CHAPTER 2

SYNTHESIS
AND
CHARACTERIZATION
OF
M (IV) PHOSPHATES
M (IV) PHOSPHONATES
METAL EXCHANGED PHASES
OF M (IV) PHOSPHATES
2.1 INTRODUCTION

The challenge for the synthetic chemist, by the demands of material technology, is to design and synthesize in high yield, novel materials, whose structures and properties can be predicted, varied and controlled, through eco-friendly routes. The interest in novel materials with predictable structures and properties for specific applications has given rise to the development of a variety of preparation methodologies. The method chosen for any material preparation, depends not only on the material composition, but also on the form in which it is required for a specific application. Some of the synthetic procedures available to the inorganic chemist for the preparation of bulk solids are –

1 Coprecipitation
2 Hydrothermal methods
3 Electrochemical methods
4 Vapor phase transport
5 High pressure synthesis
6 Pyrolysis
7 Photolysis
8 Intercalation
9 Sol-gel processes
10 Ion exchange

With an increasing concern around the world for green technologies, much attention is focused towards the development of alternative synthetic routes which have zero emission. From an industrial point of view, a method that does not employ high temperatures, could be favored, because of the ensuing energy savings.

Solid state chemistry is an important tool of material science. A combination of the two, leads to tailor made materials with desired properties. The present demands are, making use of soft chemistry routes (low
temperatures) which is popularly known as “Chemie Douce” by the French. Soft chemistry routes include, sol-gel method of synthesis, ion exchange, intercalation, hydrolysis, dehydration and reduction, that can be carried out at relatively low temperatures.

The traditional ceramic method consists of heating together two solids, with intermittent mixing and grinding, which react to form the required product. Despite the widespread use in industries as well as in the laboratories, it has certain disadvantages; high synthesis temperatures, which require large energy inputs and the reactions are slow, as they are generally carried out in the solid state. Besides, the homogeneity of the reactants, is a big issue to be taken care of, for the phasic purity of the desired product.

The present chapter deals with the synthesis and characterization of the following materials

1. AMORPHOUS MATERIALS
   Zirconium phosphate (ZrPA)
   Tin phosphate (SnPA)
   Titanium phosphate (TiPA)

2. CRystalline MATERIALS
   Zirconium phosphate (ZrPC)

3. METAL PHOSPHONATES (Hybrid materials)
   Zirconium hydroxyethylidene diphosphonate (ZrHEDP)
   Zirconium [amino tris(methylene phosphonate)] (ZrATMP)
   Zirconium [(diethylenetriaminepentakis(methylene phosphonate)]
   (ZrDETPMP)

4. METAL EXCHANGED PHASES
   Ruthenium exchanged – RuZrPA and RuZrPC
   Palladium exchanged – PdZrPA and PdZrPC
   Copper exchanged – CuZrPA
   Lithium exchanged – LiZrPA
Amorphous metal phosphates and phosphonates have been prepared by sol-gel technique, crystalline Zr(IV) phosphate has been prepared by the fluoro complex method [1] and metal exchanged phases have been prepared by ion exchange technique.

2.2 SOL-GEL PROCESS

The overall sol-gel process can be represented by the following sequence of transformations:

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Precursor -----> Sol -----> Gel -----> Product
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**Precursors** are starting materials, in which the essential basic entities for further network formation are present in the correct stoichiometry.

**Sol** is a colloidal suspension of particles in a liquid, the particles typically ranging from 1–100 nm in diameter.

**Gel** is a semi–rigid solid, in which solvent is contained in a framework of material, which is either colloidal (essentially a concentrated sol) or polymeric.

Sol-gel process can be distinguished from precipitation by its specific property to stabilize a finely dispersed (mostly colloidal) phase in solution by surface chemistry. The size of solid agglomerates is usually in the range 1-100 nm.

Important steps involved in sol-gel synthesis are –

**Hydrolysis** – It involves reaction of inorganic or organometallic precursor with water or a solvent, at ambient or slightly elevated temperature. Acid or base catalysts are added to speed up the reaction.

**Polymerization** – This step involves condensation of adjacent molecules wherein H₂O and alcohol are eliminated and metal oxide linkages are formed. Polymeric networks grow to colloidal dimensions in the liquid (sol) state.

**Gelation** – It leads to the formation of a three dimensional network through out the liquid, by the linking up of polymeric networks. The system becomes somewhat rigid, characteristic of a gel, on removing the solvent from the sol.
Aggregation of the small polymeric units, to the main network structure progressively continues on ageing the gel.

**Drying** – Here solvent is removed at moderate temperatures (< 470 K) leaving the residue behind. For obtaining high surface area and low bulk density aerogel powders, the solvent is removed supercritically.

**Dehydration** – This step is carried out between 670 and 1070 K to drive off the organic residues and chemically bound water, yielding a glassy metal oxide with up to 20–30% microporosity.

**Densification** – Temperature in excess of 1270 K are used to form the dense oxide product.

The choice of reagents, additives, concentration, ionic strength of reactants, pH, addition sequence, reaction and drying conditions, allows the control of pore structure and porosity, composition, surface polarity, surface acidity and crystallinity.

In practice however, a modified sol-gel route is followed. One of the important features in this modified route is the use of templates (structure directing agents). Templates when used at optimum concentrations, referred to as Critical Micelle Concentration (CMC), orient themselves to form an assembly with the polar head groups pointing outside, around which the anions orient to form a network. The layers of inorganic materials seem to distort and crosslink around the polar head groups to form a new mesoporous structure. The driving force for this layer folding, is most likely the ion pairing between the positively charged ammonium head groups and the negatively charged inorganic components. The template can subsequently be removed from the system, either by solvent extraction method or by calcination, to obtain finished product with predetermined pore size and structure (Fig.2.a). The sol gel method presents an attractive and easy-to-tailor alternative to conventional synthesis methods, such as ceramic firing.
Figure 2.a Mechanism of template assisted synthesis reproduced from [2].

Sol-gel process has its own advantages and disadvantages over the traditional ceramic methods:

**Advantages of Sol-Gel Process**

1. High homogeneity - intimate mixing of raw materials
2. High purity
3. Low temperature processing
   a. energy savings
   b. minimize evaporation losses
   c. minimize air pollution
   d. no reaction with container
4. More uniform phase distribution in multicomponent systems
5. New crystalline phases from new noncrystalline solids
6. Better glass products from special properties of gel
7. Materials with improved and desired properties (Tailor made materials) can be obtained
8. Porous materials using templates

**Disadvantages of the Sol-Gel Process**

1. Large shrinkage during processing
2. Residual fine pores
3. Residual hydroxyl groups when hydroxides are used
4. Residual carbon (originating from templates)
5. Health hazards of organic solvents
6. Long processing times
2.3 ION EXCHANGE

Ion-exchange is defined as a process, where an insoluble substance removes ions of positive or negative charge, from an electrolyte solution and releases other ions of like charge into solution, in a chemically equivalent amount. At some point, during the ion exchange process, ion exchange equilibrium is established.

Ion exchange is, with few exceptions, a reversible process. It resembles sorption, in that, in both cases, dissolved species is taken up by a solid. The characteristic difference between the two phenomena is that ion exchange, in contrast to sorption, is a stoichiometric process. Every ion which is removed from the solution is replaced by an equivalent amount of another ionic species of the same sign from the ion exchange material. In sorption on the other hand, a solute (an electrolyte or non electrolyte) is taken up without being replaced by equivalent species. Though this distinction seems to be clear-cut, it is sometimes difficult to apply it in practice, since every ion exchange process is accompanied by electrolyte sorption or desorption, and most of the common sorbents such as alumina and activated carbon can act, in turn, as ion exchangers.

Ion exchange process finds application in various operations [3]:

1) Removal of Ions
2) Fractionation of mixtures
3) Transformation of ionic species
4) Concentration of ions
5) Catalysis

Of late, one of the growing applications of ion exchange has been in the area of Heterogenised Homogeneous Catalysis. Homogeneous catalysts are heterogenised by supporting them onto insoluble supports, in such a manner that the environment of the catalyst is essentially unchanged. The term heterogenising refers to a process, whereby a homogeneous transition metal ion or a metal complex is immobilized or anchored onto an inert support. The supports mainly used so far are organic polymeric supports (ion exchange
resins) and the inorganic oxides – silica, alumina, zirconia etc. Though the method of anchoring on organic resins is a simple ion exchange technique, the greatest drawback is poor heat transfer ability which leads to degradation at low temperatures. On the other hand, inorganic oxides though thermally stable upto fairly high temperatures do not possess proper sites for anchoring (only weak hydroxyl groups are present on the surface). The ideal material to be used as support is therefore the tma salts. Due to cation exchange properties, the method of anchoring is simple. Besides, the material also possesses good thermal stability.

2.4 SYNTHETIC ROUTES TO HYBRID MATERIALS

Hybrid materials [4] in general can be obtained through intercalation/anchoring/pillaring/encapsulation or sol-gel method. Intercalation and pillaring occur in case of layered materials whereas anchoring generally occurs in case of amorphous materials [5]. It is reported that the nonpolar species get sorbed, whereas the polar ones get ion exchanged [6]. Encapsulation usually occurs in case of mesoporous materials [7-9].

2.4.1 Intercalation

Intercalation reactions of solids involve the insertion of a guest species (ion or molecule) into a solid host lattice without any major rearrangement of the solid structure. It may be presented as –

\[ \times \text{ (guest)} + \square \times \text{ (host)} \rightarrow \text{(Guest)}_{x} \text{ [Host]} \]

\[ \square = \text{vacant site} \]

Intercalation mainly refers to layered structures that act as hosts. A general feature of these structures are that the interlayer interactions are weak, while the intra layer bonding is strong. In this process, diffusion of ions or molecules with diameters larger than the interlayer dimension occurs, which
results in an increase of the interlayer region. Thus larger molecules and cations can be easily accommodated in the interlayer region. Intercalation leads to the development of organic-inorganic hybrids. They have been attracting significant attention as a new class of materials, since the combination of an inorganic component and an organic component has the potential to provide improved and tunable properties. [10-14].

Intercalation proceeds concomitantly in each interlayer region. The diffusion begins at the edges and proceeds towards the bulk of the crystallites with moving phase boundary, so that during the intercalation process, both the original proton form and the new intercalate phase, co-exist in the same crystal. The extent of intercalation of an organic molecule with the inorganic host is dependent on the type of host-guest interaction. Some guests such as alcohols and glycols are held to the inorganic hosts through weak bonds (van der Waals interaction or hydrogen bonds), others such as monoamines and diamines, are bound by ionic interactions [15]. In porous structures such as zeolites, the diffusion occurs in the narrow windows or small zeolitic type cavities.

2.4.2 Pillaring

It is a process whereby spacers or pillars are introduced into lamellar/layered structures. Spacers/pillars are guest molecules which increase the lateral spacing of layers, thereby allowing the diffusion of large molecules. By varying the lateral separation, the pore structure can be tailored to differentiate adsorbates on the basis of molecular size. The molecular sieving property of such a pillared material is precise enough to distinguish between molecules differing in size by a few tenths of an Angstrom unit.

Owing to the existence of a large number of layered structure types and their ability to intercalate a variety of guests, pillared derivatives can be prepared in which chemical functionality is intelligently designed into the layered host, the intercalated guest, or both.

Three important criteria for Pillared lamellar solids are
1 The gallery species must be sufficiently robust to provide vertical expansion of the galleries and prevent gallery collapse on dehydration.
2 The pillars must be laterally spaced to allow for interpillar access by molecules at least as large as nitrogen.
3 The host layers must be sufficiently rigid to sustain the desired lateral separation of pillars [16].

2.4.3 Anchoring

Traditionally, anchored systems are synthesized by the process of sorption of the organic species from solutions onto porous solid supports. Derivatization on the other hand is obtained through the process of intercalation, thereby increasing the interlayer distance [5].

Another method employed for the derivatization of inorganic compounds is that, the inorganic metal salt is directly treated with the organic reagent (sol-gel process). Sol-gel processing is one of the promising routes to inorganic-organic hybrids, since metal-oxygen networks can be formed using a “Chimie Douce” approach involving hydrolysis and polycondensation [17]. This is how M(IV) phosphonates can be synthesized. When tetravalent metal is treated with phosphonic acids, M(IV) phosphonates are obtained (phosphonic acids are obtained when the H of the OH in the tetrahedral moiety of PO(OH)₃ is replaced by R, where R=alkyl or aryl moiety, containing functional groups such as amino, alcoholic, carboxylic, sulfonic etc.).

In the present study, phosphonates with progressively increasing number of protons in the phosphonate moiety have been selected, to synthesize their zirconium based compounds. HEDP (Hydroxyethylidenediphosphonic acid), ATMP [Aminotris(methyleneephosphonic acid)] and DETPMP [Diethylenetriaminepentakis(methyleneephosphonic acid)] are phosphonic acids possessing structural hydroxyl groups, five, six and ten respectively (figure 2.b).
2.5 EXPERIMENTAL

2.5.1 Materials

Zirconium oxychloride (ZrOCl₂·8H₂O) was obtained from Loba chemicals. Stannic chloride and Titanium tetrachloride were obtained from Spectrochem India Pvt. Ltd. Sodium dihydrogen phosphate (NaH₂PO₄·2H₂O) as well as HF was obtained from Merck India. HEDP, ATMP and DETPMP were obtained from Hydro Chem. India Pvt. Ltd. Palladium chloride and Ruthenium chloride were received from S.D. Fine Chem. India Pvt. Ltd. H₂SO₄, HNO₃, HCl, NaOH, KOH and organic solvents used were of analytical grade.
A general procedure for the preparation of TMA salts [M(IV) phosphate] is presented in the following scheme

Sodium dihydrogen phosphate
- Parameters:
  - M:X (mole and volume ratio)
  - Temperature (room temperature or elevated)
  - Rate and Mode of mixing
  - Continuous stirring
  - pH = 1-2

Tetravalent metal salt solution
[M(IV) = Zr, Ti, Sn etc.]

Gelatinous precipitate
- 1) Ageing
- 2) Filtration
- 3) Washing with conductivity water (adhering ion removal)
- 4) Drying (303K)
- 5) Grinding and sieving (30-60 mesh size)

Raw product
- 1) Acid treatment (0.1 M HNO₃, 10 ml/gm); batch method (contact time - 1hr)
- 2) Washing to remove adhering acid
- 3) Drying

Active (H-form) TMA salt

Sodium dihydrogen phosphate can be replaced by salts of tungstates, arsenates molybdates etc. to obtain a variety of TMA salts. In order to obtain M(IV) phosphonates, sodium dihydrogen phosphate is replaced by phosphonic acids.

2.5.2 Preparation of zirconium phosphate (ZrPA)
ZrPA has been prepared by dropwise mixing (flow rate ~2 ml/min.) of aqueous sodium dihydrogenphosphate solution (0.2 M, 100 ml) with aqueous solution of ZrOCl₂·8H₂O (0.1 M, 100 ml, preheated to 343 K) with continuous stirring. The pH of the gel was maintained around 1-2. The gelatinous precipitates obtained was digested for 1 h, filtered, washed with conductivity water till removal of chloride ions, followed by drying at room temperature.
2.5.3 Preparation of tin phosphate (SnPA)
SnPA has been prepared by dropwise mixing (flow rate = 2 ml/min.) of aqueous sodium dihydrogenphosphate solution (0.2 M, 100 ml) with aqueous solution of stannic chloride (0.1 M, 100 ml, preheated to 343 K) with continuous stirring. The pH of the gel was maintained around 1-2. The gelatinous precipitates obtained was digested for 1 h, filtered, washed with conductivity water till removal of chloride ions, followed by drying at room temperature.

2.5.4 Preparation of titanium phosphate (TiPA)
TiPA has been prepared by dropwise mixing (flow rate = 2 ml/min.) of aqueous sodium dihydrogenphosphate solution (0.2 M, 100 ml) to acidic titanium tetrachloride solution (0.1 M in 20% HCl, 100 ml, preheated to 343 K) with continuous stirring. The pH of the gel was maintained around 1-2. The gelatinous precipitates obtained was digested for 1 h, filtered, washed with conductivity water till removal of chloride ions, followed by drying at room temperature.

2.5.5 Preparation of zirconium hydroxy ethylidene diphosphonate (ZrHEDP)
ZrHEDP has been prepared by dropwise addition (flow rate = 2 ml/min) of aqueous solution of sodium salt of HEDP (0.2 M, 100 ml) to zirconium oxychloride solution (0.1 M, 100 ml, pH = 1 with HCl, preheated to 343 K) with continuous stirring. The pH of the gel was maintained around 1-2. The gelatinous precipitates obtained was digested for 1 h, filtered, washed with conductivity water till removal of chloride ions, followed by drying at room temperature.

2.5.6 Preparation of zirconium [amino trismethylene phosphonate] (ZrATMP)
ZrATMP has been prepared by dropwise addition (flow rate = 2 ml/min.) of ATMP solution (0.2 M, 100 ml) to aqueous zirconium oxychloride solution (0.1 M, 100 ml, preheated to 343 K with continuous stirring. The pH of the gel
was maintained around 1-2. The gelatinous precipitates obtained was digested for 1 h, filtered, washed with conductivity water till removal of chloride ions, followed by drying at room temperature.

2.5.7 Preparation of zirconium [(Diethylene triamine pentakis(methyl phosphonate)] (ZrDETPMP)

ZrDETPMP has been prepared by dropwise addition (flow rate =2 ml/min.) of DETPMP solution (0.2 M, 100 ml) to aqueous zirconium oxychloride solution (0.1 M, 100 ml, preheated to 343 K) with continuous stirring. The pH of the gel was maintained around 1-2. The gelatinous precipitates obtained was digested for 1 h, filtered, washed with conductivity water till removal of chloride ions, followed by drying at room temperature.

2.5.8 Conversion to the hydrogen form (H-form)

All the materials were sized by sieving [(30-60 mesh) ASTM] and finally converted to acid form by treating 5 gm of the material with 50 mL of 1M HNO₃ for 30 min. with occasional shaking. The sample was then separated from acid by decantation and washed with conductivity water for removal of adhering acid. This process (acid treatment) was repeated at least five times. After final washing, the material was dried at room temperature. This material was used for all studies.

2.5.9 Preparation of crystalline zirconium phosphate (ZrPC)

Crystalline material was prepared by HF method [1]. To a 0.2 M solution of ZrOCl₂·8H₂O, containing HF and Zr in the molar ratio F/Zr = 5.2 was added 46 ml o-phosphoric acid (85%). It was heated on a water bath (70–75°C) for a period of 5-6 days. Distilled water was added periodically to keep the volume constant. The microcrystals obtained were filtered from the system washed thoroughly with deionised water and dried at room temperature. HF forms a complex with zirconium and when the concentration of hydrofluoric acid is sufficiently high, precipitation by phosphoric acid is inhibited. The
solution is then heated on a water bath for a period of 5-6 days maintaining the volume to be constant throughout the period. On evaporation the concentration of fluoride is lowered, zirconium fluoride complex gradually dissociates and zirconium phosphate begins to precipitate.

2.5.10 Preparation of metal exchanged phases

2.5.10.1 Preparation of RuZrPA and RuZrPC

RuZrPA and RuZrPC have been prepared by equilibrating aqueous RuCl₃ solution (0.1% w/v, 100 ml) with 2 g ZrPA or ZrPC as the case may be, with continuous stirring at 323 K for 100 h. The solid was separated by filtration and washed with conductivity water for removal of adhering ions and dried at room temperature.

2.5.10.2 Preparation of PdZrPA and PdZrPC

PdZrPA and PdZrPC have been prepared by equilibrating acidic PdCl₂ solution (0.1% w/v, 100 ml) with 2 g ZrPA or ZrPC as the case may be, with continuous stirring at 323 K for 100 h. The solid was separated by filtration and washed with conductivity water for removal of adhering ions and dried at room temperature.

2.5.10.3 Preparation of CuZrPA

CuZrPA has been prepared by equilibrating 2 g ZrPA with 200 cm³ of 0.2 M aqueous Cu (II)-acetate solution with continuous stirring at 323 K for 100 h. The solid was separated by filtration and washed with conductivity water for removal of adhering ions and dried at room temperature.

2.5.10.4 Preparation of LiZrPA

LiZrPA has been prepared by equilibrating 2 g ZrPA with 200 cm³ of 0.2 M aqueous Li-acetate solution with continuous stirring at 323 K for 100 h. The solid was separated by filtration and washed with conductivity water for removal of adhering ions and dried at room temperature.
2.6 CHARACTERIZATION

Material characterization has now become an integral part of materials science. Its ultimate goal is to understand the structure and property of a specific compound. This in turn gives an insight about the probable applications that could be explored using the material. Material characterization provides information on aspects viz., chemical composition, structure/texture etc. Chemical composition and structure, refers to elemental composition, the structure and proportions of individual phases that may be present, while surface composition means the nature and proportion of functional groups that may be present on the surface. The geometrical structure and morphology i.e. size and shape of crystallites, pore structure, pore volume and total surface area gives information on the texture of the material [29,30].

2.6.1 Physical characteristics

Physical appearance gives a general idea about the material. ZrPA, SnPA, TiPA, ZrHEDP, ZrATMP and ZrDETPMP were obtained as white hard granules. ZrPC was obtained as fine white powder.

In case of metal exchanged phases, CuZrPA was obtained as a blue powder, LiZrPA as a white powder, RuZrPA and RuZrPC were obtained as grey powders while PdZrPA and PdZrPC as light brown powders.

2.6.2 Chemical resistivity

A material to be used for various applications, is used in varied environments. Thus, it is a useful study to assess the chemical resistivity/stability in various chemical media. Chemical resistivity in various media – acids (H₂SO₄, HNO₃, HCl), bases (NaOH and KOH) and organic solvents (ethanol, benzene, acetone and acetic acid) was studied by taking 500 mg of material in 50 ml of the particular medium and allowing to stand for 24 h. The change in color, nature and weight was observed. The results presented in table 2.1 exhibit maximum tolerable limits in the particular medium.
Table 2.1 Chemical resistivity of various phosphates and phosphonates

<table>
<thead>
<tr>
<th>Material</th>
<th>Acids</th>
<th>Bases</th>
<th>Organic Solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrPA</td>
<td>36N</td>
<td>16N</td>
<td>10N 5N 5N</td>
</tr>
<tr>
<td>SnPA</td>
<td>36N</td>
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</tr>
<tr>
<td>TiPA</td>
<td>36N</td>
<td>16N</td>
<td>10N 5N 5N</td>
</tr>
<tr>
<td>ZrHEDP</td>
<td>36N</td>
<td>16N</td>
<td>10N 0.5N 0.5N</td>
</tr>
<tr>
<td>ZrATMP</td>
<td>36N</td>
<td>16N</td>
<td>10N 0.5N 0.5N</td>
</tr>
<tr>
<td>ZrDETPMP</td>
<td>36N</td>
<td>16N</td>
<td>10N 0.5N 0.5N</td>
</tr>
<tr>
<td>ZrPC</td>
<td>36N</td>
<td>16N</td>
<td>10N 5N 5N</td>
</tr>
</tbody>
</table>

2.6.3 Ion Exchange Capacity (i.e.c.)

It is defined as the number of replaceable counter ions per unit mass of the exchanger and is usually expressed as milli-equivalents per gram. The Na⁺ exchange capacity (i.e.c.) was determined by column method [31]. Further, the effect of heating on ion exchange capacity was studied by heating several 1 g portions of the exchangers for 2 h in the temperature range 100-500 °C at an interval of 100 °C in a muffle furnace and determining the Na⁺ exchange capacity by the column method [31] at room temperature.

The Na⁺ exchange capacity of all the materials is reported in table 2.2. The data for the effect of calcination on i.e.c. was studied in the temperature range 100 to 500 °C at an interval of 100 °C and the results are presented in table 2.2. An increase in the i.e.c. value for all the materials at 100 °C could be attributed to loss of moisture, thereby increasing the active exchanger content for same weight of material taken for i.e.c. determination. In case of ZrPA, SnPA and TiPA there is a small decrease in i.e.c. at 200°C, followed by a subsequently high loss of i.e.c. beyond 300 °C. This could be attributed to the condensation of structural hydroxyl groups. In case of Zr(IV) phosphonates there is a decrease in i.e.c. value up to 300 °C attributed to the condensation of structural hydroxyl groups. However, in the temperature range beyond 300 °C,
an increase in i.e.c. value is observed which could be attributed to the
decomposition of organic moiety, leading to the formation of active carbon, as
evidenced by the change in colour of the heated samples to black. At 500 °C
decrease in i.e.c. value is observed, accompanied by change in colour of the
material to almost white which could be attributed to the complete
decomposition of organic moiety/active carbon in the form of CO₂.

In case of M(IV) phosphates under study, the Na⁺ exchange capacity
evaluated at room temperature follows the order TiPA(3.09)>ZrPA(2.77)>SnPA(1.90). Since the anion HPO₄²⁻ is common for all the solids studied, the
i.e.c. of the various phosphates should bear a correlation with the acidity of the
cations, viz. Zr⁴⁺, Sn⁴⁺ and Ti⁴⁺. Acidity of a cation is related to size and ion
charge. The ionic radii for Ti⁺⁺⁺ (0.745 Å), Zr⁺⁺⁺ (0.86 Å) and Sn⁺⁺⁺ (0.83 Å) [32]. In case of TiPA the ionic radius is small and hence the positive charge
is concentrated in a small area, increasing the tendency to polarize the O−H
bond in the hydroxyl group bonded to it. The sizes of Zr⁺⁺⁺(0.86 Å) and Sn⁺⁺⁺ (0.83 Å) being almost same, similar i.e.c. could be expected, but i.e.c. of
ZrPA>SnPA. This could be attributed to complexity in structure and number of
protonic sites available for exchange.

In case of Zr (IV) phosphonates the Na⁺ exchange capacity evaluated at
room temperature, follows the order ZrHEDP(3.18)>ZrPA(2.77)>ZrDETPMP (1.92)=ZrATMP(1.89). In case of ZrPA and ZrHEDP, the phosphate and
HEDP moiety possess three and five structural hydroxyl groups respectively
that are well spaced. This explains ease of exchange. Higher i.e.c. value in case
of ZrHEDP as compared to ZrPA could be attributed to higher number of
exchangeable protons in case of ZrHEDP as compared to ZrPA. In case of
ZrATMP and ZrDETPMP, the ATMP and DETPMP moieties with six and ten
hydroxyl groups respectively, exhibit lower i.e.c. values, which could be
attributed to complexity in structure/steric effects.
Table 2.2 Effect of calcination on ion exchange capacity (i.e.c.) of phosphates and phosphonates

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (°C)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>R.T.</td>
</tr>
<tr>
<td>ZrPA</td>
<td>2.77</td>
</tr>
<tr>
<td>SnPA</td>
<td>1.90</td>
</tr>
<tr>
<td>TiPA</td>
<td>3.09</td>
</tr>
<tr>
<td>ZrHEDP</td>
<td>3.18</td>
</tr>
<tr>
<td>ZrATMP</td>
<td>1.89</td>
</tr>
<tr>
<td>ZrDETPMP</td>
<td>1.92</td>
</tr>
</tbody>
</table>

2.6.4 Elemental Analysis:

Volumetric or gravimetric techniques are well known for obtaining the elemental composition. Wet chemical analyses are routinely done using suitable procedures for solubilization of a solid and quantitative analysis of the aqueous solutions. Flame photometry, Atomic absorption spectrometry (AAS) or Inductively coupled plasma (ICP) analyzers are commonly used to estimate the chemical composition. In case of organic and organometallic materials CHN analysis is used for the estimation of various organic components present.

2.6.4.1 Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES):

ICP-AES is a widely used analytical technique for the determination of elements present in a wide variety of samples. The technique is based on atomic emission spectroscopy and as the name suggests, plasma is used as the source of excitation/ionization of atoms. Plasma is known as the fourth state of matter, which contains an appreciable fraction (>1%) of electrons and positive ions in nearly equal numbers, in addition to atoms and neutral molecules. The instrument generally uses argon plasma.
A sample solution of known concentration in the form of an aerosol is introduced in the plasma discharge. First the solvent evaporates to produce microscopic salt particles. These particles subsequently decompose to a gas, which is then atomized and finally ionized. These ionized particles in the cooler part of the plasma emit radiations that are measured by a photomultiplier tube (PMT) or by charge couple device (CCD) based solid-state detector. PMT requires slits and detectors for each element; CCD on the other hand provides simultaneous detection.

In the present study analysis was performed on a Perkin Elmer 4300 DV model, ICP-AES spectrometer. The intensity obtained for each sample is matched against a calibration plot prepared for the particular element for quantitative estimation. The concentration of different elements is actually measured at ppm level, which can be later converted into the % weight of the element, by incorporating the dilution factor (table 2.3). These values are then converted into moles of each element.

Elemental analysis performed by ICP-AES shows that the mole ratio of Zr:P in ZrPA, ZrHEDP, ZrATMP, ZrDETPMP and ZrPC to be 1:2. The % value of each element obtained is presented in table 2.3. Ruthenium was found to be 1.92% in RuZrPA and 1.41% in RuZrPC. Palladium was found to be 1.62% in PdZrPA and 1.31% in case of PdZrPC.

**Table 2.3 Elemental contents as obtained by ICP-AES**

<table>
<thead>
<tr>
<th>Material</th>
<th>Content (wt %)</th>
<th>Metal</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrPA</td>
<td>27.6 (Zr)</td>
<td>30.5 (Zr)</td>
<td>19.4</td>
</tr>
<tr>
<td>ZrPC</td>
<td>29.1 (Zr)</td>
<td>20.4</td>
<td></td>
</tr>
<tr>
<td>ZrHEDP</td>
<td>28.2 (Zr)</td>
<td>19.2</td>
<td></td>
</tr>
<tr>
<td>ZrATMP</td>
<td>26.1 (Zr)</td>
<td>18.3</td>
<td></td>
</tr>
<tr>
<td>SnPA</td>
<td>34.03 (Sn)</td>
<td>18.35</td>
<td></td>
</tr>
<tr>
<td>TiPA</td>
<td>14.4 (Ti)</td>
<td>19.3</td>
<td></td>
</tr>
</tbody>
</table>
2.6.4.2 CHN analysis

Carbon, hydrogen and nitrogen content in ZrHEDP (only C,H), ZrATMP and ZrDETPMP have been determined using Coleman USA – CHN analyzer. The content of carbon, hydrogen and nitrogen found in phosphonates has been presented in table 2.4.

<table>
<thead>
<tr>
<th>% Content</th>
<th>ZrHEDP</th>
<th>ZrATMP</th>
<th>ZrDETPMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>7.01</td>
<td>7.12</td>
<td>12.84</td>
</tr>
<tr>
<td>H</td>
<td>3.21</td>
<td>3.19</td>
<td>3.85</td>
</tr>
<tr>
<td>N</td>
<td>--</td>
<td>2.91</td>
<td>5.35</td>
</tr>
</tbody>
</table>

2.6.5 Thermal Stability

2.6.5.1 Thermogravimetric analysis (TGA): 

Thermogravimetry is the measure of quantitative changes in mass occurring in a substance as it undergoes a controlled and programmed heating or cooling as a function of temperature or time.

TGA gives an idea about the stability of the material as a function of temperature. This also gives an idea about the temperature at which the condensation of the water molecules takes place. As the materials synthesized herein are to be explored for their possible use as solid acids, as supports in heterogenised homogeneous catalysis and as proton conductors, thermal analysis will help in determining the temperature range of use. Thermal analysis (TGA) was carried out on a Shimadzu thermal analyzer at a heating rate of 10 °C/min.

Typical thermograms obtained for all the materials are shown in figures 2.c.1 – 2.c.13. All the materials exhibit two weight loss regions. The region (upto ~180 °C) is attributed to loss of moisture/hydrated water. The second weight loss above 250 °C is attributed to condensation of structural hydroxyl groups as well as decomposition and dissociation of the organic moieties when
Synthesis and Characterization

The temperature range for weight loss in each material is detailed in table 2.5.

Alberti's formula [33] has been used to determine the number of structural water molecules.

$$18n = \frac{[X(M+18n)]}{100}$$

Where,

- **n** = number of water molecules
- **M** = molecular weight of the material without water molecule
- **X** = % weight loss

Based on the above formula, ZrPA, SnPA, TiPA and ZrPC have been formulated as Zr(HPO$_4$)$_2$.2.5H$_2$O, Sn(HPO$_4$)$_2$.2H$_2$O, Ti(HPO$_4$)$_2$.5H$_2$O and Zr(HPO$_4$)$_2$.0.75H$_2$O respectively. ZrHEDP, ZrATMP and ZrDETPMP have been formulated as Zr(C$_2$H$_8$P$_2$O$_7$).2H$_2$O, Zr(C$_3$H$_{12}$P$_3$O$_9$N)$_{0.66}$1.8H$_2$O and Zr(C$_9$H$_{28}$P$_5$O$_{15}$N$_3$)$_{0.41}$.5H$_2$O, respectively.
### Table 2.5 TGA data indicating the regions for weight loss.

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature range (°C)</th>
<th>% Weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrPA</td>
<td>40-180</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>250-500</td>
<td>6</td>
</tr>
<tr>
<td>ZrPC</td>
<td>40-186</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>300-710</td>
<td>10</td>
</tr>
<tr>
<td>SnPA</td>
<td>40-160</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>200-500</td>
<td>5</td>
</tr>
<tr>
<td>TiPA</td>
<td>40-155</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>155-500</td>
<td>6</td>
</tr>
<tr>
<td>ZrHEDP</td>
<td>40-120</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>220-500</td>
<td>10</td>
</tr>
<tr>
<td>ZrATMP</td>
<td>40-105</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>200-500</td>
<td>7</td>
</tr>
<tr>
<td>ZrDETPMP</td>
<td>40-120</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td>200-500</td>
<td>16</td>
</tr>
<tr>
<td>CuZrPA</td>
<td>25-120</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>200-550</td>
<td>8.3</td>
</tr>
<tr>
<td>LiZrPA</td>
<td>40-140</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>190-620</td>
<td>9</td>
</tr>
<tr>
<td>RuZrPA</td>
<td>25-168</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>200-570</td>
<td>14.5</td>
</tr>
<tr>
<td>RuZrPC</td>
<td>25-171</td>
<td>11.4</td>
</tr>
<tr>
<td></td>
<td>200-570</td>
<td>6.5</td>
</tr>
<tr>
<td>PdZrPA</td>
<td>25-173</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>200-520</td>
<td>5.8</td>
</tr>
<tr>
<td>PdZrPC</td>
<td>25-180</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>205-650</td>
<td>10.2</td>
</tr>
</tbody>
</table>
Figure 2.c.1 TGA of ZrPA

Figure 2.c.2 TGA of SnPA
Synthesis and Characterization

Figure 2.c.3 TGA of TiPA

Figure 2.c.4 TGA of ZrHEDP
Synthesis and Characterization

Figure 2.c.5 TGA of ZrATMP

Figure 2.c.6 TGA of ZrDETPMP
Synthesis and Characterization

Figure 2.c.7 TGA of ZrPC

Figure 2.c.8 TGA of RuZrPC
Figure 2.c.9 TGA of PdZrPA

Figure 2.c.10 TGA of RuZrPA
Synthesis and Characterization

Figure 2.c.11 TGA of CuZrPA

Figure 2.c.12 TGA of LiZrPA
2.6.5.2 Differential Scanning Calorimetry (DSC):
The Differential Scanning Calorimetric technique maintains the sample and the reference materials isothermal to each other by proper application of electrical energy, as they are heated or cooled at a linear rate and gives directly the heat of a particular chemical transformation. Therefore, this technique is used to follow the phase changes occurring in the material as a function of heat treatment. DSC was recorded on a Shimadzu DSC-60 at a heating rate of 10°C min⁻¹.

Typical DSC curves obtained for all the materials are shown in figures 2.d.1 - 2.d.7. The DSC curves exhibit an endothermic peak ~100°C for ZrPA, ~105°C for SnPA, ~115°C for TiPA and ~105°C in case of ZrPC which is attributed to loss of moisture/hydrated water. An endothermic process for the materials ZrPA, SnPA, TiPA and ZrPC which starts at ~300°C could be attributed to the condensation of structural hydroxyl groups. For the Zr (IV) phosphonates, the DSC curve exhibits an endothermic peak at ~120°C for ZrHEDP, ~105°C for ZrATMP and ~120°C for ZrDETPMP, which is...
attributed to loss of moisture/hydrated water. In case of ZrHEDP and ZrATMP, however, an exothermic process which starts at \(~300\, ^\circ\text{C}\) is attributed to both decomposition of the organic moiety present in the framework as well as condensation of structural hydroxyl groups. The decomposition of the organic moiety predominates the condensation of structural hydroxyl groups which is observed as an exotherm. In case of ZrDETPMP, distinct exothermic peaks are observed in the temperature range 350–500\(^\circ\text{C}\) which could be attributed to the dissociation of bulky organic moieties.

Figure 2.d.1 DSC of ZrPA

Figure 2.d.2 DSC of SnPA
Figure 2.d.3 DSC of TiPA

Figure 2.d.4 DSC of ZrPC
Synthesis and Characterization

Figure 2.d.5 DSC of ZrHEDP

Figure 2.d.6 DSC ZrATMP
2.6.6 Surface area determination (BET Method):

The most commonly used methods for estimating the surface area of a material involves physical or chemical adsorption when it starts to level off on pressure increase near the monolayer point. Various adsorbates at different temperatures can be used depending upon the material characteristic. Measurement of total surface area of a sample requires non-specific physical adsorption [34,35], usually done with simple non-polar molecules like nitrogen and noble gases. In most cases, nitrogen adsorption method is used, however if metallic species are present, only noble gases like argon and krypton are used exclusively, as nitrogen cannot chemisorb on the metallic surface.

In principle, the total surface area of a material can be divided into the external surface area (the outer side of the particle) and the internal area (contributed by the pores of different dimensions). In case of porous materials, the contribution of the external area is only a fraction of the total surface area and hence, depending upon the nature of the materials, viz., micro, meso or macro porous types, the methodology and considerations for the use of an appropriate model for determining the surface area are important.
In heterogeneous catalysis, surface area of the catalyst plays the most important part and determines potential activity of the catalyst. While comparing the activity of different catalysts or the effect of different pretreatments to a catalyst, the major factor considered is difference in their surface areas rather than their intrinsic activity.

Brunauer, Emmett and Teller (BET) derived the equation for physical adsorption of gases on solid surfaces that leads to multilayer adsorption [36]. The assumptions made are 1) surface is energetically uniform; 2) condensation of layers of gas can proceed to multilayers and 3) adsorbed molecules do not interact laterally.

\[
P/V_{ads} (P^o-P) = 1/V_m C + P(C-1)/V_m P^o C
\]

where,

\[V_{ads}=\text{volume of gas adsorbed at equilibrium pressure}\]

\[V_m=\text{volume corresponding to monolayer coverage}\]

\[P,P^o=\text{saturated vapor pressure of the adsorbate at liquid N}_2\text{ temperature}\]

\[C=\text{isothermal constant given by exp}[(H_a-H_i)/RT]\]

Where \(H_a=\text{enthalpy of adsorption in the first layer}\)

\(H_i=\text{enthalpy of formation of second and subsequent layers}\)

A plot of \(P/V_{ads} (P^o-P)\) versus \(P/P^o\) is a straight line with the slope \(S=([C-1]/V_mC)\) and the intercept \(I=[1/V_mC]\). Knowing \(S\) and \(I\) values \(V_m\) can thus be calculated. The number of gas molecules in a monolayer is multiplied by the cross sectional area of the adsorbate, which gives the total surface area of the solid. This is calculated using the following equation:

\[\text{Specific surface area} = \frac{V_m NA_m}{22414W} \text{ m}^2\text{ g}^{-1}\]

Where, \(N\) is the Avogadro’s number, \(W\) is the weight of the catalyst sample in grams, \(A_m\) is the cross sectional area of the adsorbate molecule (0.162 nm\(^2\) for \(N_2\)) and \(V_m\) is the volume corresponding to monolayer coverage.

The surface area values of materials studied are presented in table 2.6
Table 2.6 Surface area of phosphate and its metal exchanged phases

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface area (m²g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrPA</td>
<td>282.17</td>
</tr>
<tr>
<td>ZrPC</td>
<td>2.72</td>
</tr>
<tr>
<td>RuZrPA</td>
<td>190.18</td>
</tr>
<tr>
<td>PdZrPA</td>
<td>184.27</td>
</tr>
<tr>
<td>RuZrPC</td>
<td>2.52</td>
</tr>
<tr>
<td>PdZrPC</td>
<td>2.48</td>
</tr>
</tbody>
</table>

Surface area is more in case of ZrPA as compared to ZrPC. This is attributed to amorphous nature of ZrPA. It is reported in the literature that surface area decreases with increasing crystallinity of the material [37]. In case of metal exchanged phases RuZrPA, PdZrPA, RuZrPC and PdZrPC on amorphous and crystalline zirconium phosphate the metal exchanged phases exhibit lower surface area, compared to the parent materials. This could be probably due to pore blocking in the structure by the incorporation of larger ions in place of replaceable –H⁺ ions.

2.6.7 Temperature Programmed Desorption (TPD) studies:

In acid catalyzed reactions, the measurement of acidity of the catalyst is very important, since it is the key factor in determining the activity of the catalyst. This measurement can either be done by titration with non-aqueous bases like n-butyl amine or by gaseous adsorption method.

In the present work, the acidity of different catalysts has been determined using the TPD technique. This method involves three steps. The sample is first degassed and then the pulses of 0.5 ml NH₃ are passed over it, which gets chemisorbed on the acidic sites of the catalyst. Depending upon the pulses required to saturate the catalyst, the amount of base used can be calculated. After the gas has been adsorbed, the sample is placed in an inert gas (He) stream and the temperature is increased according to a specific temperature-time program. The concentration of the desorbed gas in the
effluent gas stream is then measured as a function of the sample temperature, which is plotted. This concentration-temperature plot is referred to as the TPD profile. The area under the profile is proportional to the amount of gas desorbed. Acid sites with varying acid strength differ in their heat of adsorption, which is reflected in the TPD profile by way of a number of distinct peaks representing the acid sites of the catalyst. The acidity is reported as mmol/gm.

The surface acidity was measured for ZrPA and ZrPC as they have been used in solid acid catalysis. Surface acidity is found to be 2.34 mmol/g and 0.96 mmol/g for ZrPA and ZrPC respectively.

2.6.8 X-ray diffraction studies:

X-ray powder diffraction is a standard tool for the identification and characterization of crystalline solid phases. It gives information on the geometry of the crystal lattice, specific atoms and their arrangement in the unit cell of crystal structure. It is most effective in structure determination when the compound to be investigated is in a single phase. There are conventionally two types of diffraction studies performed using X-rays: 1) Single crystal diffraction and 2) Powder X-ray diffraction (PXRD). In comparison to the information obtained by single crystal intensity data, the PXRD profiles yield far poorer information mainly due to equivalent and overlapping reflections. Compared to the three dimensional location of each reflection in a single crystal diffraction experiment, the powder diffraction pattern can give only one dimensional data, due to the rotational projection of the randomly oriented reciprocal lattices. PXRD is a long-range order technique sensitive to the basic periodic structure of a solid sample.

Any diffraction pattern consists of: peak position ($\theta$), peak intensity (cps) and the shape of the peak (broad or sharp). The peak positions are dependent on the geometry of the crystal lattice i.e. size and shape of the unit cell. The intensities of the peaks in a profile are related to the specific atoms in a crystal and their arrangement in the unit cell of the crystal. The shape of the
peak is related to the size and the perfection of the crystallites and various instrumental parameters. The diffraction profile obtained through constructive interference, obeys Bragg’s law

\[ n \lambda = 2d \sin \theta \]

where, 
- \( n \) = order of diffraction
- \( \lambda \) = wavelength of intercept X-ray (in Å)
- \( d \) = distance between two parallel scattering planes (in Å)
- \( \theta \) = incident angle

A plot of cps v/s 2θ is obtained where, 2θ is an experimental parameter (angle between the diffracted and the undeviated X-ray waves).

Phase identification is done by comparison of the pattern with the data base-powder diffraction files distributed by International Center for diffraction data (ICDD), (Formerly ASTM and then JCPDS), which is a collection of single phase X-ray diffraction patterns in the form of tables.

X-ray diffractogram (2θ = 5–80°) was obtained on X-ray diffractometer (Rigaku Dmax 2200) with Cu-Kα radiation and nickel filter. Typical diffractograms obtained are presented in figure 2.e.1-2.e.13. The absence of any sharp peaks in the X-ray diffractogram for ZrPA, SnPA, TiPA, ZrHEDP, ZrATMP, ZrDETPMP, CuZrPA, LiZrPA, RuZrPA and PdZrPA indicates the amorphous nature of the materials. In case of ZrPC, PdZrPC and RuZrPC sharp peaks are obtained confirming the crystalline nature of the material. The crystalline phase of ZrPC was confirmed from the JCPDS files available (Card no. 340127).
Synthesis and Characterization

Figure 2.e.1 XRD of ZrPA

Figure 2.e.2 XRD of ZrPC
Figure 2.e.3 XRD of SnPA

Figure 2.e.4 XRD of TiPA
Figure 2.e.5 XRD of ZrHEDP

Figure 2.e.6 XRD of ZrATMP
Synthesis and Characterization

Figure 2.e.7 XRD of ZrDETPMP

Figure 2.e.8 XRD of CuZrPA
Synthesis and Characterization

Figure 2.e.9 XRD of LiZrPA

Figure 2.e.10 XRD of RuZrPA
Synthesis and Characterization

Figure 2.e.11 XRD of RuZrPC

Figure 2.e.12 XRD of PdZrPA
2.6.9 Infrared Spectroscopy (FTIR):

Infrared spectroscopy is based on the interaction of electromagnetic radiation with matter. Every solid, liquid or gaseous material is built up of aggregates of molecules or periodic lattice of well-defined molecules or atoms. Majority of such systems of matter exhibit local or global dipole moment depending upon masses, binding forces, distances and relative angle of atoms, which make up molecules. Each of these has a set of characteristic vibrational states, which are typical of a material. The various properties of a material are dependent upon its microstructure, which can be understood from IR spectra of the material. Vibrational spectroscopy is the most promising and widely used method for material characterization. The advantage being that, detailed microstructural information is obtained from the vibrational spectra. The information obtained from IR spectra serves both complementary and supplementary to those obtained from other techniques like XRD, e.g. information regarding phase transition, compositional changes or presence of...
surface functional groups in a material. Most of the limitations of other methods are overcome in the application of IR spectroscopy to study the surface of solid materials.

In the present study, the IR absorption spectra of the synthesized materials were recorded to obtain information regarding the functional groups present in the material.

FTIR spectra of M(IV) phosphates and Zr(IV) phosphonates were recorded using KBr wafer on a Bomem MB series with Epson Hi 80 printer/plotter. The FTIR spectra for all the metal phosphates and phosphonates are presented in figure 2.f.1–2.f.7.

The FTIR spectra of M(IV) phosphates (ZrPA, SnPA, TiPA and ZrPC) and Zr(IV) phosphonates (ZrHEDP, ZrATMP and ZrDETPMP) exhibit a broad band in the region ~3400 cm\(^{-1}\) which is attributed to asymmetric and symmetric \(-OH\) stretches. A sharp medium band at ~1635 cm\(^{-1}\) is attributed to aquo \((\text{H–O–H})\) bending. A band in the region ~1035 cm\(^{-1}\) is attributed to the presence of \(\text{P}=\text{O}\) stretching. A medium intensity band at 1400 cm\(^{-1}\) is attributed to the presence of \(\delta(\text{POH})\) [38].

Zr(IV) phosphonates (ZrHEDP, ZrATMP and ZrDETPMP) exhibit additional bands at ~1150 cm\(^{-1}\) indicating to the presence of aliphatic \(\text{P}=\text{O}\) group. Further, in case of ZrHEDP a combination of bands at ~1450 cm\(^{-1}\) and ~1375 cm\(^{-1}\) is attributed to \(\delta_{\text{as}}\text{CH}_3\) and \(\delta_{\text{s}}\text{CH}_3\), respectively. Bands in the region 1445–1475 cm\(^{-1}\) in case of ZrATMP and ZrDETPMP indicates the presence of secondary and tertiary amine, respectively [39].
Synthesis and Characterization

Figure 2.f.1 FTIR of ZrPA

Figure 2.f.2 FTIR of ZrPC
Synthesis and Characterization

Figure 2.f.3 FTIR of TiPA

Figure 2.f.4 FTIR of SnPA
Synthesis and Characterization

Figure 2.f.5 FTIR of ZrHEDP

Figure 2.f.6 FTIR of ZrATMP
2.6.10 Scanning Electron Microscopy (SEM):

It is a type of electron microscopy capable of producing high resolution images of a sample surface. Due to the manner in which the image is created, SEM images have a characteristic three-dimensional appearance and are useful for judging the surface structure of the sample. In a typical SEM, electrons are thermionically emitted from a tungsten or lanthanum hexaboride (LaB₆) cathode and are accelerated towards an anode; alternatively electrons can be emitted via field emission (FE). The electron beam, which typically has an energy ranging from a few hundred eV to 50 keV, is focused by one or two condenser lenses into a beam with a very fine focal spot sized 1 nm to 5 nm. The beam passes through pairs of scanning coils in the objective lens, which deflect the beam over a rectangular area of the sample surface. Through these scattering events, the primary electron beam, effectively spreads and fills a teardrop-shaped volume, known as the interaction volume, extending from less than 100 nm to around 5 μm into the surface. Interactions in this region lead to the subsequent emission of electrons which are then detected to produce an image. The most common imaging mode monitors low energy (<50 eV) secondary electrons. Due to their low energy, these electrons originate within a

Figure 2.f.7 FTIR of ZrDETPMP
few nanometers from the surface. The electrons are detected by a scintillator-photomultiplier device and the resulting signal is rendered into a two-dimensional intensity distribution, that can be viewed and saved as a digital image. The brightness of the signal, depends on the number of secondary electrons reaching the detector. If the beam enters the sample, perpendicular to the surface, then the activated region is uniform about the axis of the beam and a certain number of electrons "escape" from within the sample. As the angle of incidence increases, the "escape" distance of one side of the beam will decrease and more secondary electrons will be emitted. Thus, steep surfaces and edges tend to be brighter than flat surfaces, which results in images with a well-defined, three-dimensional appearance. Using this technique, resolutions less than 1 nm are possible. In addition to the secondary electrons, backscattered electrons can also be detected. Backscattered electrons may be used to detect contrast between areas with different chemical compositions. These can be observed especially when the average atomic number of the various regions is different.

Figure 2.g Schematic representation of SEM setup

Scanning electron micrographs (figure 2.h.1–2.h.2) shows the general morphology of the materials. The metal exchanged phases show different morphological features as compared to the parent materials.
Synthesis and Characterization

Figure 2.h.1. SEM of various phosphates and phosphonates
Figure 2. SEM of various metal exchanged phases of zirconium phosphate

Figure 2.h.2. SEM of various metal exchanged phases of zirconium phosphate

Figure 2. SEM of various metal exchanged phases of zirconium phosphate
REFERENCES


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Synthesis and Characterization


