powder diffraction study of layer compounds. The crystal structure of* α-$Ti(HPO_4)_2 \cdot H_2O$ *and a proposed structure for* α-$Ti(HPO_4)_2 \cdot (PO_4).2H_2O$, Acta Chem Scan, 44 **(1990)** 865-872.
40. Poojary D M, Shpeizer B, Clearfield A, *X-Ray powder structure and Rietveld refinement of* γ*-zirconium phosphate,* $Zr(PO_4)(H_2PO_4) \cdot 2H_2O$, J. Chem. Soc. Dalton Trans. **(1995)** 111-113.
41. Alberti G, Cardini Galli P, Constantino U, Torracca E, *Crystalline insoluble salts of polybasic metals—I Ion-exchange properties of crystalline titanium phosphate*, J. Inorg. Nucl. Chem. 29(2) **(1967)** 571-578.

42. Alberti G, Giammari G, Grassini-strazza G, *Chromatographic behaviour of inorganic ions on crystalline titanium phosphate or zirconium phosphate thin layers*, J. Chromato. 28 **(1967)** 118-123.
43. Kobayashi E, *Studies of Inorganic Ion Exchangers. IV. Ion Exchange Equilibrium between Titanium(IV) Bis(hydrogenphosphate) and NaCl-KCl aqueous solutions*, Bull. Chem. Soc. Jpn. 52(5) **(1979)** 1359-1362.
44. Clearfield A, Blessing R, Stynes J, *New crystalline phases of zirconium phosphate possessing ion-exchange properties*, J. Inorg. Nucl. Chem. 30(8) **(1968)** 2249-2258.
45. Alluli S, Ferragina C, La Ginestra A, Massucci M, Tomassi N, *Preparation and ion-exchange properties of a new phase of the crystalline titanium phosphate -* $Ti(HPO_4)_2{\cdot}2H_2O$, J. Inorg. Nucl. Chem. 39(6) **(1977)** 1043-1048.
46. Alberti G, Constantino U, Luciani G, *Crystalline insoluble acid salts of tetravalent metals - XXVIII synthesis of crystalline* $Ti(HPO_4)_2{\cdot}2H_2O$ *by the HF procedure and some comments on its formation and structure*, J. Inorg. Nucl. Chem. 41(5) **(1979)** 643-647.
47. Clearfield A, *Design of New Materials*, Cocke O L, Clearfield A (Eds), Pelnum Press, New York **(1987)**.
48. Bhaumik A, Inagaki S, *Mesoporous titanium phosphate molecular sieves with ion-exchange capacity*, J. Am. Chem. Soc. 123 **(2001)** 691-696.
49. Wang J, Clearfield A, Peng G, *Preparation of layered zirconium phosphonate/phosphate, zirconium phosphonate/phosphite and related compounds*, Mater. Chem. Phys. 35 **(1993)** 208-216.
50. Stein E, Clearfield A, Subramanian N, *Conductivity of group IV metal sulfophosphonates and a new class of interstratified metal amine-sulfophosphonates*, Solid State Ionics 83 **(1996)** 113-124.
51. Vermeulen L, Thosmson M, *Stable photoinduced charge separation in layered viologen compounds*, Nature 358 **(1992)** 656-658.
52. Clearfield A, Thakur D, *Cyclohexanol dehydration over zirconium phosphates of varying crystallinity*, J. Catal. 69 **(1981)** 230-233.
53. Clearfield A, Thakur D, *Zirconium and titanium phosphates as catalysts: a review*, Appl. Catal. 26 **(1986)** 1-26.
54. Clearfield A, Thakur D, *The acidity of zirconium phosphates in relation to their activity in the dehydration of cyclohexanol*, J. Catal. 65 **(1980)** 185-194.

55. Frianeza T, Clearfield A, *Catalytic studies on the dehydration of cyclohexanol by crystalline titanium phosphate and mixed titanium-zirconium phosphates: I. Effect of thermal phase changes on catalytic activity*, J. Catal. 85 **(1984)** 398-404.
56. Cheung H, Clearfield A, *The oxidative dehydrogenation of cyclohexene catalyzed by* $ZrCu(PO_4)_2$, J. Catal. 98(2) **(1986)** 335-342.
57. Alberti G, Cavalaglio S, Marmottini F, Matusek K, Megyeri J, Szirtes L, *Preparation of a composite γ-zirconium phosphate-silica with large specific surface and its first characterisation as acid Catalyst*, Appl. Catal. A: Gen. 218 **(2001)** 219-228.
58. Dume C, Hölderich W F, *Amination of 1-octanol*, Appl. Catal. A: Gen. 183 **(1999)** 167-176.
59. Dume C, Kervennal J, Hub S, Hölderich W F, *Synthesis of dimethylethylamine from ethylamine and methanol over phosphate catalysts*, Appl. Catal. A: Gen. 180 **(1999)** 421-433.
60. Fougret C M, Hölderich W F, *Ethylene hydration over metal phosphates impregnated with phosphoric acid*, Appl. Catal. A: Gen. 207 **(2001)** 295-301.
61. Johnstone R, Liu J, Whittaker D, *Mechanism of cyclohexanol dehydration catalysed by zirconium phosphate*, J. Chem. Soc. Perkin Trans. 6 **(1998)** 1287-1288.
62. Johnstone R, Liu J, Whittaker D, *Mechanism of heterogeneous gas phase dehydration of 1- methylcyclohexanol catalysed by metal(IV) phosphates*, J. Mol. Catal. A: Chem. 174 **(2001)** 159-168.
63. Johnstone R, Liu J, Lu L, Whittaker D, *Hydrogenation of alkenes over palladium and platinum metals supported on a variety of metal(IV) phosphates*, J. Mol. Catal. A: Chem. 191 **(2003)** 289-294.
64. Al-Qallaf A, Hodson L, Johnstone R, Liu J, Lu L, Whittaker D, *Heterogeneous liquid phase catalysis by metal (IV) phosphates of cyclic ether formation and a reverse Prins reaction*, J. Mol. Catal. A: Chem. 152 **(2000)** 187-200.
65. Costa M, Hodson L, Johnstone R, Liu J, Whittaker D, *The mechanism of gas-phase dehydration of cyclohexanol and the methylcyclohexanols catalysed by zirconium phosphate and zirconium phosphate*, J. Mol. Catal. A: Chem. 142 **(1999)** 349-360.
66. Costa M, Johnstone R, Whittaker D, *Catalysis of terpene rearrangements by zirconium phosphates and zirconium organo-substituted phosphonates*, J. Mol. Catal. A: Chem. 129 **(1998)** 79-89.

67. Costa M, Johnstone R, Whittaker D, *Catalysis of gas and liquid phase ionic and radical rearrangements of α- and β-pinene by metal(IV) phosphate polymers*, J. Mol. Catal. A: Chem. 104 **(1996)** 251-259.
68. Costa M, Johnstone R, Whittaker D, *Properties of polymeric zirconium phosphates as Friedel-Crafts catalysts*, J. Mol. Catal. A: Chem. 103 **(1995)** 155-162.
69. Pavlova S, Sadykov V, Zabolotnaya G, Kochubey D, Maximovskaya R, Zaikovskii V, Krivcntsov V, Tsybulya S, Burgina E, Volodin A, Chaikina M, Kuznetsova N, Lunin V, Agrawal D, Roy R, *The novel acid catalysts - framework zirconium phosphates: the bulk and surface structure*, J. Mol. Catal. A: Chem. 158 **(2000)** 319-323.
70. Sadykov, *Scientific bases for the synthesis of highly dispersed framework zirconiumphosphate catalysts for paraffin isomerization and selective oxidation*, Kinet. Catal. 42 **(2001)** 391-398.
71. Isobe A, Yabuuchi Y, Takezawa I, *Gas-phase hydration of ethene over Me(HPO4)2·nH2O (Me=Ge, Zr, Ti and Sn)*, Appl. Catal. A: Gen. 194-195 **(2000)** 395-401.
72. Benvenuti F, Carlini C, Patrono P, Galletti A, Sbrana G, Massucci M, Galli P, *Heterogeneous zirconium and titanium catalysts for the selective synthesis of 5-hydroxymethyl - 2 - furaldehyde from carbohydrates*, Appl. Catal. A: Gen. 193 **(2000)** 147-153.
73. Parikh A, Shivanekar A, Chudasama U, *Recent Trends in Catalysis,* Vishwanathan B, Pillai C N (Eds), Narosa Publishing House, New Delhi **(1999)** 732.
74. Patel P, Shivanekar A, Chudasama U, *Use of zirconium tungstate in acid catalysis: some esterification reactions*, Ind. J Chem. 31A **(1992)** 803-805.
75. Shivanekar A, Chudasama U, *Recent Trends in Catalysis*, Vishwanathan B, Pillai C N (Eds), Narosa Publishing House, New Delhi **(1990)** 489.
76. Parikh A, Patel A, Chudasama U, *Recent Trends in Catalysis,* Murugesan V, Arbindoo B, Palanichamy M (Eds), Narosa Publishing House, New Delhi **(1999)** 421.
77. Beena B, Chudasama U, *$[Cu(NH_3)_4]^{2+}$ SnP as a catalyst*, Indian J. Chem. Tech. 16 **(2009)** 188-191.

78. Patel S, Chudasama U, *Synthesis, characterization and catalytic application of tin phosphate*, Indian J. Chem. 41A **(2002)** 1864-1866.
79. Parikh A, Chudasama U, *Metal (IV) Tungstates as Solid Acid Catalysts for the Synthesis of Phthalate Diester-Dioctyl Phthalate (DOP)*, Indian J. Chem. Tech. 10 **(2003)** 44-47.
80. Joshi R, Chudasama U, *Synthesis of monoester and diesters using eco-friendly solid acid catalysts M(IV) Tungstates and phosphates*, Indian J. Chem. Tech. 15 **(2008)** 238-243.
81. Patel H, Joshi R, Chudasama U, *Use of zirconium(IV) phosphate as a solid acid catalyst in some esterification reactions*, Indian J. Chem. 47A **(2008)** 348-352.
82. Parangi T, Wani B, Chudasama U, Synthesis of monoesters and diesters using eco-friendly solid acid catalysts – Cerium(IV) and Thorium(IV) Phosphates, App. Cata. A: Gen. 467 **(2013)** 430-438.
83. Patel S, Ganeshpure P, Chudasama U, *Metal (IV) Phosphates as solid acid catalysts for selective cyclodehydration of 1,N - diols,* Green Chem. 3 **(2001)** 143-145.
84. Patel S, Chudasama U, Ganeshpure P, *Cyclodehydration of 1,4-butanediol catalyzed by metal (IV) phosphates*, React. Kinet. Catal. 76 **(2002)** 317-325.
85. Patel S, Chudasama U, Ganeshpure P, *Tetravalent metal acid salts: Solid acid catalysts for hydration of nitriles to amindes* Indian J. Chem. 42B **(2003)** 1168-1169.
86. Patel S, Chudasama U, Ganeshpure P A, *Ketalization of Ketones with diols catalyzed by Metal (IV) phosphates as solid acid catalysts,* J. Mol. Catal. A: Chem. 194 **(2003)** 267-271.
87. Joshi R, Chudasama U, *Synthesis of coumarins via the pechmann condensation using inorganic ion exchangers as solid acid catalysts*, J. Sci. Ind. Res. 67 **(2008)** 1092-1097.
88. Thakkar R, Chudasama U, *Synthesis of mono and diesters using eco-friendly solid acid catalyst - zirconium titanium phosphate,* Green Chem. Lett. Rev. 2(2) **(2009)** 61-69.
89. Devassy B M, Halligudi S B, Hegde S G, Halgeri A B, Lefebvre F, *12-Tungstophosphoric acid/zirconia—a highly active stable solid acid—comparison with a tungstated zirconia catalyst,* Chem. Comm. **(2002)** 1074-1075.