CHAPTER 4

Applicability of Cerium (IV) and Thorium (IV) Phosphates as Solid Acid Catalysts

4.1 INTRODUCTION

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, 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 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.

4.2 PRINCIPLES OF GREEN CHEMISTRY

Twelve principles **[1]** 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 ofall 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.

4.3 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.

SolidAcidCatalysts-Analternate approach toliquid acid catalysts

Liquid acids such as H_2SO_4, HF, H_3PO_4etc. 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.**[2]**.

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 Brønsted 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 **[3].**

Solid acid catalysts are appealing, since the nature of the acid sites is 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.**[4]** 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**[5-7].**

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.

4.4 AIM AND SCOPE OF THE PRESENT WORK

A drive for clean technology associated with the problems encountered while using 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 super acids, sulfated oxides and TMA salts.

As already described in **Chapter I**, TMA salts indicate good potential for application as solid acid catalysts due to presence of surface protons/acidity,H^+ of the structural –OH providing acid sites**[8-10]**. Besides they possess excellent thermal and chemical stability. TMA salts have been used as catalysts in several organic transformations by various groups -Dr. A. Clearfield (USA), Dr. G. Alberti (Italy), Dr. W. Holderich (Germany),Dr. D. Whittaker (UK) andDr. 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 [**11**]. Clearfield et al[**9,12**] 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 [**13**] 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 [**14**].

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 [**15**]. Holderich has reported zirconium phosphate as solid acid catalyst, in amination reactions that exhibit 100 % selectivity for 1-octylamine [**16**], formation of dimethyl ethyl amine from ethyl amine and methanol [**17**], and ethylene hydration [**18**].

David Whittaker [**19, 20**] 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 organic transformations, such as hydrogenation of alkenes [**21**], reverse Prins reaction [**22**], dehydration of cyclohexanol and methylcyclohexanols [**23**], terpene rearrangements [**10**], ionic and radical rearrangements of α and β-pinene [**24**], alkylation of anisole with alcohols (Friedel-Crafts) [**25**] 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 [**26**]. Cheng et al [**27**] have reported the catalytic properties of zirconium phosphate, titanium phosphate, and their organically pillared derivatives, towards methanol conversion.Ivanova et al have used zirconium phosphate for paraffin isomerization and selective oxidation [**28**]. Balandin et al [**29**] reported zirconium phosphate for the dehydration of C_2-C_4 olefins. Malendberg found zirconium phosphate to be a better catalyst for propanol dehydration showing a conversion efficiency of 97 % [**30**]. The gas phase hydration of ethane was studied over various metal phosphates and high activity and selectivity were reported with tin phosphate [**31**]. Benvenuti et al [**32**] 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 that include esterification [**33-42**], dehydration of alcohols [**43, 44**], hydration of nitriles to amides [**45**], ketalization of ketones [**46**] and Pechmann condensation reactions [**47, 48**].Most of the reports outlined earlier/abovereveal the use of phosphates of Zr, Ti and Sn as solid acid catalysts. However, not much work has been explored on phosphates of Ce and Th as solid acid catalysts.

The present study involves practicing and achieving green chemistry goals, wherein cerium phosphate (CP) and thorium phosphate (TP), materials of the class of TMA salts have been explored as solid acid catalysts. The catalytic performance of these materials has been evaluated by studying Esterification and Acetal Formation as model reactions.

4.5 ESTERS AND ESTERIFICATION

Esters represent an imperative class of aroma compounds. Esters are useful as solvents, plasticizers, perfumes, fragrance in cosmetics, flavours in foods, diluents in paints and coatings as well as intermediates in drugs, dye stuffs, fine chemicals and pharmaceutical industries. Monoesters are very important industrially and find a wide range of applications in perfumery, flavours, pharmaceuticals and as solvents. Diesters diethyl malonate (DEM), diethyl succinate (DES), dioctyl phthalate (DOP) and dibutyl phthalate (DBP) are important bulk chemicals. DEM occurs naturally in grapes and strawberries as a colourless liquid with an apple-like odour, and is used in perfumes. It is also used to synthesize other compounds such as barbiturates, artificial flavourings and as intermediates for synthesis of vitamin B_1, and vitamin B_6. Succinate esters are intermediates in the production of poly butylene succinate (PBS) polymers, a polyester composed of succinic acid and 1,4-butanediol having attractive properties for broad application in automobiles and consumer goods. The 1,4-butanediol is produced by hydrogenation of succinate ester, hence the entire PBS polymer is a succinate based, bio-renewable material. Esters of succinic acid (primarily dimethyl esters) are also being investigated for their insulinotropic potential in rats **[49]**. DOP and DBP are used as additives in the form of plasticizer, to the important plastic polyvinyl chloride.

Esterification is an industrially important reaction. The reaction between an organic acid and an alcohol is known as “esterification”. The synthesis of monoesters can be presented as shown in **Scheme 4.1**.The reaction is generally carried out with large excess of alcohol and in presence of a strong acid catalyst. The esterification procedure introduced by E. Fischer and A. Speier (1895) consists in refluxing acid and excess methanol or ethanol in the presence of about 3 % hydrogen chloride.

$$\mathrm{RCOOH} + \mathrm{R`OH} \overset{\overset{+}{\mathrm{H}}}{\rightleftharpoons} \mathrm{RCOOR`} + \mathrm{H_2O}$$

where, R and R` are alkyl and aryl groups

Scheme 4.1 *Esterification reaction*

Esterification is a reversible reaction and gives water as the second product. Fora stoichiometric mixture of acid and alcohol, equilibrium generally reaches ~68% **[50]** of conversion for the straight chain saturated alcohol. In order to obtain maximum yields, Le Chatlier's principle is followed and the reaction is driven to the right hand side/forward direction, as follows:

Addition of one of the reactants in excess: The reaction usually reaches a point of equilibrium at ~60% conversion, but in a small scale experiment a conversion of 60-80% can be achieved by use of a large excess of either acid or alcohol.

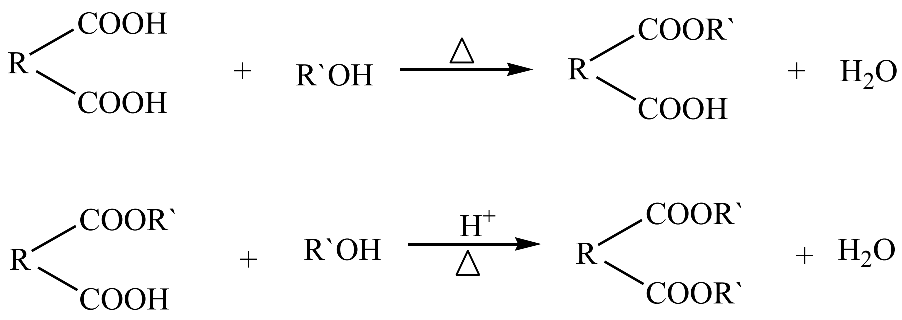
Removal of one of the products:Either ester or water formed is removed as soon as it is formed. Generally, suitable organic solvents are employed to remove the water formed during the reaction as a binary azeotrope or employing dehydrating agents such as anhydrous magnesium sulfate or molecular sieves **[51]**.

To avoid equilibrium reaction, other paths have been suggested for ester synthesis. Such reactions involve the use of acyl halides or anhydrides or by alkylation of salts of carboxylic acids with alkyl halides. With acid halides, though the reactions are rapid and irreversible, HCl is obtained as a byproduct which is difficult to remove from the product. Mostly pyridine is used as an HCl acceptor. However, these reactions are efficient for only primary alcohols, secondary alcohols give lower yields and no reaction occurs at all with tertiary alcohols. Further, aromatic acid chlorides are considerably less reactive than aliphatic acid chlorides.

Esters are also synthesized from anhydrides, the reaction being same as acid chlorides, however anhydride yields a molecule of carboxylic acid instead of corrosive HCl. This reaction is widely used in industry in esterification of polyhydroxy compounds such as carbohydrates, cellulose etc.

Other methods include the use of alkyl tert-butyl ether or by alkylation of salts of carboxylic acids with alkyl halides, trans-esterification, carbonylation of olefins, alcoholysis of nitriles etc.

Reaction involved for diester synthesis is presented in **Scheme 4.2**.



where, R = $(\text{-CH}_2\text{-})_n$; R`= alkyl groups

Scheme 4.2 *Di-esterification reaction*

Diesters can be prepared using dicarboxylic acid or anhydride. Diesters are prepared in two stages (**Scheme 4.2**) [**52-54**], the first stage is very rapid and can be carried out in the absence of a catalyst. However, esterification of the second carboxylic group is very slow and needs to be facilitated by an acid catalyst, resulting in the formation of water as a byproduct. The reaction is an equilibrium one and hence to facilitate it in the forward direction, the water molecule must be removed by azeotrope formation. The current commercial process is a batch method which is very efficient with respect to its feed stocks. Conversion (based on phthalic anhydride) and selectivity can reach 99.2 and 99.8 %, respectively[**52**]. To reach this high conversion, a 20 % excess of alcohol is used[**52**]. The excess is recovered after reaction by a steam stripping process. Hardly any purification is required after synthesis because of the high selectivity, usually only a decolorization is carried out. A typical byproduct is the dialkyl ether formed by the condensation of two molecules of alcohol.

Problems/Limitations in Esterification

For the preparation of perfumery and flavour grade esters, only a few of the above mentioned routes can be considered, due to the stringent specifications of the final product. Normally, liquid phase catalysts such as sulphuric acid, *p*-toluene sulfonic acid, methanesulfonic acid, hydrochloric acid, phosphoric acid etc. have been used, that are cited as potential environmentally hazardous chemicals that pose problems such as difficulty in handling, causing acidic waste water, difficulty of catalyst recovery etc. [**2, 55**]. These catalysts are known to colour the product and cannot be reused. As already mentioned, these liquid acids have several disadvantages. Due to these problems, accompanied by the increasing environmental awareness, there is a global effort to replace the conventional liquid acids by suitable solid acids. The most widely employed and supposedly cleaner production technique for such esters, involves the reaction of the appropriate carboxylic acid with an alcohol using a heterogeneous catalyst such as solid acid catalyst under reflux conditions, followed by separation of the ester by distillation.

4.6 LITERATURE SURVEY IN THE CURRENT AREA OF STUDY

Monoesters using various Solid Acid Catalysts

Cation exchange resins Dowex 50W and Amberlite IR-120 [**56, 57**] have been used as solid acid catalysts in the esterification of acetic acid with isobutanol. Esterification of acrylic and lactic acids with butanol using Amberlyst-15 [**58,59**] and lactic and salicylic acids with methanol using Dowex 50W resin as solid acid catalysts [**60, 61**] has been reported. Salmi et al have studied methyl acetate formation on new polyolefin supported sulfonic acid catalysts [**62**]. Meunier [**63**] has reported esterification reactions using Nafion as solid acid catalyst. Kaolinite [**64**] as well as montmorillonite [**65**] clay has been used as catalyst in the esterification of carboxylic acids. Sartori has written an excellent review on clay catalyst for monoesterification reaction [**66**].Manohar et al [**67**] have reported esterification of acetic acid and benzoic acid using ZrO_2 and Mo-ZrO_2 as solid acid catalysts and found that Mo-ZrO_2 exhibits better catalytic activity than ZrO_2. Valdeilson et al [**68**] have studied esterification of acetic acid with alcohols using supported niobium pentoxide on silica-alumina catalysts.Vishwanathan et al [**69**] have reported esterification by solid acid catalysts including clays, zeolites, sulphated metal oxides and heteropolyacids.Toor et al [**70**] have reported kinetic study of esterification of acetic acid with n-butanol and isobutanol catalyzed by ion exchange resin. Silicotungstic acid supported zirconia is reported as an effective catalyst for esterification reactions using formic, acetic, propionic, *n*-butyricacid and *n*-butyl alcohol, isobutyl alcohol and *sec*-butyl alcohol [**71**]. Chu et al [**72**] have reported the vapour phase synthesis of ethyl and butyl acetate by immobilized dodecatungstosilicic acid on activated carbon. The rate of esterification was found to be dependent on the partial pressure of the reactants. Dupont et al [**73**] have reported heteropolyacids (HPA) supported on activated carbon as catalysts for the esterification of acrylic acid by butanol. Deactivation of the catalyst was observed under flow conditions (from 43 to 32% conversion) which wereattributed to the dissolution of the supported HPA in the reaction medium (25 %). Timofeeva et al [**74**] have reported esterification of acetic acid and *n*-butyl alcohol using Keggin and Dawson type HPAs and found that the reaction rate depends on the acidity, as well as on the structure and composition of HPAs. 12-TPA supported on hydrous zirconia was used as solid acid catalyst in esterification of primary and secondary alcohols [**75**]. Sharath et al [**76**] studied benzyl acetate formation in the presence of zeolites and their ion exchanged forms. They reported reasonably good yield with 100 % selectivity. Ma et al [**77**] have reported the synthesis of ethyl, butyl and benzyl acetates with high yields using zeolitecatalyst. Jiang et al[**78**] have studied catalytic activity of mesoporous TiO_2 solid super acid for esterification of iso-amyl alcohol and salicylic acid. Sugi et al [**79**] have reported 12-TPA supported onto MCM-48 as an efficient catalyst for the esterification of long chain fatty acid and alcohols in supercritical CO_2.Yarmo et al [**80**] have reported 12-TPA supported on MCM-41 for esterification of fatty acid under solvent free condition. The workers have also reported synthesis, characterization and catalytic performance of porous nafion resin/silica nano-composites for esterification of lauric acid and methanol [**81**]. Nascimento et al have reported catalytic esterification of oleic acid over SO_4^{2-}/MCM-41 nano-structured materials [**82**]. Helen et al [**83**] have reported use of mesoporous silica supported diarylammonium catalysts for esterification of free fatty acid in greases.Zhu et al [**84**] have reported synthesis, characterization and application of sulfated zirconia/hexagonal mesoporous silica (HMS) catalyst in the esterification of gossypol.Pandurangan et al have [**85**] reported vapour phase esterification of butyric acid with 1-pentanol and tert-butylbenzene with iso-propyl acetate over Al-MCM-41 mesoporous molecular sieves. Srinivas et al[**86**] have reported the kinetics of esterification of fatty acids over solid acid catalysts including large pore zeolite-β (Hβ), micro-mesoporous Fe/Zn double-metal cyanide (DMC) and mesoporous Al-MCM-41.Said et al have [**87**] reported perspective catalytic performance of Brønsted acid sites during esterification of acetic acid with ethyl alcohol over 12-TPA supported on silica. Rhijn et al [**88**] have reported sulfonic acid functionalized ordered mesoporous materials as catalysts for condensation and esterification reactions.Zhang Yijun et al [**89**] have reported synthesis, characterization and catalytic application of HPA/MCM-48 in the esterification of methacrylic acid with n-butyl alcohol. Lingaiah et al [**90**] have reported 12-TPA with varying contents on SnO_2 as efficient solid acid catalysts for esterification of free acids with methanol for the production of biodiesel.These catalysts were found to be highly stable and active in esterification reaction .Guo et al [**91**] have reported simultaneous esterification and transesterification of soybean oil with methanol catalyzed by mesoporous Ta_2O_5/SiO_2–$[H_3PW/R]$ (R = methyl or phenyl) hybrid catalysts. Khire et al [**92**] have reported esterification of lower aliphatic alcohols with acetic acid in presence of sulfated zirconia and silica supported zirconia catalysts and these catalysts have been evaluated and compared with other acid catalysts. Chopade et al have [**93**] reported use of various heterogeneous solid acid catalysts for production of biodiesel viatransesterification of triglycerides with methanol. Feng et al have [**94**] reported the use of sulfonated based NKC-9 cation exchange resin for acidic oil continuous esterificationprocess in a fixed bed reactor. Nage and Kulkarni et al have [**95**] reported biodiesel production by a continuous process using heterogeneous catalysts (mixed oxides of Zr and Al).Keat Teong Lee et al [**96**] have written an excellent review on heterogeneous catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel. Park et al [**97**] have reported heterogeneous catalyst system for the continuous conversion of free fatty acids in used vegetable oils for the production of biodiesel The authors also have reported esterification of used vegetable oils using heterogeneous WO_3/ZrO_2 catalyst for production of biodiesel [**98- 99**]. Gang et al [**100**] have reported solvent free esterifications of various carboxylic acids and alcohols catalyzed by surfactant-combined catalysts dodecylbenzene sulfonic acid (DBSA) and copper dodecylbenzene sulfonate (CDBS) in moderate to excellent yield at room temperature. Liao Sen et al [**101**] have reported use of ammonium cerium phosphate for benzyl acetate synthesis.

From our laboratory, TMA salts have been widely investigated as solid acid catalysts for synthesis of monoesters such as ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA) and benzyl acetate (BzAc) [**33-42**].

Diesters using various Solid Acid Catalysts

Suter [**102**] has reported a noncatalytic process for the manufacture of DOP, at very high temperatures, at which autocatalysis occurs. Bekkum and Schwegler [**103**] investigated the use of HPAs (homogeneous and carbon supported) for DOP synthesis. They obtained a superior activity at low temperatures in both homogeneous and supported form. Thorat et al [**104**] have reported the use of solid super acids (sulfated and HPA supported onto oxides) for the synthesis of DOP. They have reported a selectivity > 99 % and demonstrated that selection of optimum calcination temperature is a must for optimum yield. Yadav et al[**105**] also have reported esterification of maleic acid with ethanol over cation-exchange resinsas catalysts.G Lu [**106**] has investigated DOP synthesis over solid superacids SO_4^{2-}/Ti-M-O (M = Al, Fe, Sn). They obtained superior activity in case of SO_4^{2-}/Ti-Al-Sn-O system and found that acid strength, surface area and catalytic activity of the system is affected by the preparation conditions. Ma et al [**107**] studied the synthesis of DOP using ZSM-5 and HY zeolites. Z H Zhao [**108**] has also reported the use of aluminophosphate and silicoaluminophosphate molecular sieves as solid acid catalyst for the synthesis of DOP. Amini et al [**52**] have reported the use of heteropoly acids for the production of DOP and DBP. DEM synthesis has been reported by Reddy et al [**109**] using montmorillonite clay, but the yield is low (41 %) and relatively high amount of catalyst (0.5 g) was used. In another report, DEM was synthesized by Jiang et al [**110**] using the reaction of CO with $ClCH_2COOC_2H_5$. In this case high yield was observed but the reaction was carried out at high pressure.Kolah et al[**49**] have reported esterification of succinic acid with ethanol and have also reported esterification of tri-ethyl citrate via mono and di-ethyl citrate catalyzed by macroporous Amberlyst-15 ion exchange resin.Patel et al [**111**] have reported synthesis and characterization of 12-TPA anchored to MCM-41 and its use as environmentally benign catalyst for synthesis of succinate and malonate diesters. Ren et al [**112**] have reported catalytic activity of a novel carbon-based solid acid catalyst for esterification of succinic acid with ethanol. Okudan et al [**113**] have reported esterification reaction of polystyrene modified with maleic anhydride in the presence of resin catalyst.

From our laboratory, TMA salts have been widely investigated as solid acid catalysts for synthesis of diesters such as dioctyl phthalate (DOP), dibutyl phthalate (DBP),diethyl malonate(DEM) and diethyl succinate (DES) [**40-42**, **114**].

As seen in the foregoing discussion, esterification reactions have been investigated using several solid acids such as sulphated zirconia, zeolites, sulfonic acid based resins, heteropoly acids, metal oxides, pillared clay etc [**115-120**]. Though, sulphated zirconia is a good esterification catalyst, it gets easily deactivated by losing the sulphate ions, thereby restricting recycling of the catalyst. The main disadvantage of heteropoly acids is low efficiency due to low surface area, rapid deactivation and poor stability and when supported on carbon the activity decreases [**121**]. Sulfonic acid based resin (Nafion-H) has also been found to be unsatisfactory due to its low operating temperature.

In the present study the potential use of CP, TP, CP_M and TP_M as solid acid catalysts has been explored by studying esterification as a model reaction wherein mono esters ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA), benzyl acetate (BzAc) and diesters such as diethyl malonate (DEM), diethyl succinate (DES), dibutyl phthalate (DBP) and dioctyl phthalate (DOP) have been synthesized optimizing several parameters viz reaction time, catalyst amount and mole ratio of reagents including regeneration and reuse of catalysts. The catalytic activity of the materials has been compared and correlated to surface acidity of the materials.

4.7 SYNTHESIS OF ESTERS

4.7.1 Experimental

Materials**:** Acetic acid, ethanol, 1-propanol, 1-butanol, benzyl alcohol, cyclohexane xylene and toluene were procured from Merck, India.

Catalyst Synthesis:The synthesis and characterization of CP, TP, CP_M, and TP_Mhave been discussed in **Chapter II**, **Section 2.3 and 2.4**.

Synthesis of monoesters (EA, PA, BA and BzAc): Monoester synthesis were carried out varying several parameters such as reaction time, catalyst amount, mole ratio of reactants and these parameters optimized. In a typical reaction, a 100 mL round bottomed flask was equipped with a Dean and Stark apparatus, attached to a reflux condenser and charged with acetic acid (0.05 - 0.10 M), alcohol (0.05 - 0.10 M), catalyst (0.10 - 0.20 g) and a suitable solvent (15 mL) used as azeotrope to remove water formed during the reaction. Cyclohexane (80°C) was used as a solvent for the synthesis of ethyl acetate and toluene (110°C) for propyl acetate, butyl acetate and benzyl acetate. The temperature parameter has not been varied as the reaction temperature is sensitive to boiling points of reactants [ethanol (78°C), 1-propanol (97°C), 1-butanol (118°C) and benzyl alcohol (205°C)] as well as solvents used as azeotrope. After completion of reaction, catalyst was separated by decantation and reaction mixture was distilled to obtain the product.

Synthesis of diesters (DEM, DES, DBP and DOP):The diesters were synthesized in two steps. The mono ester was prepared in first step by taking equimolar proportion (0.025 mole) of acid and alcohol (malonic acid and ethanol for DEM, succinic acid and ethanol for DES, phthalic anhydride and 1-butanol for DBP, phthalic anhydride and 2-ethyl 1-hexanol for DOP) in a round bottomed flask and the reaction mixture stirred at ~80°C for DEM and DES, ~110°C for DBP and ~140°C for DOP for about 10-15 min in absence of any catalyst and solvent. The dicarboxylic acid and anhydride gets completely converted to the monoester, so that the acid concentration at this stage is taken as the initial concentration. The obtained product (monoester) was then subjected to esterification reaction by addition of a second mole (0.025 mole) of respective alcohol, catalyst (0.10 - 0.20 g) and 15 mL solvent {toluene (110°C) for DEM, DES and DBP, and xylene (140°C) for DOP}. The reactions were carried out optimizing several parameters such as reaction time, catalyst amount and mole ratio of reactants. The temperature parameter has not been varied as the reaction temperature is sensitive to boiling points of reactants as well as solvents used as azeotrope. In all cases round bottomed flask was fitted with Dean and Stark apparatus, with a condenser to remove water formed during the reaction. After completion of reaction, catalyst was separated by decantation and reaction mixture distilled to obtain the product.

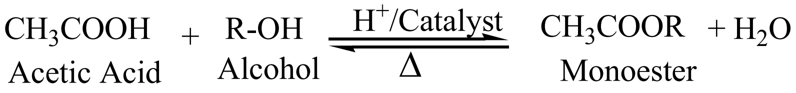
Calculation of % yield of esters: The yields of the mono and diesters formed were determined by titrating the reaction mixture with 0.1 M alcoholic KOH solution. The yields of the esters were calculated using the formula, $\% \, yield = [(A - B) / A] \times M \times 100$, where A and B are acid values of the sample withdrawn before and after reaction and M is mole ratio of acid: alcohol. The yield of ester formed was also determined using GC. (Oven temperature: 150 °C, injector temperature: 200 °C, detector temperature: 220 °C and split ratio is 1:2).

***Regeneration of catalyst*:**After separation of catalyst from reaction mixture by decantation, it is first refluxed in ethanol for 30 minutes to solubilise and remove adsorbed molecules, followed by drying at room temperature (~30 ºC) and acid treatment using 1 M HNO_3 (as discussed in **Chapter II, Section 2.3**). This material was used as recycled catalyst. This regeneration procedure was followed in subsequent recycle reaction.

4.7.2 Results and Discussion

Synthesis of monoesters

Monoester synthesis EA, PA, BA and BzAc is presented as shown in **Scheme 4.3**and were prepared as described in experimental section. Equilibrium constants of the esterification reactions are low. As in any equilibrium reaction, the reaction may be driven to the product side by controlling the concentration of one of the reactants (Le Chatlier's Principle). In order to obtain higher yield of esters, solvents cyclohexane and toluene were employed to remove the water formed during the reaction as a binary azeotrope.



$$\underset{\text{Acetic Acid}}{CH_3COOH} + \underset{\text{Alcohol}}{R\text{-}OH} \xrightleftharpoons[\Delta]{H^+/\text{Catalyst}} \underset{\text{Monoester}}{CH_3COOR} + H_2O$$

R = -C_2H_5 for ethyl acetate, -C_3H_7 for propyl acetate,
-C_4H_9 for butyl acetate and -CH_2-Ph for benzyl acetate

Scheme 4.3*Synthesis of monoesters (EA, PA, BA and BzAc)*

Firstly, reaction conditions were optimized for EA synthesis, varying parameters such as reaction time, catalyst amount and initial mole ratio of the reactants using CP as solid acid catalyst.(**Table 4.1** and a graphical presentation **Figures 4.1 to 4.3**)

It is observed that as reaction time increases, percentage yield increases. However, there is not much gain in product after 8 h. With increasing amount of the catalyst, the % yield increases which is probably due to proportional increase in the number of active sites. The influence of reactant mole ratio was studied by increasing mole ratio from 1:1.5 to 1.5:1 (acid:alcohol).According to Le Chatlier's principle, ester yields can be increased by increasing the concentration of either alcohol or acid. As observed from**Table 4.1**, the % yield of ester increases with increase in mole ratio of acid while decreases with increasing mole ratio of alcohol. This may be attributed to preferential adsorption of alcohol on the catalyst which results in blocking of active sites. For economic reasons also, the reactant that is usually less expensive of the two is taken in excess. In the present study, acids were used in excess. The temperature parameter has not been varied as the reaction temperature is sensitive to boiling points of reactants as well as solvents used as azeotrope.

Further, at optimized conditions (mole ratio of reactants = 1:1.5 (alcohol:acid); catalyst amount = 0.15 g; reaction time = 8 h) synthesis of EA, PA, BA and BzAc was performed using CP, CP_M, TP and TP_M as solid acid catalysts, (**Table 4.2**).

Esterification of monoesters EA, PA and BA has been reported [**108**] in absence of catalyst and exhibit poor yields. Therefore catalyst is a must for these reactions. In case of BzAc however, it is observed that with an excess of acetic acid and in the absence of any catalyst the yield is as high as 90.6 % which is attributed to auto catalysis. In another report **[76]** high yields of BzAc were obtained with small amount of the catalyst but the reaction time was relatively high. Higher yields in case of benzyl acetate could be attributed to an enhanced nucleophilicity due to presence of aromatic ring in benzyl alcohol. The order of % yield of ester formed for both CP and TP is BzAc > BA > PA > EA could be explained due to increase in carbon chain length in the respective alcohols used for ester formation. When the boiling point of the alcohol is less than the temperature of the reaction, most of the alcohol will end up in the vapor phase and not be available in the liquid phase. This is the reason why the heavier alcohols react more than the lighter ones. Turn over number (TON)reflects the effectiveness of a catalyst and this also follows the order of ester formation.

The order of monoesters formed with reference to performance of catalyst (**Table 4.2, Figures 4.4 and 4.5**) is CP_M> CP > TP_M> TP could be attributed to higher surface acidity as well as protonating ability. (**Chapter II, Table 2.6**)

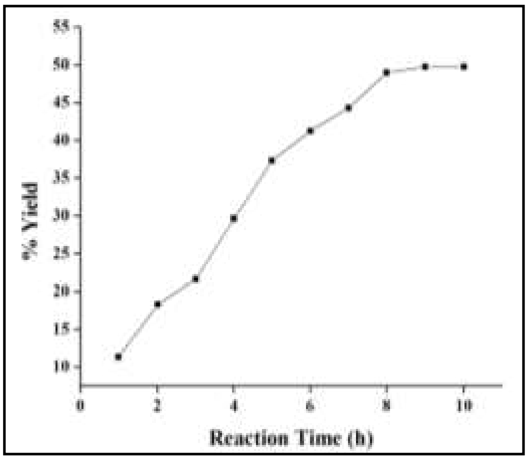


Figure 4.1*Reaction time optimization for EA synthesis using CP*

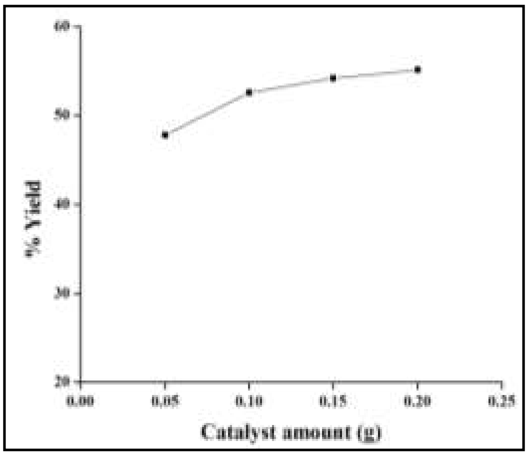


Figure 4.2*Catalyst amount optimization for EA synthesis using CP*

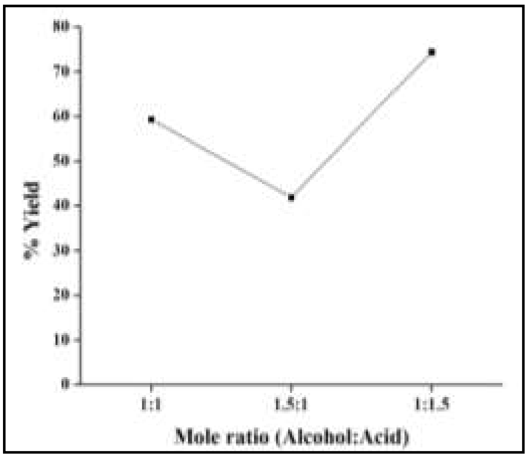


Figure 4.3*Mole ratio optimization for EA synthesis using CP*

Table 4.1*Optimization of reaction conditions for monoesters using CP*

Sr. No.	Reactants with their mole ratio	Product	Catalyst Amount (g)	Time (h)	Temperature (ºC)	%Yield CP
(A)	Time variation					
1	E + AA (1:1)	EA	0.05	1	80	12.2
2	E + AA (1:1)	EA	0.05	2	80	23.1
3	E + AA (1:1)	EA	0.05	3	80	25.2
4	E + AA (1:1)	EA	0.05	4	80	33.5
5	E + AA (1:1)	EA	0.05	5	80	39.6
6	E + AA (1:1)	EA	0.05	6	80	44.4
7	E + AA (1:1)	EA	0.05	7	80	48.2
8	E + AA (1:1)	EA	0.05	8	80	52.3
9	E + AA (1:1)	EA	0.05	9	80	53.1
10	E + AA (1:1)	EA	0.05	10	80	53.1
(B)	Catalyst amount variation					
12	E + AA (1:1)	EA	0.10	8	80	57.1
13	E + AA (1:1)	EA	0.15	8	80	59.1
14	E + AA (1:1)	EA	0.20	8	80	59.3
(C)	Mole ratio variation					
15	E + AA (1.5:1)	EA	0.15	8	80	41.8
16	**E + AA (1:1.5)**	**EA**	**0.15**	**8**	**80**	**74.4**

E=Ethanol; AA= Acetic acid

Table 4.2*% yields of monoesters using CP, TP, CP$_M$ and TP$_M$ at optimized condition*

Sr. No	Reactants	Product	CP		TP	
			% Yield	*TON	%Yield	*TON
1	E+ AA	EA	74.4	33.7	70.7	32.0
2	P + AA	PA	75.6	37.8	72.1	36.0
3	B + AA	BA	78.5	42.9	74.8	40.9
4	BzA + AA	BzAc	81.3	53.6	78.0	51.4
(A)	Microwave irradiated catalysts		CP$_M$		TP$_M$	
			% Yield	*TON	%Yield	*TON
5	E+ AA	EA	77.8	35.2	75.0	33.9
6	P + AA	PA	80.7	40.3	77.5	38.7
7	B + AA	BA	82.2	44.9	80.0	43.7
8	BzA + AA	BzAc	89.1	58.8	85.4	56.3

AA= Acetic acid; E=Ethanol; P= 1-Propanol; B=1-Butanol; BzA= Benzyl alcohol
*Mole ratio of the reactants = 1:1.5 (Alcohol: Acid); Reaction Time = 8 h; Catalyst amount = 0.15 g; Reaction temperature 80˚C for EA; and 115˚C for PA, BA and BzAc; *TON = Turn over number, gram of ester formed per gram of catalyst.*

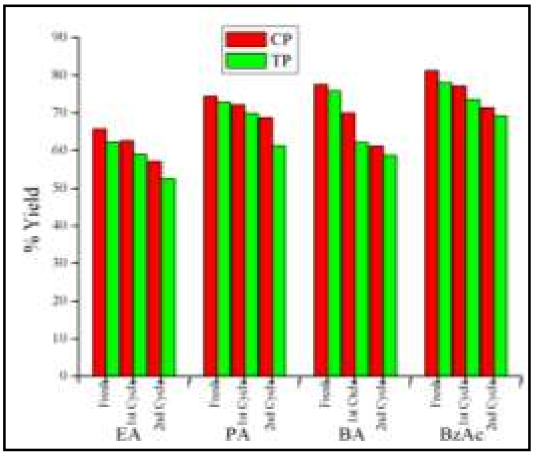


Figure4.4*Comparative catalytic performance of CP and TP for synthesis of monoesters*

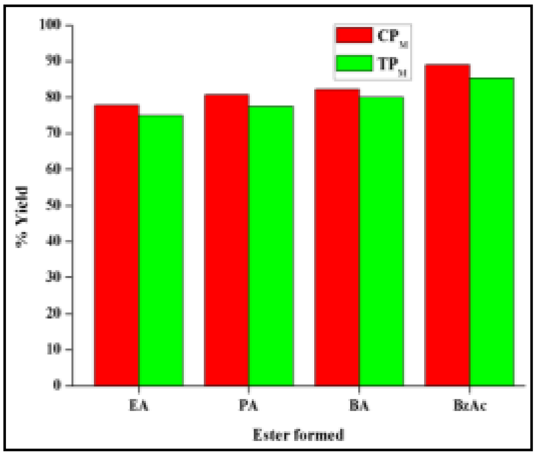


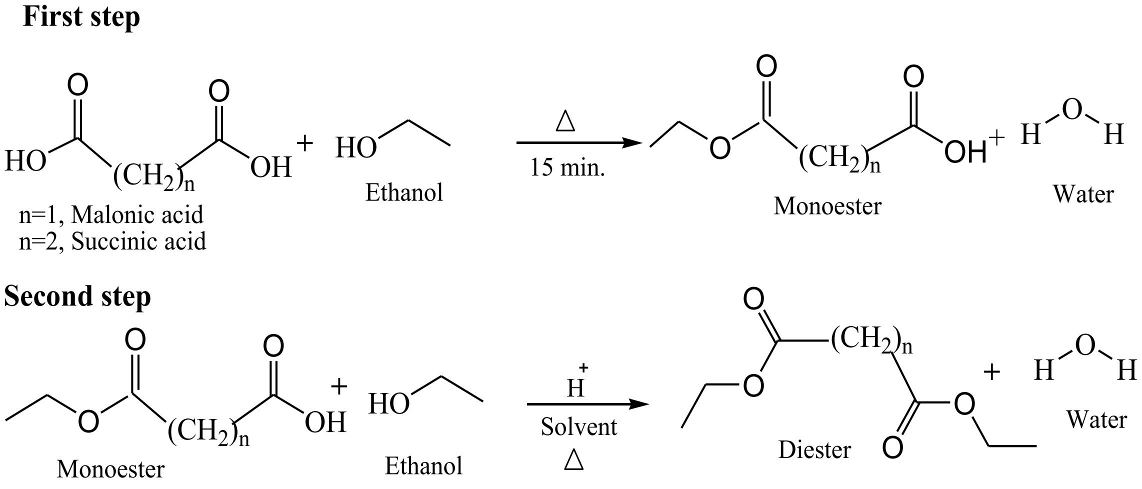
Figure4.5*Comparative catalytic performance of CP_M and TP_M for synthesis of monoesters*

Synthesis of diesters

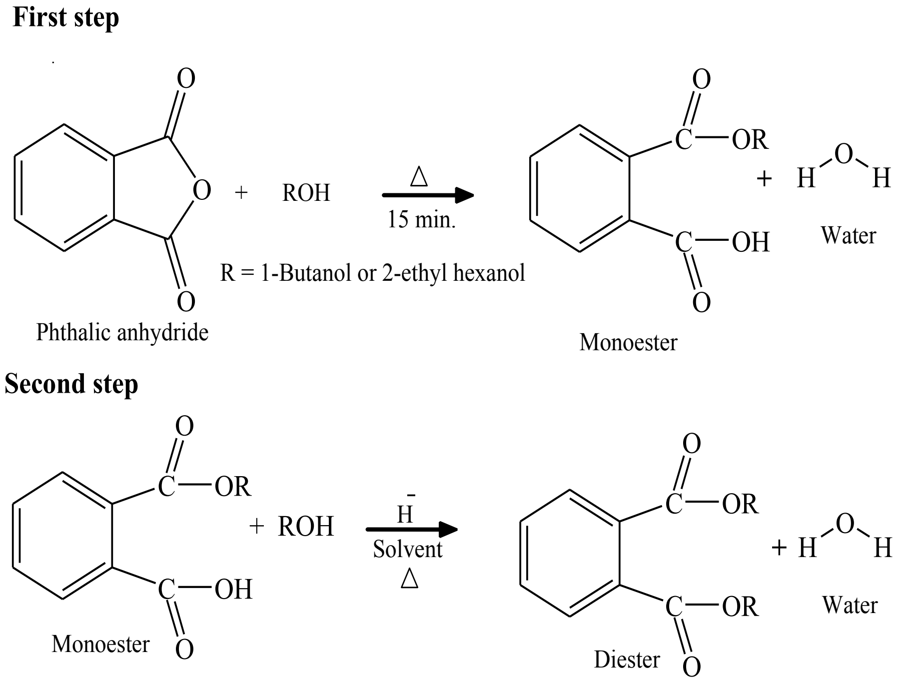
Diestersynthesis, DEM, DES, DBP and DOP canbe presented as shownin **Schemes4.4** (DEM and DES) and**4.5** (DOP and DBP).

Firstly, reaction conditions were optimized for DEM synthesis, varying parameters such as reaction time, catalyst amount and initial mole ratio of the reactant using CP as solid acid catalyst. The optimized reaction conditions for diesters have been presented in **Table 4.3** and a graphical presentation **Figures 4.6 to 4.8**).

At optimized conditions (mole ratio of reactant = 1:2 (diacid/anhydride: alcohol), catalyst amount = 0.15 g and reaction time = 10 h) synthesis of DEM, DES, DBP and DOP was performed using CP, TP, CP_M and TP_M (**Table 4.4**).



Scheme 4.4*Schematic presentation of synthesis of DEM and DES*



Scheme 4.5 *Schematic presentation of synthesis of DOP and DBP*

In all cases, order of diesters formed is DEM > DES > DOP > DBP. The % yields of DOP are higher than DBP which could be attributed to higher boiling point of 2-ethyl 1-hexanol compared to 1-butanol. When boiling point of the alcohol is less than the temperature of the reaction, most of the alcohol will end up in the vapor phase and not be available in the liquid phase. This is the reason why the heavier alcohols react more than the lighter ones. Further, higher yields in case of DEM and DES compared to DOP and DBP is probably due to less steric hindrance felt by incoming ethanol from monoethyl malonate formed in the first step.

The order of diesters formed with reference to performance of catalyst (**Table 4.4, Figures 4.9 and 4.10**) is CP_M> CP > TP_M> TP could be attributed to higher surface acidity as well as protonating ability.

DEM synthesis has been reported by Reddy et al [**109**] using montmorillonite clay, but the yield is low (41 %) and relatively high amount of catalyst (0.5 g) was used. In another report, DEM has been synthesized by Jiag et al using the reaction of CO with $ClCH_2COOC_2H_5$. In this case high yield was observed but the reaction was carried out at high pressure [**120**]. Succinic acid esterification (diethyl succinate – DES) kinetics has been studied by Kolah et al using Amberlyst-15 ion exchange resin as solid acid catalyst [**49**]. However, study on % yields of DES has not been discussed. DOP formation has been catalyzed by solid super acids [**104**] and heteropoly acids [**110**]. Though, % yields of DOP are high, these solid acid catalysts suffer leaching and cannot be reused. Suter [**102**] has reported a non-catalytic process for the manufacture of DOP, at very high temperatures, at which autocatalysis occurs.

When homogeneous liquid acids are used as catalysts for synthesis of diesters, the result is a product that is coloured and of a poor quality. In the present work good % yields of diesters are obtained (**Table 4.4**) with the advantage that the diester is the single product and colourless.

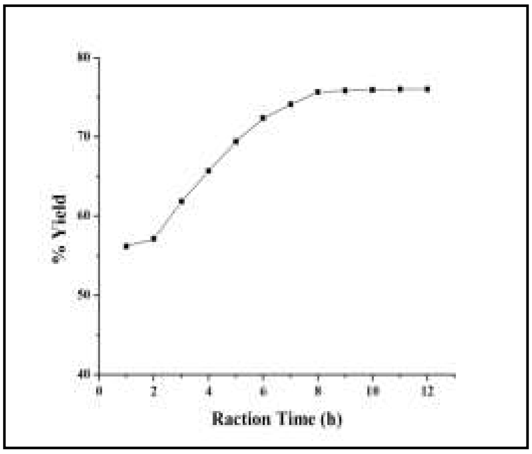


Figure 4.6*Reaction time optimization for DEM synthesis using CP*

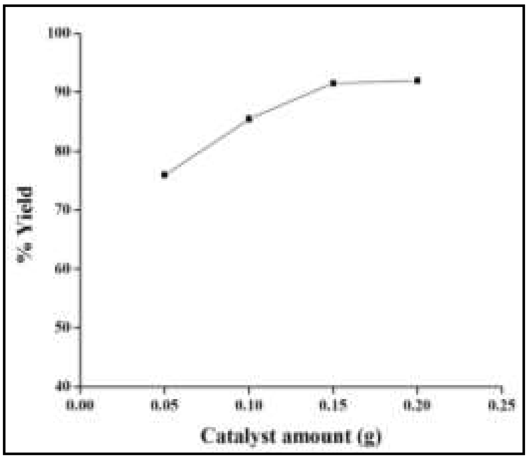


Figure 4.7*Catalyst amount optimization for DEM synthesis using CP*

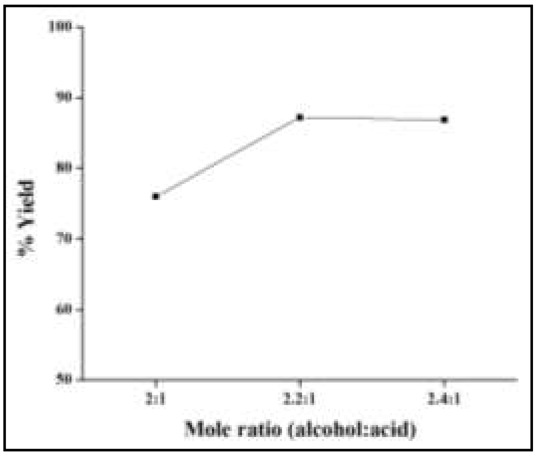


Figure 4.8 *Mole ratio optimization for DEM synthesis using CP*

Table 4.3 *Optimization of reaction conditions for diesters using CP*

Sr. No.	Reactants with their mole ratio	Product	Catalyst Amount (g)	Time (h)	Temp. (^0C)	%Yield
						CP
(A)	Time variation					
1	E + MA (2:1)	DEM	0.05	1	115	56.2
2	E + MA (2:1)	DEM	0.05	2	115	57.1
3	E + MA (2:1)	DEM	0.05	3	115	61.8
4	E + MA (2:1)	DEM	0.05	4	115	65.7
5	E + MA (2:1)	DEM	0.05	5	115	69.4
6	E + MA (2:1)	DEM	0.05	6	115	72.3
7	E + MA (2:1)	DEM	0.05	7	115	74.1
8	E + MA (2:1)	DEM	0.05	8	115	75.6
9	E + MA (2:1)	DEM	0.05	9	115	75.8
10	E + MA (2:1)	DEM	0.05	10	115	75.9
11	E + MA (2:1)	DEM	0.05	11	115	76.0
12	E + MA (2:1)	DEM	0.05	12	115	76.0
(B)	Catalyst amount variation					
13	E + MA (2:1)	DEM	0.10	8	115	85.5
14	**E + MA (2:1)**	**DEM**	**0.15**	**8**	**115**	**91.5**
15	E + MA (2:1)	DEM	0.20	8	115	92.0
(D)	Mole ratio variation					
16	E + MA (2.2:1)	DEM	0.15	8	115	87.2
17	E + MA (2.4:1)	DEM	0.15	8	115	86.9

E=Ethanol; MA=Malonic Acid, DEM = Dimethyle melonate

Table 4.4*% yields of diesters using CP, TP, CP_M and TP_M at optimized condition*

Sr. No	Reactants	Product	CP		TP	
			%Yield	*TON	%Yield	*TON
1	E + MA	DEM	91.5	29.8	89.0	29.0
2	E + SA	DES	67.1	23.4	64.5	22.5
3	B + PhA	DBP	44.0	21.7	42.8	21.1
4	O + PhA	DOP	69.7	47.4	60.0	40.8
(A)	Microwave irradiated catalysts		CP_M		TP_M	
			%Yield	*TON	%Yield	*TON
5	E + MA	DEM	95.5	31.1	93.0	30.3
6	E + SA	DES	73.4	25.6	70.1	24.5
7	B + PhA	DBP	53.7	24.4	50.5	24.9
8	O + PhA	DOP	76.8	52.3	67.4	45.8

*E=Ethanol; B=1-Butanol; O=2-ethyl 1-hexanolMA=Malonic Acid; SA=Succinic Acid; PhA=Phthalic Anhydride;Mole ratio of the reactants = 2:1(Alcohol: Acid); Reaction time = 8 h. Catalyst amount = 0.15 g; Reaction temperature 115˚C for DEM, DES and DBP, 140˚C for DOP; *TON = Turn over number, gram of ester formed per gram of catalyst.*

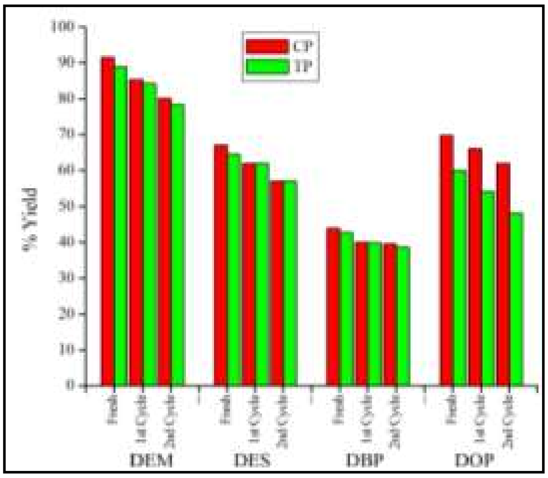


Figure 4.9 *Comparative catalytic performance of CP and TP for synthesis of diesters*

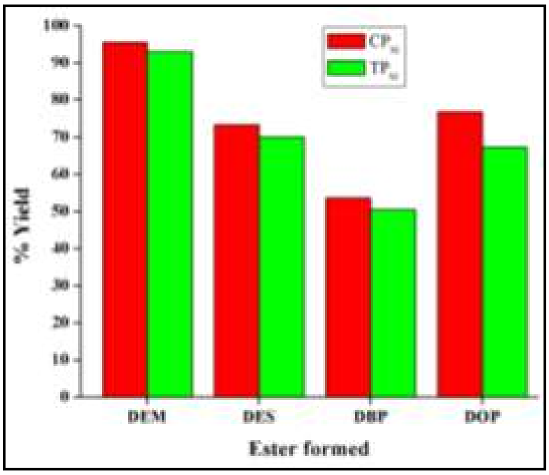


Figure 4.10 *Comparative catalytic performance of* CP_M *and* TP_M *for synthesis of diesters*

Comparing catalyst efficiency/performance of CP and TP with M(IV) phosphates of the class of TMA salts {M(IV) = Zr, Ti and Sn} [**40, 42**], the % yields are observed to be ranging from low to marginal to comparative to high yields (**Table 4.5**).

Regeneration and reuse of catalysts

During the course of the reaction, many a time the catalyst colour changes. This is probably due to the fact that reactant molecules come onto surface of catalyst and enters into reaction to give the product, while a few of them get adsorbed on surface. In each subsequent run, the acid sites in catalysts were regenerated as described in experimental section. Almost 100% catalyst recovery is observed. After regeneration and reuse, decrease in yields are observed which is probably due to the deactivation of catalysts because of substrate molecules getting adsorbed on surface or also entering interstices of the catalyst material [**48**]. Reusability of CP and TP was tested by conducting two runs **(Table 4.6, Figures 4.4 and 4.9**) wherein only a marginal decrease in % yields was observed by 4 - 7 % (**Table 4.6**).

EDX of spent catalysts has been performed for both CP and TP in case of EA synthesis after first catalytic run. EDX of spent CP **(Figure 4.11)** shows atomic % of Ce and P to be 38.24% and 61.76% respectively while EDX of fresh CP **(Figure 2.3a)** shows atomic % of Ce and P to be 34.95 and 65.05%respectively. EDX of spent TP **(Figure 4.12)** shows atomic % of Th and P to be 37.52% and 62.48% respectively while EDX of fresh TP **(Figure 2.5a)**shows atomic % of Th and P to be 35.75 % and 64.25 %. In both cases atomic % of P is observed to have decreased. Probably, decrease in % yield of monoesters and diesters may be due to the leaching of P in catalysts.

Table 4.5 *Comparison of % yields of EA, BzAc, DEM and DOP using TMA salts*

Catalysts	**Substrates (mole ratio)**	**Catalyst Amount (g)**	**Product formed**	**Reaction Temperature (°C)**	**Reaction Time (h)**	**Yields (%)**
TiP **[40]**	E + AA (1:1.5)	0.15	EA	80	8	76.1
SnP **[40]**	E + AA (1:1.5)	0.15	EA	80	8	89.5
ZrP [**42**]	E + AA (1:2)	0.20	EA	80	10	78.1
CP*	E + AA (1:1.5)	0.15	EA	80	8	74.4
TP*	E + AA (1:1.5)	0.15	EA	80	8	70.7
CP_M*	E + AA (1:1.5)	0.15	EA	80	8	77.8
TP_M*	E + AA (1:1.5)	0.15	EA	80	8	75.0
TiP **[40]**	BzA + AA (1:1.5)	0.15	BzAc	115	8	82.3
SnP **[40]**	BzA + AA (1:1.5)	0.15	BzAc	115	8	100
ZrP [**42**]	BzA + AA (1:1.2)	0.20	BzAc	115	10	100
CP*	BzA + AA (1:1.5)	0.15	BzAc	115	8	81.3
TP*	BzA + AA (1:1.5)	0.15	BzAc	115	8	78.0
CP_M*	BzA + AA (1:1.5	0.15	BzAc	115	8	89.1
TP_M*	BzA + AA (1:1.5	0.15	BzAc	115	8	85.4
TiP [**42**]	E + MA (2.5:1)	0.20	DEM	115	10	74.6
ZrP [**42**]	E + MA (2.5:1)	0.20	DEM	115	10	72.8
CP*	E + MA (2:1)	0.15	DEM	115	8	91.5
TP*	E + MA (2:1)	0.20	DEM	115	10	89.0
CP_M*	E + MA (2:1)	0.15	DEM	115	8	95.5
TP_M*	E + MA (2:1)	0.15	DEM	115	8	93.0
TiP [**40**]	O + PhA (1.8:1)	0.15	DOP	145	10	51.7
SnP [**40**]	O + PhA (2.2:1)	0.15	DOP	145	8	65.2
ZrP [**42**]	O + PhA (2.5:1)	0.20	DOP	145	10	72.8
CP*	O + PhA (2:1)	0.15	DOP	145	8	69.7
TP*	O + PhA (2:1)	0.15	DOP	145	8	60.0
CP_M*	O + PhA (2:1)	0.15	DOP	145	8	76.8
TP_M*	O + PhA (2:1)	0.15	DOP	145	8	67.4

**: Present work.*

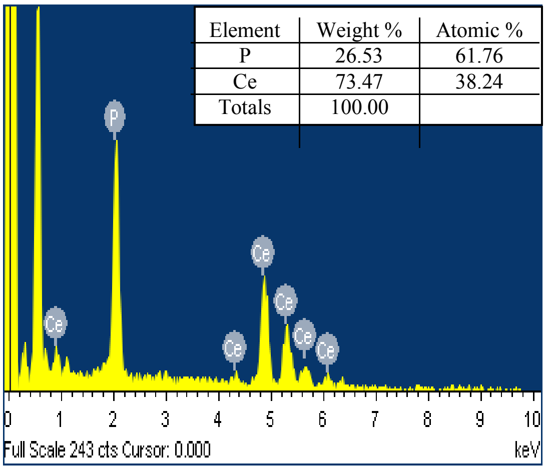
TiP = Titanium(IV) phosphate, SnP = Tin(IV) phosphate and ZrP = Zirconium(IV) phosphate; E = Ethanol; AA = Acetic Acid; BzA= Benzyl Alcohol, MA=Malonic Acid, PhA = Phthalic Anhydride and O = 2-ethyl 1-hexanol;

Solvents: Toluene for EA (Ethyl Acetate),BzAc(Benzyl Acetate) and DEM (Dimethyle Melonate); Xylene for DOP (Dioctyl Phthalate).

Table 4.6*Performance of recycled catalysts*

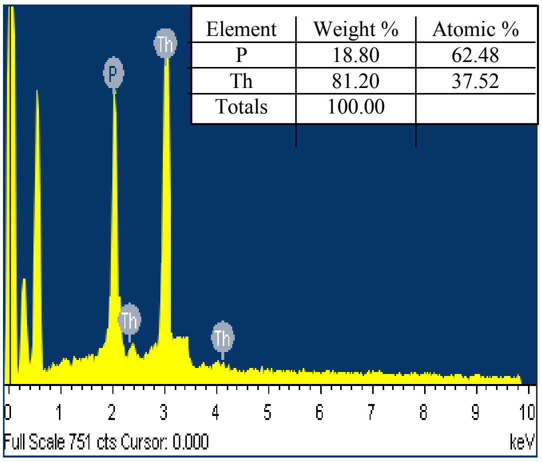
Recycled Catalyst	Catalytic Run	% Yield							
		EA	PA	BA	BzAc	DEM	DES	DBP	DOP
CP	Fresh	74.4	75.6	78.5	81.3	91.5	67.1	44.0	69.7
	First	72.1	88.2	72.0	73.2	85.4	61.9	40.1	66.1
	Second	67.8	87.3	66.1	67.8	80.2	57.1	39.6	62.0
TP	Fresh	70.7	72.1	74.8	78.0	89.0	64.5	42.8	60.0
	First	66.9	68.1	70.1	71.7	84.3	59.1	40.0	54.2
	Second	61.1	62.0	66.6	65.1	78.5	54.1	38.7	48.2

Reaction conditions:
Monoesters: Mole ratio of the reactants = 1:1.5 (Alcohol: Acid); Reaction Time = 8 h; Catalyst amount = 0.15 g; Reaction temperature 80˚C for EA; and 115˚C for PA, BA and BzAc; 115˚C for DEM, DES and DBP, 140˚C for DOP; Diesters: Mole ratio of the reactants = 2:1 (Alcohol: Acid); Reaction time = 8 h. Catalyst amount = 0.15 g; Reaction temperature 115˚C for DEM, DES and DBP, 140˚C for DOP.



Element	Weight %	Atomic %
P	26.53	61.76
Ce	73.47	38.24
Totals	100.00	

Figure 4.11*EDX of spent CP*



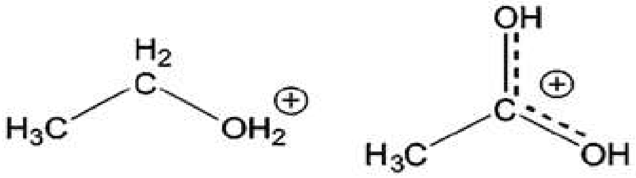
Element	Weight %	Atomic %
P	18.80	62.48
Th	81.20	37.52
Totals	100.00	

Figure 4.12*EDX of spent TP*

4.7.3 Reaction Mechanism in Solid Acid Catalyzed Esterification Reaction

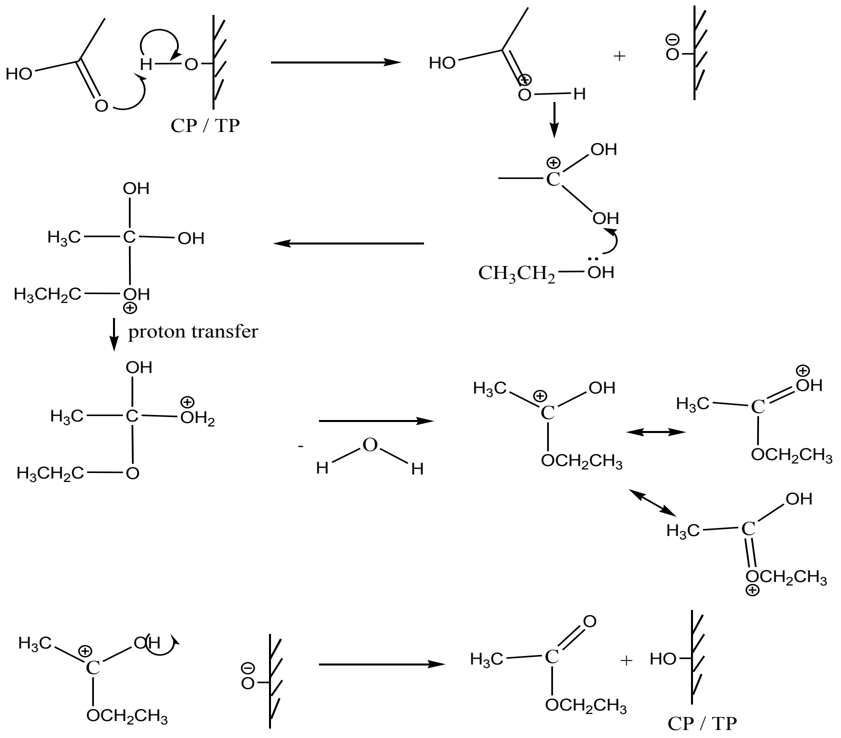
The mechanism of esterification can be different for the various solid acid catalysts and also depends on gas- or liquid-phase operation as well as the substrate. Chu et al [**72**] claim that the esterification mechanism of acetic acid with butanol over carbon-supported HPA catalysts proceeds via a protonated alcohol intermediate, but most authors [**122-124**] proposed a protonated carboxylic acid as the reaction intermediate. The two possible intermediates, protonated ethanol and protonated acetic acid, are shown in **Scheme 4.6.**

The mechanism of diester formation over solid acid catalyst is similar to that of conventional mechanism involving the formation of protonated dicarboxylic acid, using proton donated by the catalyst, followed by nucleophilic attack of alcoholic group to yield the respective monoester. The second carboxylic group present in monoester gets further esterified by the same mechanism in a repeat reaction, which ultimately results in the diester formation [**125**].



Scheme 4.6*Possible protonated intermediates in esterification reaction*

Based on the classical mechanism for acid catalyzed esterification reaction, a mechanism is proposed (**Scheme 4.7**) for esterification of ethanol with acetic acid as a typical case, involving a protonated acetic acid intermediate [**42**].



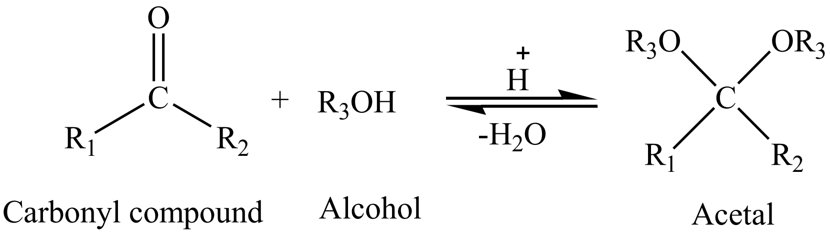
Scheme 4.7*Proposed reaction mechanism for esterification*

4.7.4 Conclusions

The study reveals good performance of all catalysts under study, with advantages of operational simplicity, mild reaction conditions as well as regeneration/reuse of catalysts. Further there is no catalyst or colour contamination in products formed, nor acid waste generation, a limitation in the conventional process. The highlighting feature of the present work is the synthesis of CP_M and TP_M under microwave irradiation in much shorter reaction time, with higher surface acidity including good % yields of esters formed.

4.8 ACETAL FORMATION

Acetalization is an acid catalyzed reaction wherein acetals are derived from carbonyl compounds and alcohols**(Scheme 4.8)**, intensely used in organic synthesis to protect the carbonyl group of ketones and aldehydes, which is sometimes necessary in the manipulation of organic molecules with multiple functional groups[**126, 127**]. Protection of the carbonyl groups of aldehydes and ketones can be accomplished by alcohols [**128**], diols[**129**] or trioxanes[**130**]. Based on the alcohol used, a variety of mono and di-acetal derivatives are obtained. Most of the acetalization processes involve the reaction of carbonyl compound with ethylene glycol in presence of an appropriate acid catalyst.



R_1 = H/alkyl/aryl groups, R_2 and R_3 = alkyl/aryl groups

Scheme 4.8*Acetalization reaction* **[126,127]**

Acetals are oxygenated compounds that can be prepared following different types of reactions:

- Filley et al have studied the reaction between methyl 9,10-dihydroxystearate and long chain aldehydes to form the corresponding cyclic acetal in the presence of *p*-toluenesulfonic acid (PTSA) [**131**].
- Reaction of glyoxylic acid with aliphatic alcohols using cation exchange resins as catalysts [**132**].
- From allylic ethers using cobalt compounds as catalysts [**133**].
- Reacting aldehydes and ketones with trimethyl/triethyl orthoformate at room temperature in the presence of copper(II) tetrafluoroborate as catalyst [**134**].
- Reacting ethanol and acetaldehyde in the presence of an acid catalyst. The main reaction implies the production of 1,1-diethoxy ethane and water [**135**].
- Acetalization of D-gluconolactones with long-chain aldehydes. [**136**]
- Preparing a peroxyacetal from the aldehyde and 1,1-dimethylprop-2-enyl hydroperoxide [**137-140**].

Sharma and Chopade et al have reported innovative reaction systems like reactive distillation or reactors integrating dehydration membranes in order to achieve high conversions for acetal formation [**138-143**]. In both these systems the reaction products, or at least one of the products, are removed from the reaction, shifting the reaction in the forward direction following Le Chatlier's principle.

The importance of acetals lies in the great synthetic utility and their stability to a variety of organic environments/reagents. Cyclic acetals and ketals are the most useful protective groups for the carbonyl functionality widely used in carbohydrate synthesis[**144**].

Besides, the interest of acetals as protecting groups, many of them have found direct applications as solvents in fragrance industries [**145, 146**], cosmetics[**146**], food and beverage additives[**127, 147**], pharmaceuticals[**148**], in the synthesis of enantiomerically pure compounds[**149, 150**], in detergent and lacquer industries[**146**], and in polymer chemistry[**151**].

Pentaerythritol (PET) is an alcohol with formula $C(CH_2OH)_4$[2,2-bis(hydroxymethyl)propane-1,3-diol]. It is a white, crystalline polyol with the neopentane backbone, a versatile building block for the preparation of many polyfunctional compounds. The pentaerythritol react with carbonyl compounds to give pentaerythritol acetals which are useful in many fields. They can be applied as plasticizers and vulcanizers for various polymeric materials, as raw materials for production of valuable resins and lacquers, as physiologically active substances, [**152**] defoamers for washing solution containing anionic surfactant, in motor oils, lubricating oils and hydraulic fluids[**153**]. 1,2-diacetals are efficient protecting groups for vicinal 1,2-diol units in carbohydrates. Acetonide formation is the commonly used protection for 1,2-(*cis*)- and 1,3-diols, which have extensively been used in carbohydrate chemistry to selectively mask the hydroxyls of different sugars [**154**].

4.9 LITERATURE SURVEY IN THE CURRENT AREA OF STUDY

A number of acetalization procedures include the use of corrosive protic acids (HCl, H_2SO_4), Lewis acids ($ZnCl_2$, $FeCl_3$) [**127, 155**], *p*-toluenesulphonic acid[**156**], camphorsulphonic acid[**157**], iodine[**158**], formic acid[**159**] and a series of cationic diphosphine Lewis acid complexes of Pt(II), Pd(II), and Rh(III) etc. [**160, 161**]

However, acetalization procedures mentioned above, require expensive reagents, tedious work-up procedures and neutralization of the strongly acidic media leading to the production of harmful wastes. Though the conventional catalysts are very effective, they produce highly corrosive media and chemically reactive waste streams, whose treatment can be both difficult and hazardous.Hence, these methods suffer limitations, derived from high E-factors and low atom utilization as the catalysts are irreversibly lost[**162**]. In this context, the use of heterogeneous acid catalysts for the reaction is attractive and it may allow carrying it out without the generation of wastes.

In contrast, solid acid catalysts are easier to handle, the general operation of a large chemical process is safer and eco-friendly, obtained product is of high purity and finally the possibility of recycling and reuse of catalysts[**43**]. Environmentally benign solid acid catalysts such as SO_4^{-2}/ZrO_2, SO_4^{-2}/TiO_2[**163**], Ce exchanged montmorillonite[**164**], acidic zeolites[**165-167**], mesoporous silica[**168**] and siliceous mesoporous material[**169, 170**], $Al(HSO_4)_3$[**171**], SBA-15[**172**] and $CeCl_3$[**173**] have been reported to be active for the acetalization reactions. Latcher et al[**154**] have reported catalytic activity of ion exchange resins such as niobium phosphate and amberlyst-35 as solid acid catalyst for the acetalization of hexanal with 2-ethyl-hexanol and also observed higher performance of niobium phosphate compared with Amberlyst-35.

Kannan et al[**152**] have reported acetalization of pentaerythritol with several carbonyl compounds in the presence of an Al-pillared saponite. Firouzabadi et al[**174**] have described application of solid silica chloride, an easily available and efficient catalyst for the preparation of diacetal of pentaerythritol from aldehydes that gives good yields with short reaction times. Pandurangan et al[**175**] have reported synthesis of diacetal from pentaerythritol with carbonyl compounds using MCM-41 molecular sieves. However, catalyst regeneration and reuse studies have not been reported [**174, 175**].It has been earlier reported that Ce exchanged H-Y zeolites and K-10 montmorillonite clays possess more acid sites and produce larger amount of acetal compared to other rare earth exchanged zeolites and clays[**164**].Shaterian et al have reported application of P_2O_5/SiO_2 and P_2O_5/Al_2O_3 as a heterogeneous recoverable catalyst in acetalization of carbonyl compounds with pentaerythritol [**176**].

In the present study the catalytic activity of CP, TP, CP_M and TP_M as solid acid catalysts has been explored using acetal formation as model reaction. A simple, efficient and highly eco-friendly protocol is described for the acetalization of benzaldehyde, cyclohexanone, acetophenone and benzophenone with PET by varying parameters such as reaction time, catalyst amount and mole ratio of the reactants including regeneration and reuse of catalysts. The catalytic activity of the materials has been compared and correlated to surface acidity of the materials.

4.10 ACETALIZATION OF CARBONYL COMPOUNDS WITH PENTAERYTHRITOL(PET)

4.10.1 Experimental

Materials:Pentaerythritol, benzaldehyde, cyclohexanone, acetophenone, benzophenone, silica, ethyl acetate and petroleum etherwere obtained from Across Organics.

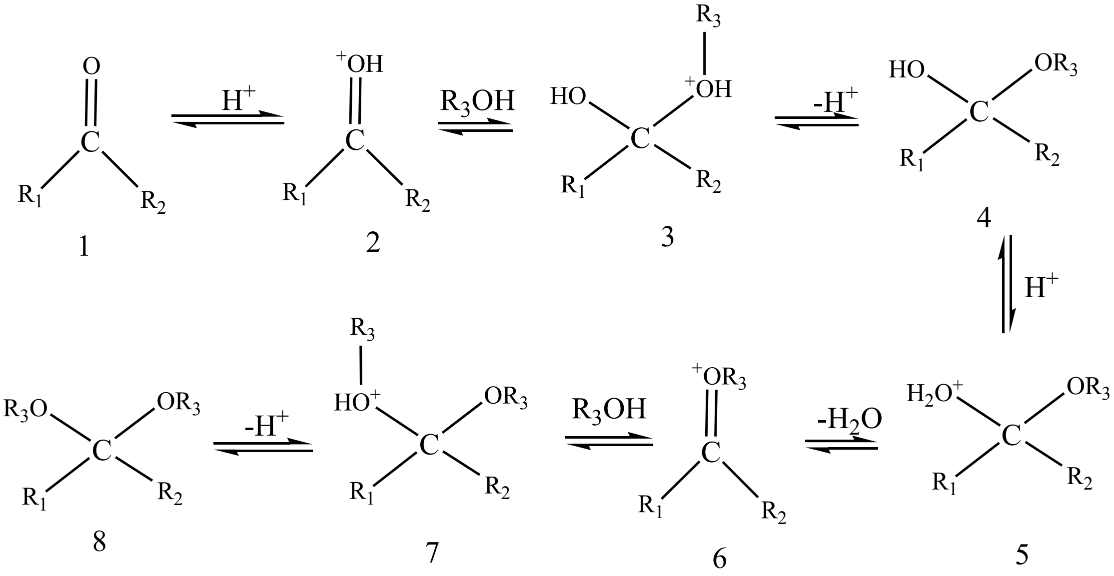
Catalyst Synthesis:The synthesis and characterization of CP, TP, CP_M, and TP_M have been discussed in **Chapter II**, **Section 2.3 and 2.4**.

Experimental setup for acetal formation: In a typical reaction, a 100 mL round bottomed flask equipped with a Dean and Stark apparatus, attached to a reflux condenser was used and charged with carbonyl compound (5-20 mmol), PET (5-10 mmol), catalyst (0.1 - 0.6 g) and toluene as solvent (10 mL) in nitrogen atmosphere. The reactions were carried out varying several parameters such as reaction time,catalyst amount and mole ratio of reactants and these parameters optimized. The progress of the reaction was monitored by TLC (20% of ethyl acetate in petroleum ether). After cooling, the catalyst was filtered off and washed with CH_2Cl_2. The crude product was isolated by distillation and purified through recrystalization (ethanol).

Regeneration of catalyst: The regeneration procedure was performedas described earlier in the text**(Section 4.5.1)**.

4.10.2 Results and Discussion

Acetal formation is a reversible reaction (**Scheme 4.8**) which proceeds by a two-step mechanism (**Scheme 4.9)[139, 140, 163**]. **Scheme 4.9**outlines the mechanism of the acetal formation of carbonyl compounds using solid acid catalyst. In the mechanism presented, carbonyl compound is first protonated by the Brønsted acid sites (H^+ ions of the catalyst) to produce the intermediate 2 which then combines with alcohol to form the hemiacetal 4. Protonation of 4 leads to intermediate 5 which undergoes subsequent dehydration to give 6. Reaction of 6 with a molecule of alcohol gives intermediate 7. Removal of a proton from 7 leads to the formation of the acetal 8**[139, 140, 163]**.

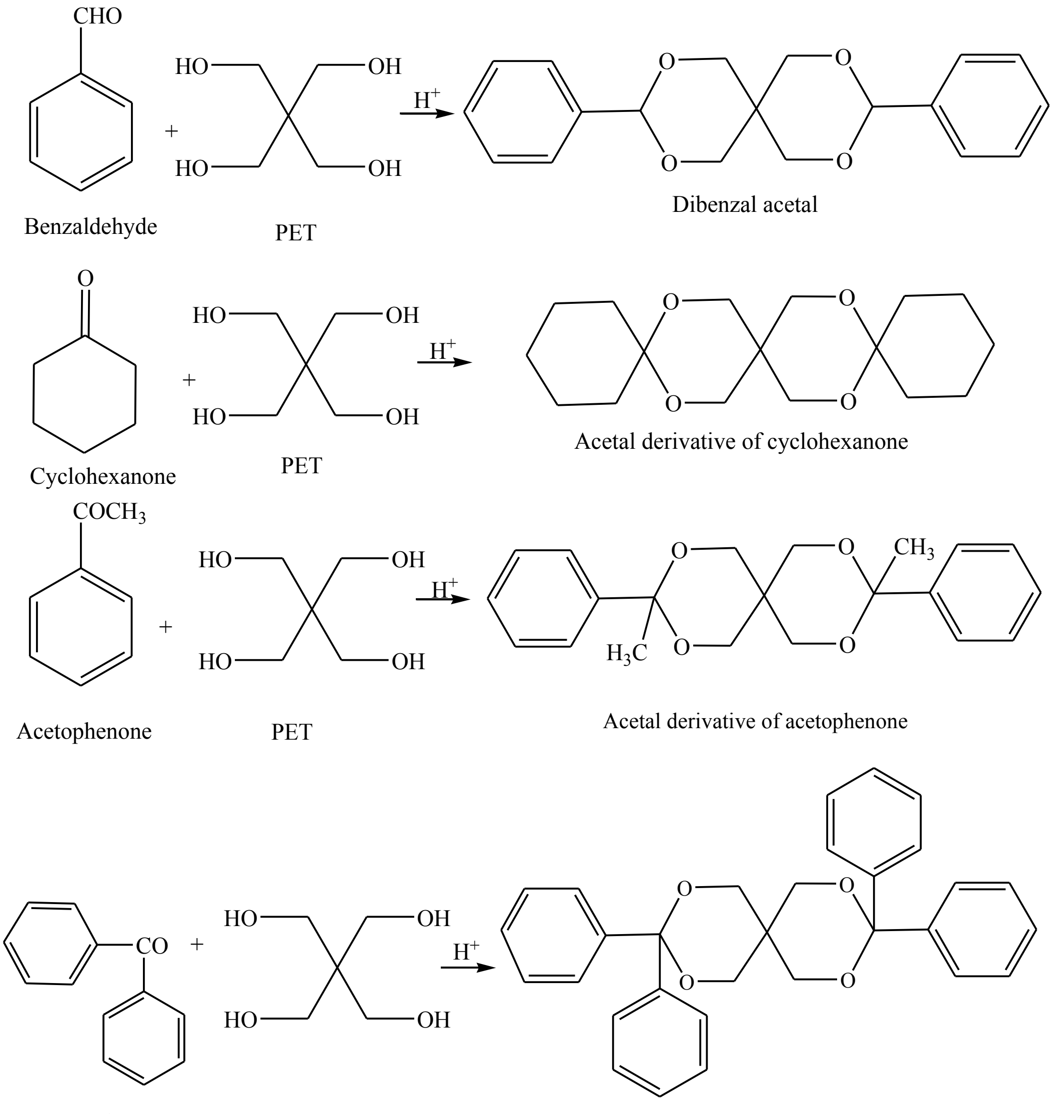


Scheme 4.9*General mechanism for acetalization of carbonyl compounds***[164]**

In the present study acetalization of aldehyde (benzaldehyde) and ketones (cyclohexanone, acetophenone, benzophenone) with PET has been performed as described in experimental section. The acetalization reaction of aldehydes/ketones with PET can be presented as **Scheme 4.10**.

Firstly, reaction conditions were optimized for preparation of diacetal from benzaldehyde and ketones (cyclohexanone and acetophenone) with PET by varying parameters such as reaction time, catalyst amount and initial mole ratio of the reactants using CP as solid acid catalyst. The optimized reaction conditions are presented in **Tables 4.7 to 4.9** and a graphical presentation (**Figures 4.13 to 4.15**).

The effect of reaction time on the product yield of diacetal formed in all cases was studied at refluxing temperature (110˚C) using toluene as solvent with 1:1 mole ratio of PET:benzaldehyde/ketones and 0.1g of catalyst (CP). The reaction reached equilibrium within 4 h (benzaldehyde), 6 h (cyclohexanone) and 8 h (acetophenone). With increasing catalyst amount, which was varied from 0.1g to 0.6 g, % yield increases probably due to increase in the number of acid sites. With reference to mechanism described in **Scheme 4.9**, step 1 is protonation whereas step 3 is formation of hemiacetal followed by deprotonation. For deprotonation to occur, an optimum acidity is required or else if acidity is higher, then the further reaction to form the acetal is inhibited or reaction slows down and thus, the excess acid amount may promote the occurrence of the reverse reaction. Therefore in all cases, optimum catalyst amount was taken as 0.3 g (**Tables 4.7 to 4.9**).



Scheme 4.10 *Reaction of a carbonyl compound and PET to form the corresponding diacetal derivatives*

Equilibrium constants of the acetalization reactions are low. As in any equilibrium reaction, the reaction may be driven to the product side by controlling the concentration of one of the reactants (Le Chatlier's Principle). In order to obtain higher yield of acetal, Le Chatlier's Principle has been followed. The influence of mole ratio of reactants on product yield was studied using 0.3 g of catalyst at the refluxing temperature at optimized reaction time. The mole ratio PET: benzaldehyde/ketones were varied from 1:1 to1:5 and 2:1. It is observed that when the mole ratio increased from 1:1 to 1:4, the product yield increased which is attributed to an increase in chemisorption of benzaldehyde/ketones on the Brønsted acid sites which leads to the polarization of the carbonyl bond where PET makes a nucleophilic attack. Further, for mole ratio 2:1, yield decreased which may be due to the dilution of benzaldehyde/ketones. In the present study, 1:4 mole ratio of PET: benzaldehyde/ketones were used. Diacetal of PET was observed as the single product over all mole ratios of PET and benzaldehyde/ketones.

At optimized condition (reaction time = 4 h (benzaldehyde), 6 h (cyclohexanone), 8 h (acetophenone and benzophenone), catalyst amount = 0.3 g, mole ratio of PET:benzaldehyde/ketones = 1:4 and reaction temperature = 110˚C), acetalization of benzaldehyde, cyclohexanone, acetophenone and benzophenone with PET was performed using CP, TP, CP_M and TP_M (**Table 4.10**).

In all the reactions, acetal derivative of benzaldehyde (dibenzal acetal) was obtained with high % yield. This is probably due to the fact that aldehyde undergoes nucleophilic addition more readily than ketones. Compared to benzophenone and acetophenone, benzophenone being more bulky than acetophenone, shows the lowest reactivity and thus low yields. The rate determining step of acetalization is the formation of a cation from the protonated hemiacetal (**Scheme 4.9**) Hence, the bulkiness of hemiacetals might prevent the attack of the alcohol on the carbonyl carbon atom thereby effecting a change in the rate-determining step. Further, the electron withdrawing power of phenyl group (1 for acetophenone and 2 for benzophenone) in these compounds reduces the easy release of the pair of electron on the carbonyl carbon during the reaction. However, cyclohexanone is more reactive towards nucleophiles than both acetophenone and benzophenone[**163**]. Therefore the reactivity of the ketones decrease in the order cyclohexanone > acetophenone > benzophenone (**Table 4.10**).Turn over number (TON)reflects the effectiveness of a catalyst and this also follows the order of diacetal formation(**Table 4.10**).

The order of % yields obtained with reference to performance of catalyst (**Table 4.10, Figures 4.16 and 4.17**) is CP_M> CP > TP_M> TP could be attributed to higher surface acidity as well as protonating ability (**Chapter II, Table 2.6**).

Regeneration and reuse of catalysts

During the course of the reaction, many a time the catalyst colour changes. This is probably due to the fact that reactant molecules come onto surface of catalyst and enters into reaction to give the product while a few of them get adsorbed on surface. In each subsequent run, the acid sites in catalysts were regenerated as described in experimental section. After regeneration and reuse, decrease in yields are observed which is probably due to the deactivation of catalysts because of substrate molecules getting adsorbed on surface or also entering interstices of the catalyst material [**48**]. Reusability of CP and TP was tested by conducting two runs **(Table 4.11, Figure 4.18**) wherein only a marginal decrease in % yields was observed by 4 - 7 % (**Table 4.11**). When catalyst was used as such (without regeneration) a 7 - 10 % decrease in yields are observed (**Table 4.11**).

EDX of spent catalyst has been performed for both CP and TP in case of dibenzal acetal formation after first catalytic run. EDX of spent CP **(Figure 4.18)** shows atomic % of Ce and P to be 37.97% and 62.03% respectively while EDX of fresh CP **(Figure 2.3a)** shows atomic % of Ce and P to be 34.95 and 65.05%respectively. EDX of spent TP **(Figure 4.19)** shows atomic % of Th and P to be 37.65 % and 62.35 % respectively while EDX of fresh TP **(Figure 2.5a)**shows atomic % of Th and P to be 35.75 % and 64.25 %. In both cases atomic % of P is observed to have decreased. Probably, decrease in % yields of diacetal derivatives may be due to the leaching of P in catalysts.

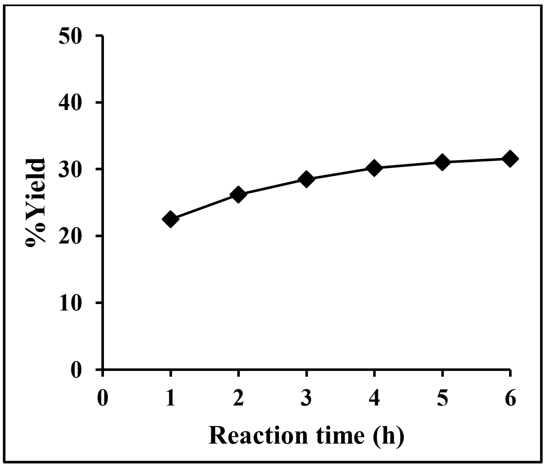


Figure 4.13 *Reaction time optimization of for preparation of diacetal from benzaldehyde and PET using CP*

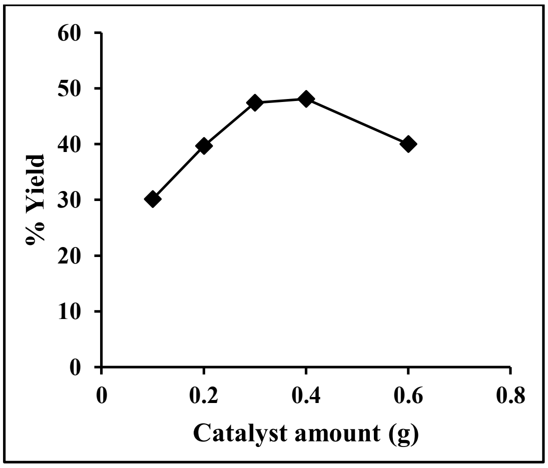


Figure 4.14 *Catalyst amount optimization of for preparation of diacetal from benzaldehyde and PET using CP*

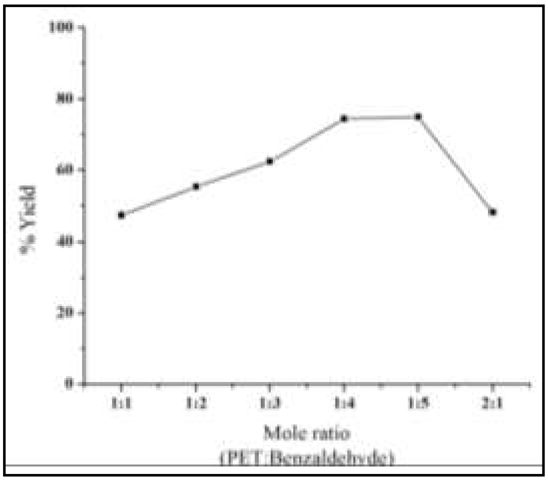


Figure 4.15 *Mole ratio optimization for preparation of diacetal from benzaldehyde and PET using CP*

Table 4.7*Optimization of reaction conditions for preparation of diacetal from benzaldehyde and PET using CP*

No.	Reactants with their mole ratio	Catalyst Amount(g)	Time(h)	*% Yield
(A)	Reaction time variation			
1	PET : Benzaldehyde (1:1)	0.1	1	-
2	PET : Benzaldehyde (1:1)	0.1	2	18.1
3	PET : Benzaldehyde (1:1)	0.1	3	24.4
4	**PET : Benzaldehyde (1:1)**	**0.1**	**4**	**30.1**
5	PET : Benzaldehyde (1:1)	0.1	5	31.0
6	PET : Benzaldehyde (1:1)	0.1	6	31.5
(B)	Catalyst amount variation			
7	PET : Benzaldehyde (1:1)	0.2	4	39.6
8	**PET : Benzaldehyde (1:1)**	**0.3**	**4**	**47.4**
9	PET : Benzaldehyde (1:1)	0.4	4	48.2
10	PET : Benzaldehyde (1:1)	0.6	4	40.6
(C)	Mole ratio variation			
11	PET : Benzaldehyde (1:2)	0.3	4	55.4
12	PET : Benzaldehyde (1:3)	0.3	4	62.4
13	**PET : Benzaldehyde (1:4)**	**0.3**	**4**	**74.5**
14	PET : Benzaldehyde (1:5)	0.3	4	75.0
15	PET : Benzaldehyde (2:1)	0.3	4	48.1

Reaction temperature=110°C *(Toluene)*; **Yields based on conversion of benzaldehyde*

Table 4.8*Optimization of reaction conditions for preparation of diacetal from cyclohexanone and PET using CP*

No.	Reactants with their mole ratio	Catalyst amount (g)	Time (h)	*% Yield
(A)	Reaction time variation			
1	PET : Cyclohexanone (1:1)	0.1	1	--
2	PET : Cyclohexanone (1:1)	0.1	2	12.2
3	PET : Cyclohexanone (1:1)	0.1	3	17.8
4	PET : Cyclohexanone (1:1)	0.1	4	21.2
5	PET : Cyclohexanone (1:1)	0.1	5	25.5
6	**PET : Cyclohexanone (1:1)**	**0.1**	**6**	**29.7**
7	PET : Cyclohexanone (1:1)	0.1	7	31.2
8	PET : Cyclohexanone (1:1)	0.1	8	32.0
(B)	Catalyst amount variation			
9	PET : Cyclohexanone (1:1)	0.2	6	36.2
10	**PET : Cyclohexanone (1:1)**	**0.3**	**6**	**44.2**
11	PET : Cyclohexanone (1:1)	0.4	6	45.0
12	PET : Cyclohexanone (1:1)	0.6	6	40.0
(C)	Mole ratio variation			
13	PET : Cyclohexanone (1:2)	0.3	6	51.4
14	PET : Cyclohexanone (1:3)	0.3	6	58.4
15	**PET : Cyclohexanone (1:4)**	**0.3**	**6**	**72.0**
16	PET : Cyclohexanone (1:5)	0.3	6	72.4
17	PET : Cyclohexanone (2:1)	0.3	6	44.4

*Reaction temperature=110°C (Toluene); *Yields based onconversion ofcyclohexanone*

Table 4.9*Optimization of reaction conditions for preparation of diacetal from acetophenoneand PET using CP*

No.	Reactants with their mole ratio	Catalyst Amount (g)	Time (h)	*% Yield
(A)	Reaction time variation			
1	PET : Acetophenone (1:1)	0.1	1	--
2	PET : Acetophenone (1:1)	0.1	2	9.0
3	PET : Acetophenone (1:1)	0.1	3	13.2
4	PET : Acetophenone (1:1)	0.1	4	16.0
5	PET : Acetophenone (1:1)	0.1	5	18.5
6	PET : Acetophenone (1:1)	0.1	6	21.1
7	PET : Acetophenone (1:1)	0.1	7	25.4
8	**PET : Acetophenone (1:1)**	**0.1**	**8**	**27.0**
9	PET : Acetophenone (1:1)	0.1	9	28.2
10	PET : Acetophenone (1:1)	0.1	10	29.1
(B)	Catalyst amount variation			
11	PET : Acetophenone (1:1)	0.2	8	32.8
12	**PET : Acetophenone (1:1)**	**0.3**	**8**	**38.1**
13	PET : Acetophenone (1:1)	0.4	8	39.0
14	PET : Acetophenone (1:1)	0.6	8	31.0
(C)	Mole ratio variation			
15	PET : Acetophenone (1:2)	0.3	8	41.6
16	PET : Acetophenone (1:3)	0.3	8	52.2
17	**PET : Acetophenone (1:4)**	**0.3**	**8**	**61.0**
18	PET : Acetophenone (1:5)	0.3	8	61.7
19	PET : Acetophenone (2:1)	0.3	8	34.2

*Reaction temperature=110 °C (Toluene); *Yields based onconversion ofacetophenone*

Table 4.10% *Yields of diacetals from benzaldehyde/ketones and PET using CP, TP, CP_M and TP_M*

No.	Reactants	Time (h)	*% Yield (TON)	
			CP	TP
1	PET : Benzaldehyde	4	74.5 (6.9)	68.1 (6.3)
2	PET : Cyclohexanone	6	72.0 (6.3)	59.4 (5.2)
3	PET : Acetophenone	8	61.0 (6.3)	54.7 (5.6)
4	PET : Benzophenone	8	48.2 (7.1)	44.1 (6.5)
(A)	Catalyst reusability			
5	PET : Benzaldehyde 1st Cycle	4	70.0 (6.5)	64.0 (5.9)
6	PET : Benzaldehyde 2nd Cycle	4	64.1 (5.9)	59.2 (5.5)
7	PET : Cyclohexanone 1st Cycle	6	68.2 (6.0)	56.2 (4.9)
8	PET : Cyclohexanone 2nd Cycle	6	61.3 (5.4)	53.4 (4.7)
9	PET : Acetophenone 1st Cycle	8	58.7 (6.0)	50.4 (5.2)
10	PET : Acetophenone 2nd Cycle	8	53.6 (5.5)	48.0 (4.9)
11	PET : Benzophenone 1st Cycle	8	42.1 (6.2)	37.7 (5.6)
12	PET : Benzophenone 2nd Cycle	8	38.4 (5.7)	33.4 (5.0)
(B)	Microwave irradiated catalysts		CP_M	TP_M
1	PET : Benzaldehyde	4	86.1 (8.0)	72.3 (6.7)
2	PET : Cyclohexanone	6	80.3 (7.0)	68.5 (6.0)
3	PET : Acetophenone	8	73.4 (7.6)	62.2 (6.4)
4	PET : Benzophenone	8	54.0 (7.9)	48.3 (7.1)

*Mole ratio of reactants, PET:benzaldehyde/ketones = 1:4; Catalyst amount = 0.3 g;Reaction temperature = 110°C (Toluene); *Yields based on conversion of carbonyl compound taken; TON = Turn over number, gram of diacetal formed per gram of catalyst.*

Table 4.11 *Results for reusability of catalysts (with and without regeneration) in case of dibenzal acetal formation at optimized condition*

Catalyst used	Catalytic Run	%Yield	
		CP	TP
Fresh	--	74.5	68.1
With regeneration	First	70.0	64.0
	Second	64.1	59.2
Without regeneration	First	66.1	60.8
	Second	53.8	52.0

**Yields based on conversion of benzaldehyde*

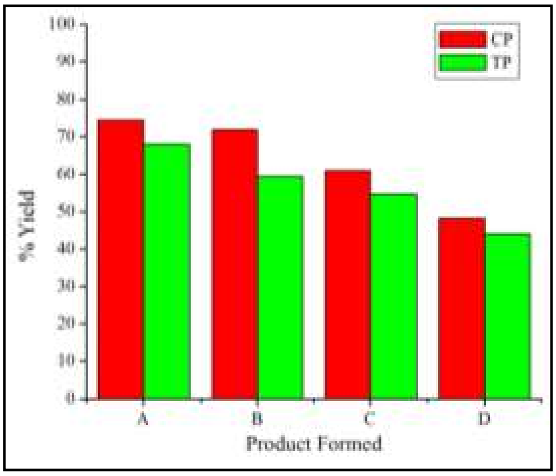


Figure 4.16 *Comparative catalytic performance of CP and TP for preparation of diacetals*

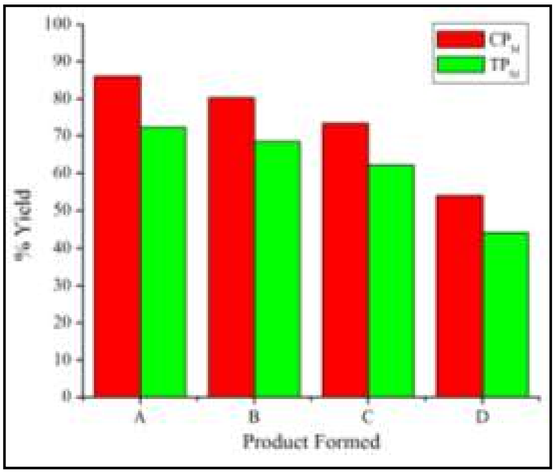


Figure 4.17 *Comparative catalytic performance of CP_M and TP_M for preparation of diacetals*

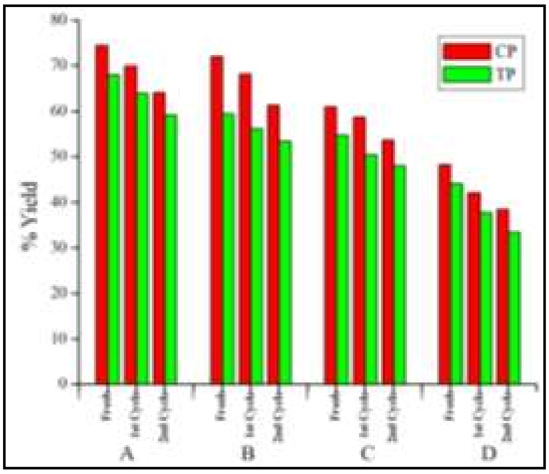
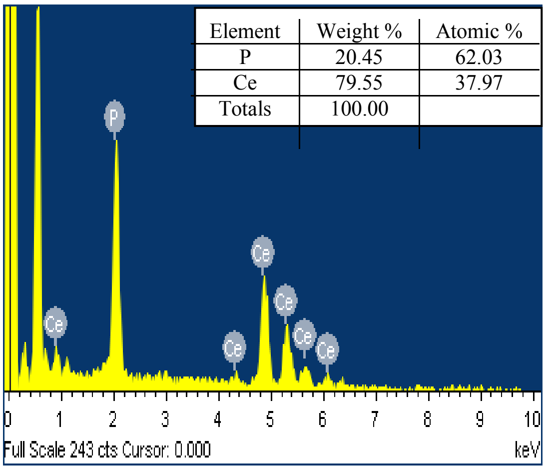


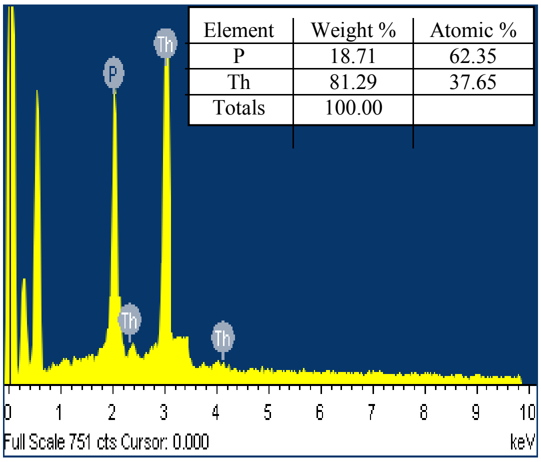
Figure 4.18 *Reusability of CP and TP for preparation of diacetals*

A=Dibenzal acetal; B= Acetal derivative of Cyclohexanone; C=Acetal derivative of Acetophenone; D=Acetal derivative of Benzophenone



Element	Weight %	Atomic %
P	20.45	62.03
Ce	79.55	37.97
Totals	100.00	

Figure 4.19 *EDX of spent CP*



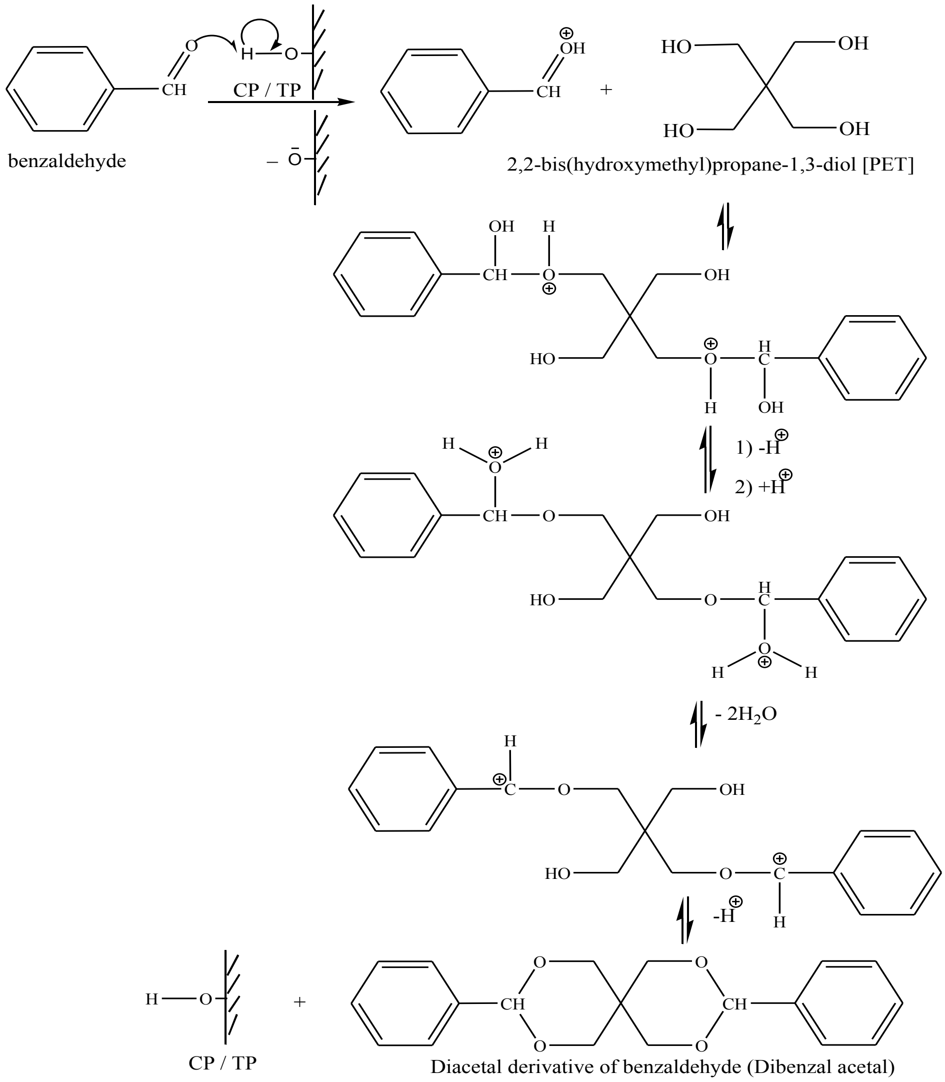
Element	Weight %	Atomic %
P	18.71	62.35
Th	81.29	37.65
Totals	100.00	

Figure 4.20 *EDX of spent TP*

4.10.3 Reaction Mechanism inSolid Acid Catalyzed Acetalization Reaction

Acetal formation is believed to proceed through hemiacetal intermediates [**154**]. Kanan et al [**154**] have reported acetalization mechanism for cyclohexanone with PET using pillared clay catalyst. The carbonyl compound is first protonated by Brønsted acid sites of the catalyst, which provides successive protonation to produce intermediates which combine with hydroxyl groups of PET to form hemiacetals. Protonation and subsequent dehydration gives corresponding acetal. The rate determining step of acetalization is the formation of a cation from the protonated hemiacetal.The bulkiness of hemiacetals might prevent the attack of the second alcohol groupthereby changing the ratedetermining step [**155**].

Based on earlier reports [**155**], a mechanism is proposed (**Scheme 4.11**) for acetalization of benzaldehyde with PET catalyzed by CP and TP.



Scheme 4.11*Proposed mechanism for acetalization of benzaldehyde with PET catalyzed by CP and TP*

4.10.4 Characterization of the Products

The isolated products were characterized by FTIR, ^{1}H-NMR spectroscopy and melting point.

Dibenzal acetal

IR absorptions

υ_{max}/cm^{-1} 2910 (CH), 2862 (CH), 1600 (C=C Aromatic), 1460 (C=C Aromatic), 1390 (CH), 1050 (C-O-C), 805 (C_6H_5), 710 (C_6H_5)

NMR data

δH (100 MHz; $CDCl_3$; Me_4Si), 3.51 (6H, m, $H_{ax,}$ H_{eq}), 4.70 (2H, d, J 11.7, 2 H_{eq}), 5.42 (2H, s, 2 × PhCH), 7.10–7.60 (10H, m, 2 × Ph)

Melting Point: 155°C (Ethanol)

Acetal derivative of cyclohexanone

IR absorptions

υ_{max}/cm^{-1} 2960 (CH), 2870 (CH), 1140 (C-O-C)

NMR data

δH H(100 MHz; $CDCl_3$; Me_4Si) 1.4-1.7(20H, m, 2 × $(CH_2)_5$), 3-3.5 (8H, m, $(CH_2O)_4$)

Melting Point: 116°C (Ethanol)

Acetal derivative of acetophenone

IR absorptions

υ_{max}/cm^{-1} 2970 (CH), 2890 (CH), 1600 (C=C Aromatic), 1468 (C=C Aromatic), 1365 (CH), 1150 (C-O-C), 790 (C_6H_5), 700 (C_6H_5)

NMR data

δH (100 MHz; $CDCl_3$; Me_4Si) 1.51 (6H, s, 2 × Me), 3.15 (2H, dd, J 11.1, 2.4, 2 × H_{eq}), 3.30 (2H, d, J 11.1, 2 × H_{ax}), 3.60 (2H, d, J 11.7, 2 × H_{ax}), 4.48 (2H, dd, J 11.7, 2 × H_{eq}), 7.25-7.70 (10H, m, 2 × Ph).

Melting Point: 146°C (Ethanol)

Acetal derivative of benzophenone

IR absorptions

υ_{max}/cm^{-1} 2975 (CH), 2880 (CH), 1615 (C=C Aromatic), 1480 (C=C Aromatic), 1390 (CH), 1050 (C-O-C), 755 (C_6H_5), 770 (C_6H_5)

NMR data

δH (100 MHz; $CDCl_3$; Me_4Si) 3.6 (8H, s, $(CH_2O)_4$), 7.14–7.32 (20H, m, 2 × $(Ph)_2$).

Melting Point: 160°C (Ethanol)

4.10.5 Conclusions

The work outlined herein reveals the promising use of CP and TP as solid acid catalysts in acetal formation with high selectivity of the products, advantages being operational simplicity, mild reaction conditions, no catalyst contamination in products formed, no acid waste generation as well as regeneration and reuse of catalysts. Further, the catalysts CP_M and TP_M synthesized (under microwave condition) in a much shorter reaction time with higher surface acidity and good % yields of diacetal is encouraging.

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