SUMMARY

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.

The current global scenario demands environmental compatibility [1] that includes, E-factor, Environmental Quotient (EQ), Atom efficiency and Zero Emission Technology.A lot of attention is focused towards 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.

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 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.

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 [2] provide a significant guideline in dealing with the concept of betterment of the environment.

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.

In recent times a new type of catalysis has emerged having advantages of both homogeneous and heterogeneous catalysis, termed as "Heterogenised homogeneous catalysis" which may be achieved by supporting the homogeneous catalyst onto a solid support (inorganic or polymer) 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.

Organic/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 (oxides), 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.

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 [3].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 [4].

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 [5]. 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.

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.

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 [6-9].

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 behavior and stability towards thermal, chemical and ionizing radiations.

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 [9] 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.

The supports used in heterogenised homogeneous catalysis are generally organic (polymers) and inorganic (oxides). Both organic polymers and inorganic oxides 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 oxides, 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. TMA salts being cation exchangers, homogeneous catalysts (metal ion or metal complexes) can be supported by ion exchange method. Besides TMA salts also exhibit good thermal and chemical stability.

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.

Esterification is an industrially important reaction, monoesters being very important industrially, and find a wide range of applications in perfumery, flavours, pharmaceuticals and as solvents. Diesters dioctyl phthalate (DOP), dibutyl phthalate (DBP), diethyl malonate (DEM) are important bulk chemicals. DOP and DBP are used as additives in the form of plasticizer. DEM is used in perfumes, to synthesize compounds such as barbiturates, artificial flavourings and as intermediates for synthesis of vitamin B_1 and vitamin B_6. The conventional catalyst used in esterification reactions is sulphuric acid[10] cited as a potential environmentally hazardous chemical, posing several disadvantages in industrial processes, which include wasting large amount of catalyst, corroding reactors, causing an acidic waste water, difficulty of catalyst recovery etc. Esterification reactions have been widely investigated using several solid acids[11-19]. To mention a few, sulphated zirconia, zeolites, sulfonic acid based resins, heteropoly acids, metal oxides etc. However, it has been observed that though sulphated zirconia is a very good esterification catalyst, it gets easily deactivated by losing the sulphate ions and thereby recycling of the catalyst is restricted. In case of heteropoly acids, the separation is difficult and when supported on carbon the activity decreases. Sulfonic acid based resin (Nafion–H) has also been found to be unsatisfactory due to its low operating temperature.

Coumarins are used as additives in food and cosmetics, optical brightening agents, dispersed fluorescent and laser dyes [20], exhibit useful and diverse biological activity and serve as anticoagulant agents [21].Synthetic routes to coumarins include Pechmann, Perkin, Knoevenagel and Reformatsky reactions [22]. Pechmann reaction is most widely applied method for coumarin synthesis, since it proceeds from simple starting materials (phenols and β keto ester) and gives good yields of coumarins with substitution in either pyrone or benzene ring or in both. Conventionally, coumarins (4-methyl 7-hydroxy coumarin) can be obtained in high yields upon reaction of ethyl acetoacetate with resorcinol using sulphuric acid as solvent and condensing agent[23]. Aluminium chloride and trifluoroacetic acid are also reported as condensing agent for synthesis of coumarins [23]. The conventional process requires long reaction times, corrodes the reactor and creates by-products and salt waste due to neutralisation of the acid. In view of the deficiencies encountered, there is a global effort to replace the conventional homogeneous liquid acids by heterogeneous solid acids.

Friedel–Crafts acylation of aromatic compounds is an omnipresent reaction in the production of aromatic ketones largely used as intermediates in the synthesis of pharmaceuticals, dyes, fragrances, agrochemicals,paint additives, photoinitiators, plasticizers and other commercial products[24,25]. Traditional Friedel-Crafts acylation uses acyl halides or anhydrides as acetylating agents, with soluble Lewis acids(anhydrous $AlCl_3$ and BF_3) and mineral acids(H_2SO_4, HF) as catalysts which are polluting and difficult to work with. These acids are consumed in more than stoichiometric amounts due to the formation of 1:1 molar adduct with the product. Besides, the subsequent separation of the product by hydrolysis is cumbersome and generates a large amount of environmentally hazardous and corrosive waste.

The liquid phase benzylation of benzene and other aromatic compounds by benzyl chloride is important for the production of diphenylmethane and substituted diphenylmethanes which are industrially important compounds used as pharmaceutical intermediates and fine chemicals[26].Friedel-Crafts alkylation reactions catalysed by homogeneous Lewis acid catalysts generally give complex reaction mixtures. The formation of reactant (and product) catalyst complexes, the increased tendency of alkylated products toward further alkylation and isomerization, coupled with the long contact of the reactant with the catalyst, result in decreased product selectivity. The major draw back in these processes is that the Lewis acid is non-regenerable. There is, therefore, substantial interest to carry out alkylation reactions with solid acid catalysts which decrease these side reactions. The acid sites in solid acids being milder than the conventional lewis acids, would also inhibit side reactions such as polyalkylation, isomerization, transalkylation, dealkylation and polymerization that occur under normal reaction conditions.

Ruthenium catalysed reactions are both mild as well as versatile. Ruthenium supported onto polyoxometallates, zirconia and polystyrene have been studied for various hydrogenation and oxidation reactions[27-29].In recent years, significant advances have been observed in the development of active and selective catalysts for liquid phase oxidation of organic compounds[30] and considerable attention focused towards the choice of environmentally benign oxidants from the view point of improving reaction atom efficiencies[31-33].The factors that influence the choice of oxidant include, active oxygen content, availability, selectivity and nature of the waste produced. Hydrogenolysis is the reduction of organic functional groups by addition of hydrogen to unsaturated groups, such as the reduction of ketones to alcohols or the addition of hydrogen across single bonds, leading to cleavage of functional groups.

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 I of the thesis is a brief introduction to catalysis in general and solid acid catalysis and heterogenised homogeneous catalysis in particular.

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 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. Amongst mono esters, catalytic activity/TON increases with increasing chain length of alcohol and the trend in TON is BzA>BA>PA>EA. Higher yields of BA obtained could be attributed to an enhanced nucleophilicity due to presence of aromatic ring in benzyl alcohol. Amongst diesters, high yields in case of DEM, compared to DOP and DBP is probably due to less steric hindrance felt by incoming ethanol from monoethyl malonate formed in the first step. When homogeneous liquid acids are used as catalysts for synthesis of DOP and DBP, the result is a product that is coloured and of a poor quality. In the present work, the advantage is that the diester is the unique product and colourless. In general M(IV) phosphates exhibit better catalytic activity compared to tungstates. The activity of the regenerated catalyst was reduced by ~10%.

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 (4M7HC), 4-methyl 7,8-dihydroxy coumarin (4M7,8HC) and 4-methyl 5,7-dihydroxycoumarin (4M5,7HC) involving condensation of resorcinol(R), pyrogallol(P) and phloroglucinol(Ph) 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. Electron-donating substituents in the position meta to the phenol hydroxyl group makes P and Ph, more active compounds for Pechmann condensation compared to R. In case of crystalline materials, though surface area is less there is no decrease in the catalytic activity/TON. This can be attributed to the fact that though the number of surface acid sites are less for crystalline materials, the desorption temperatures are higher, indicating the presence of strong acidity/ active sites enhancing the catalytic activity. The activity of the regenerated catalyst was reduced by ~10%.

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. Product yield and TON are higher for veratrole compared to anisole. The presence of an additional electron donating methoxy group in veratrole makes it a more active compound for electropholic substitution of acyl group in the para position than anisole due to an increased electron density at para position and resultant increased susceptibility for attack by the electrophile. TiP and TiW exhibit highest yield of PBT amonst M(IV) phosphates and tungstates respectively.The activity of the regenerated catalyst was reduced by ~10%.

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. Higher yield of benzaldehyde is obtained when benzyl alcohol is used as substrate compared to styrene. This could be attributed to the oxidative cleavage that has to occur in case of 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. Catalytic activity/TON is maximum for 1-octene followed by nitrobenzene and then cyclohexanone. The reaction mixture shows no further conversion on removing the catalyst from the system, indicating that Ruthenium is not leaching from the support. The activity of the regenerated catalyst was reduced by ~5%.

REFERENCES:

[1] Sheldon R A 2000 *Pure Appl Chem* **72** 1233

[2] Sanghi R 2003 *Green Chemistry Environment Friendly Alternatives* (Eds.) Sanghi R and Srivastava M M. Narosa Publishing House, New Delhi **Ch. 3** 30

[3] Sivasanker S 2002 *Catalysis Principles and Applications* (Eds.) Vishwanathan B, Sivasanker S and Ramaswamy A V. Narosa Publishing House, New Delhi **Ch. 19** 215

[4] Mukherji S M and Singh S P 1976 *Reaction Mechanism in Organic Chemistry* McMillan India Ltd

[5] Tanabe K 1981 *Catalysis- Science and Technology* (Eds.) Anderson J R and Boudart M. Vol-2 Springer-Verlag, Berlin

[6] 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

[7] Clearfield A 1982 *Inorganic Ion Exchange Materials* CRC Press, Boca Raton, Florida

[8] Clearfield A, Nancollas G H and Blessing R H 1973 *Ion Exchange and Solvent Extraction* (Eds.) Marinsky J H and Marcs Y. Marcel Dekker, New York **Vol 5**

[9] Amphlett C B 1964 *Inorganic Ion Exchangers* Elsevier Amsterdam

[10] Vogel A I *Vogel's Textbook of Practical Organic Chemistry* 1987 *Longman Group Ltd England* 4th edn 501

[11] Santacesaria E, Gelosa D, Danje P and Carra S 1983 *J Catal* **80** 427

[12] Izuka T and Tanabe K, 1984 *Chem Lett* 1085

[13] Okazaki S and Wada N 1993 *Catal Today* **16** 349

[14] Hino M and Arata K 1981 *Chem Lett* 1671

[15] Guttmann A T and Grasselli R K, 1983 *Appl Catal* **9** 57.

[16] Izumi Y, Haseba R and Urabe K 1983 *J Catal* **84** 402.

[17] Baba T and Ono Y 1986 *Appl Catal* **22** 321

[18] Dupont P, Vedrine J C, Aumard E P, Hecquet G and Lefebrve F 1995 *Appl Catal* **129** 217

[19] Dupont P and Lefebrve F 1996 *J Mol Catal* **114** 299.

[20] Bogdal D 1998 *J Chem Res* 468

[21] Li Tong-Shuang, Zhang Z H and Yang F and Fu C G, 1998 *J Chem Res* 38

[22] Reddy B M, Patil M and Lakshmanan P 2006 *J Mol Catal A: Chemical* **256** 290.

[23] Gunnewegh E A, Hoefnagel A J and van Bekkum H 1995 *J Mol Catal A:Chemical* **100** 87.

[24] Kantam M L, Ranganath K V S, Sateesh M, Shivakumar K B and Chaudhary B M 2005 *J Mol Catal A:Chemical* **225** 15

[25] Jasra R V 2003 *Bull Catal Soc India* **2** 157

[26] Vinu A, Sawant D, Arigu K, Harfmann M, Halligudi S B 2005 *Microporous and Mesoporous Mat* **80** 195

[27] Neumann R and Khenkin A 1995 *Inorg Chem* **34** 5753

[28] McNamara C A, Dixon M J and Bradley M 2002 *Chem Rev* **102** 3275

[29] Leadbeater N E, Scott K A and Scott L J 2000 *J Org Chem* **65** 3231.

[30] Seneci P *Solid Phase Synthesis and Combinatorial Techniques* 2000 *John Wiley* ,New York.

[31] Arends I W C E, Sheldon R A, **2001** *Appl Catal A: Generel* **212** 175.

[32] Sheldon R A 1996 *J Mol Catal A: Chemical* **107** 75.

[33] Trost B M 1991 *Science* **254** 1471