

1. Introduction

1.1 Necessity, Research Problem and Solutions

Recently Peter Drucker said:

“The best way to predict the future is to discover it”

Understanding of the natural world is science and ability to manipulate it, is Technology. The early human came out of the caves and realised for few minimum needs for their survival. Scientific processes are the ways through which scientists investigate and communicate about the natural world. The scientific body of knowledge includes concepts, principles, facts, laws, and theories about the way how the world works around us.

The "Urban Revolution" began when simple communities aggregated into complex societies that built large cities, developed forms of writing, metallurgy and perhaps most important mastered the hydraulic technologies and more sophisticated agricultural techniques that enabled their civilizations to flourish in arid lands. Egyptians, Chinese, Mesopotamians, Indians living in the Indus River Valley, Mesoamericans and Incans, all refined the astronomical, mathematical, and monument-building skills of their forbears at different points in chronological time but within the trajectory of technological development for all human societies. During this revolution and trajectory, needs of mankind also increased which leads to discovery. Mankind utilised “reward of discovery” making better life style. But this interrupted nature’s balance and few unwanted results are in front of the world (with the more weighted advantages) in the form of pollution, global warming, hazardous wastes etc. Chemistry has played main role in both aspects of this revolution and is expected & committed to give solution too.

1.1.1 Current concern and status of research

During the development of technologies and revolution or transformation, mankind has created an environment of complex systems around it which help to live him as the super creature of our planet. Development of research institute, industries, and other means of daily need exploit nature and mankind. Natural disaster, pollution, and imbalance in the behaviour of the nature are its main examples. Pollution and consequent problems (e.g. diseases) are the main concerns of the environment. Recent reports on the industry effluents are 900 billion ton processing of crude oil, which

uses about 50 billion ton of metal catalyst ^[1]. After three years, these catalysts are replaced by fresh one and disposed off in the environment ^[2] which causes problem for all livings on earth (e.g. contaminated water and food) because the discharged catalyst has been considered by Environmental Protection Agency as a hazardous material ^[3]. Thus catalysts without no such problems are required. Aluminophosphate as a catalyst may be good alternative for this purpose.

The concept of green chemistry is devoted to solve these issues by utilising green chemistry principles. Catalysis is a high potential tool which helps green chemistry to get solution for mentioned problem. The design and preparation of catalysts not only has an impact on the economic strategies but also control and minimise the research problems of all the chemical industries affecting the environment and health. The U.S. Environmental Protection Agency ^[4] estimated that they are recycling 8 million tons of metal catalyst in United States.

Governments and industries worldwide must urgently address the management of chemicals in order to curtail the escalating health and environmental risks associated with the widespread production, use and disposal of these chemicals (e.g. used catalysts).

1.1.2 Green Chemistry concept and management of problems by catalysis

The term “*green chemistry*” was coined by Paul Anastas in 1991^[5]. However, concept was originated by Trevor Kletz ^[6] in his 1978 paper where he proposed that chemists should seek alternative processes to those involving more dangerous substances and conditions. Green chemistry, also called sustainable chemistry, is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances ^[7]. Green chemistry seeks to reduce the bad impacts of chemistry on the environment by preventing pollution at its source level and using alternative natural resources.

Paul Anastas and John C. Warner developed 12 principles of green chemistry ^[5] which help to explain green chemistry concept in practice. The green chemistry concept can be understood by these 12 principles where Catalysis is one of them to regulate, manage and fulfil the requirement of green approach and solve the environmental issues. The 12 principles are:

1. It is better to prevent waste than to treat or clean up waste after it is formed.

2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. 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.
7. A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. Reduce derivatives – Unnecessary derivatization (blocking group, protection and temporary modification) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Substances and the form of a substance used in a chemical process should be chosen to minimize potential for chemical accidents, including releases, explosions, and fires.

It is clear from the above points that the focus is on minimizing the hazard and maximizing the efficiency of any chemical choice. Catalysis may play an important role in this particular regard. Research work on catalysis is also a main point out of these 12 principles of green chemistry. Particularly, zeolite and zeotype catalyst materials have become sparking as they account for the concept of green chemistry e.g. prevents wastes, no hazardous synthesis, benign chemicals, good solid catalyst etc. Zeolite and zeotype materials have a great importance (used to control radioactive

waste in Fukushima Daiichi nuclear disaster). Attempts are also being made not only to quantify the *greenness* of a chemical process but also to affect other variables such as chemical yield, price of reaction components, safety in the handling of chemicals, hardware demands, energy profile and ease of product workup and purification. In the statement for the 2005 Nobel Prize for Chemistry for "the development of the metathesis method in organic synthesis", the Nobel Prize Committee stated; *this represents a great step forward for 'green chemistry', reducing potentially hazardous waste through smarter production.* Metathesis is an example of how the important basic science has been applied for the benefit of mankind, society and the environment. The concept of green pharmacy was developed recently based on similar principles. All these issues and potential energetic are expected to be solved by the green chemistry, where the use of zeolite, zeotype (as catalyst) and catalysis may play an important role.

1.2 Catalysis

Catalysis = Greek words *kata* meaning down and *lyein* meaning loosen.

1.2.1 History

About one hundred and seventy nine years ago it was possible for one man to prepare an annual report on the progress of the whole chemistry. And this task was undertaken for several initial years by Swedish chemist J. J. Berzelius for the Stockholm Academy of Sciences. He introduced the concept of catalysis after the review of a number of earlier findings on the chemical change of the catalytic reactions in both homogeneous and heterogeneous systems. In his short paper ^[8] (1835-1836) he proposed a new force responsible for his finding, "catalytic force" and named the decomposition process as "catalysis". He wrote;

"It is, then, proved that several simple or compound bodies, soluble and insoluble, have the property of exercising on other bodies an action very different from chemical affinity. By means of this action they produce, in these bodies, decompositions of their elements and different recombinations of these same elements to which they remain indifferent."

Joseph Priestley (before 1800) and Dutch chemist Martinus van Marum made observations on the dehydrogenation of alcohol on the metal catalysts. Louis Jacques Thenard discovered that ammonia is decomposed into nitrogen and hydrogen when

passed over various red-hot metals, and ten years later, with Pierre Dulong, he found that the activity of iron, Platinum derivatives, copper, silver, gold, and platinum for decomposing ammonia decreased in the order given. Homogeneous catalytic processes have been used by mankind from thousands of years, for example, in fermentation. Clear statement and observation of catalytic effect was given by Humphry Davy ^[9] (Royal Society, 1817) when he fixed a fine platinum wire above a coal-gas flame in a safety-lamp. When additional coal gas was introduced into the lamp, the flame went out but the platinum wire remained hot for many minutes. Davy immediately deduced that the oxygen and coal gas combined without flame when in contact with the hot wire, thereby producing enough heat to keep the wire incandescent. When a hot platinum wire introduced into a mixture of coal gas and air immediately became incandescent. Furthermore, many combustible vapours mixed with air were found by Davy to produce the same effect. Davy had discovered the phenomenon of heterogeneous catalytic oxidation. This is one of the earliest recorded pattern of catalytic activity. In these researches Davy was assisted by Faraday but it is unclear whether Faraday contributed to the development of the ideas or acted mainly by carrying out Davy's instructions.

The industrial possibilities of heterogeneous catalytic oxidation were appreciated as early as 1831 by Peregrine Phillips, Junior, who in that year took out a British Patent (No. 6096) for "Certain Improvements in Manufacturing Sulphuric Acid commonly called Oil of Vitriol". History of catalysis is very wide and interesting. In current scenario, various catalyst type materials have been introduced. Supercritical conditions, ionic liquids, metal organic frameworks and various forms of zeolite (aluminosilicate) and zeotype (aluminophosphate) materials are few of the recent potential talk. History of catalysis and recent progress can be studied here ^[10-13]. Few of the known earliest examples of catalysis used by civilization are:

- 6000 BC Beer brewing by malting procedure (**Malt enzymes**)
- 3000 BC Wine making by fermentative conversion of grape juice sugars (**Yeast**)
- 2000 BC Alcohol by fermentation of various carbohydrate sources (**Yeast**)
- Bread & leavened bakery products by carbon dioxide and alcohol (**Baker's yeast**)
- Vinegar (acetic acid) by aerobic fermentation of ethanol (**Acetobacter**)
- 800 BC Cheese making (coagulation) by casein hydrolysis with calf stomach extracts
- 1850 Yogurt formation from milk by lactose to lactic acid conversion (**Lactobacillus**)

1.2.2 Principle of catalysis

Catalysis is the increase in rate of a chemical reaction of one or more reactants due to the participation of an additional substance called a catalyst. A catalyst may participate in multiple chemical transformations.

Catalyzed reactions have lower activation energy (rate-limiting free energy of activation) than the corresponding un-catalyzed reaction, resulting in a higher reaction rate at the same temperature and reactant concentrations. Catalysts may affect the reaction environment favourably, or bind to the reactants to polarize its bonds, e.g. acid catalysts for reactions of carbonyl compounds. In catalysis, a catalyst lowers the kinetic barrier and speeds up the attainment of chemical equilibrium. In addition, catalysts affect the forward and reverse rates equally; this means that catalysts have no effect on the equilibrium constant and thus on the composition of the equilibrium state. Catalysts function by allowing the reaction to take place through an alternative mechanism that requires smaller activation energy. This change is brought about by a specific interaction between the catalyst and the reaction components. Recall that the rate constant of a reaction is an exponential function of the activation energy, so even a modest reduction of E_a (energy of activation) can yield an impressive increase in the rate of reaction (Fig. 1).

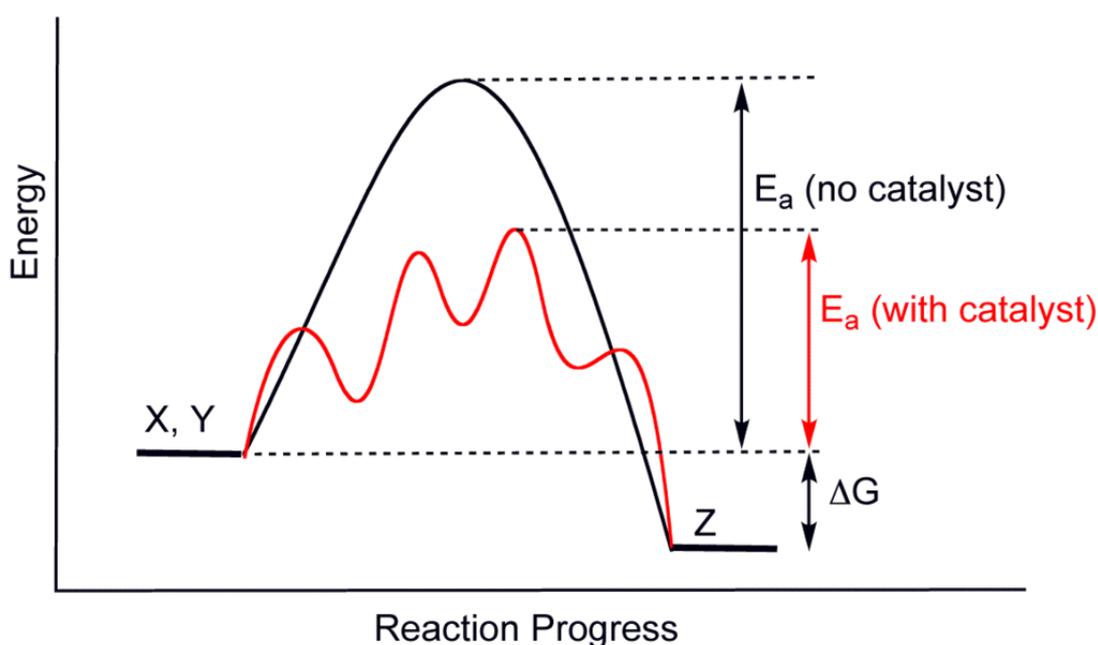


Fig. 1. Change in the activation energy of a reaction equilibrium in presence of catalyst.

1.2.3 Types of catalysts

Catalysts are conventionally divided into two categories: *homogeneous* and *heterogeneous*. *Enzymes*, natural biological catalysts, are often included in the former group, but because they share some properties of both the types of catalysts and they also exhibit some very special properties of their own. Thus they are treated sometimes as a third category.

1.2.3.1 Homogeneous catalyst

In chemistry, homogeneous catalysis is a sequence of reactions that involve a catalyst in the same phase as the reactants. Phase here refers to solid, liquid, or gas. Most commonly, a homogeneous catalyst is co-dissolved in a solvent with the reactants. The reaction needs a collision between two negative ions in these types of catalytic reactions.

1.2.3.2 Heterogeneous catalyst

In chemistry, heterogeneous catalysis is referred to the type of catalysis where the phase of a catalyst differs from that of the reactants. Phase here refers not only to solid, liquid or gas, but also immiscible liquids, e.g. oil and water. The great majority of practical heterogeneous catalysts is solids and the great majority of reactants is gases or liquids. Heterogeneous catalysis is of a paramount importance in many areas of the chemical and energy industries. Heterogeneous catalysis has attracted Nobel prizes for Fritz Haber and Carl in 1918, Irving Langmuir in 1932 and Gerhard Ertl in 2007 ^[14].

In heterogeneous catalysis, the reactants diffuse to the catalyst surface and adsorb onto it via the formation of chemical bonds. After reaction, the product desorbs from the surface and diffuses away (Fig. 2). If the diffusion rates are not taken into account, the reaction rates for various reactions on the surface of catalyst depend solely on the rate constants and reactant concentrations. For solid heterogeneous catalysts, the surface area of the catalyst is a critical parameter because it determines the availability of catalytic sites for reactants. Surface areas can be so large, for example some mesoporous silicates have surface areas of 1000 m²/g. The most common approach to maximize surface area is the use of a catalyst support in which a catalyst material is spread over a material which has a high surface area.

Adsorption is commonly an essential first step in heterogeneous catalysis. Adsorption is, when a molecule in the gas phase or in solution binds to the atoms on the solid or liquid surface. The molecule that is binding to a surface is called the adsorbate and the surface to which it binds is called the adsorbent. The process of the adsorbate binding to the adsorbent is called adsorption. The reverse of this process (the adsorbate splitting from adsorbent) is called desorption. In terms of catalyst support, the catalyst is the adsorbate and the support is the adsorbent.

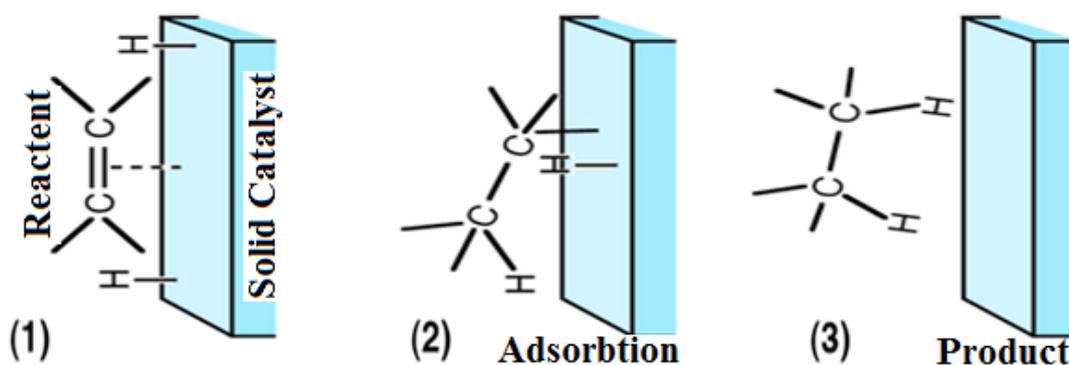


Fig. 2. The mechanism of reaction over solid catalyst-surface

Two types of adsorptions are recognized in heterogeneous catalysis. In the first type, physisorption, induces only small changes to the electronic structure of the adsorbate. Typical energies for physisorption are from 2-10 kcal/mol. The second type is chemisorption, in which the adsorbate is strongly perturbed, often leading to bond-breaking. Energies for typical chemisorptions range from 15 to 100 kcal/mol. For physisorption, adsorbate is attracted to the surface atoms by van-der Waals forces. The analysis of physisorption for a polar or an ionic species is more complex. Chemisorption results in the sharing of electrons between the adsorbate and the adsorbent. Chemisorption is traditionally described by the Lennard-Jones-Potential which considers various cases. In the industrial scale chemistry, many processes are catalysed by "solid acids" because these heterogeneous catalysts do not get dissolved in the reaction medium and thus can be separated easily. Well known examples include zeolites, alumina and various others metal oxides. Aluminophosphate materials and zeolites are among the few advanced examples of heterogeneous catalysts ^[7, 15-17].

1.3 Zeolite and aluminophosphate materials

1.3.1 What are zeolite and aluminophosphate?

Zeolites are aluminosilicates microporous crystalline solid frameworks with well-defined structures. Generally they contain silicon, aluminium and oxygen in their framework and cations, water and/or other molecules within their pores and voids. Many zeolites occur naturally as mineral, and are extensively mined in many parts of the world. Others are synthetic and are made commercially for specific uses or produced by researchers/scientists trying to understand more about their chemistry. Because of their unique porous properties, zeolites are used in the variety of applications with a global market of several million tonne per annum. In the western world, major uses of zeolites are in the petrochemical cracking, ion-exchange (water softening and purification), separation & removal of gases and solvents. Other applications are in agriculture, animal husbandry and construction. They are often also referred to as *molecular sieves*.

The term zeolite was originally coined in 1756 by Swedish mineralogist Axel Fredrik Cronstedt, who observed that upon rapidly heating, the material stilbite produce large amount of steam due to the water that had been absorbed by the material stibite. Based on this, he called the material “**zeolite**”, which is from the Greek words ζέω, meaning "to boil" and λίθος (*lithos*), meaning "stone" (boiling stone) ^[18].

Similar to the zeolite materials, aluminophosphates (zeotype) are novel class of crystalline microporous framework with regular/hierarchical pores and voids that represents the first family of the molecular sieves synthesized without silica ^[19], although most widely known molecular sieves are the aluminosilicate and microporous silica polymorphs. The novel aluminophosphate molecular sieves are very similar to zeolites in properties. The anhydrous form of these materials is found in nature as the mineral berlinite. These aluminophosphate are structure analogue of zeolite materials, thus called zeotype. Silica is replaced by phosphorus atom in the aluminophosphates and aluminum is common in both the zeolites and aluminophosphates.

In the late 1970's, the Union Carbide Laboratories set out to discover a new generation of molecular sieves. The strategy was to explore new framework composition of oxides out of the known aluminosilicates and silica molecular sieves.

The first elements, explored as the tetrahedral framework cations were aluminum and phosphorus. Initial success resulted in the discovery of the aluminophosphate (AlPO-n, n represents here specific structure number of framework which reflects geometry, structure and crystallography of that aluminophosphate) molecular sieves reported in 1982 by Wilson et al. ^[19]. The addition of silicon to the aluminophosphate framework resulted in the silicoaluminophosphate (SAPO-n) molecular sieves reported by Lok et al. ^[20]. The metal aluminophosphate (MeAPO-n) molecular sieves with frameworks containing aluminium, phosphorus and metal cations (Me = Mg²⁺, Fe^{2+,3+}, Co²⁺, Mn²⁺ and Zn²⁺ etc., were reported by Messina et al. ^[21] and Wilson et al. ^[22] in 1985 and 1986. IZA commission has classified more than 218 Framework Type Codes (FTC) and 42 additional codes have since been approved for AlPO-n and zeolites together [November 2014-09-28] however several analogue types for each FTC, are listed at IZA.

Many synthetic (mostly) forms of anhydrous aluminophosphate [IZA] are known and have framework structures similar to zeolites which are used as catalysts or molecular sieves. The term molecular sieve is the ability to selectively sort molecules, based primarily on size exclusion process. This is because a sieve refers to a particular property of these materials, i.e. the very regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter the pores of a zeolite, is controlled by the dimensions of the channels of molecular sieves.

1.3.2 Structure of aluminophosphates and zeolites

Aluminophosphates are microporous materials similar to zeolites. Few of the structures are having 3D-framework and few are having 2D-layer type structure or 1D-chain structure. Most of the three-dimensional (3D) structures are noble and some appear to be structurally related/analogue to the zeolite family as the same building units (SBU) construct framework of both. At the time of discovery of aluminophosphates, Union Carbide reported about 20 framework structures, of which at least 14 were microporous 3D-framework and 6 are 2-D layer-type materials. One of the noble 3D structures that is AlPO-5 (MFI), was also determined by single-crystal X-ray methods at that time.

Aluminophosphate molecular sieves are made up by corner-sharing of AlO_4 and PO_4 tetrahedral units (via oxygen bridge) which are in strict alternation in the framework (Fig. 4) to fulfil the requirement of Loewenstein's rule ^[23] (Al-O-Al bonding avoidance) as aluminium atoms are in tetrahedral coordination here. These tetrahedral units form a three dimensional network containing channels and pores which make them particularly attractive for adsorption and catalytic reaction. $[\text{AlO}_4]^-$ and $[\text{PO}_4]^+$ tetrahedral units have one negative and one positive charge respectively. These tetrahedral units neutralise charge of each other when combined to form the framework and therefore produce electrically neutral framework. But when transition metal ions (generally in divalent state) replace any of the framework atom (Al or P), charge imbalance is caused on the framework ^[24] which leads to Brønsted acid sites and may also cause Lewis acid centres, if any metal ion remains coordinatively unsaturated in the framework or due to unfilled d orbital in metal ions.

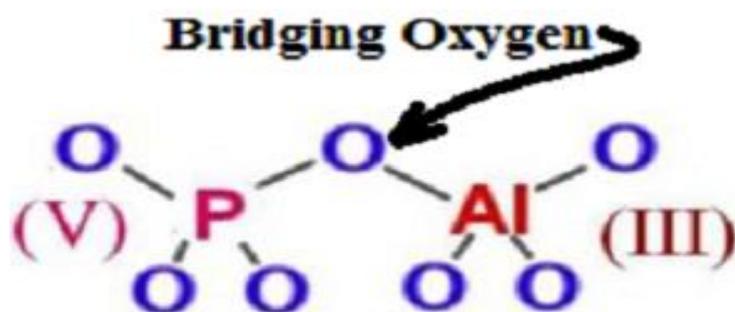


Fig. 4. Chemical bonding in the framework of an aluminophosphate structure

Their general formula can be expressed as $[(\text{AlO}_2)_x \cdot (\text{PO}_2)_x] \cdot y\text{H}_2\text{O}$ which indicates that unlike most of the zeolites, the aluminophosphate molecular sieves are ordered with an Aluminium/Phosphorus (Al/P) ratio of one i.e. always unity. Apart from their structural similarity, the crystal chemistry of AlPO-n molecular sieves and zeolites differ considerably as aluminophosphate frameworks are neutral in contrast to the negatively charged aluminosilicate. The aluminophosphate framework structures vary in the orientation of the AlO_4 tetrahedra and PO_4 tetrahedra to form different framework types and in this respect they are similar to the zeolites which differ in having electrically charged frameworks, however only some structure are noble but some are analogue of zeolites.

Zeolites and zeotypes are open-structure framework, consisted of many channels and/or interconnected voids of discrete size (in the range 0.3-20 Å) which are occupied by cations and water molecules. The primary building unit (PBU) of these structures is the individual tetrahedral $[TO_4]$ tetrahedral unit [Fig. 5A], where T refers to Si & Al (in aluminosilicate), Al, Si & P (in aluminophosphate) or metal ion (Me) e.g. Co^{2+} or Mn^{2+} .

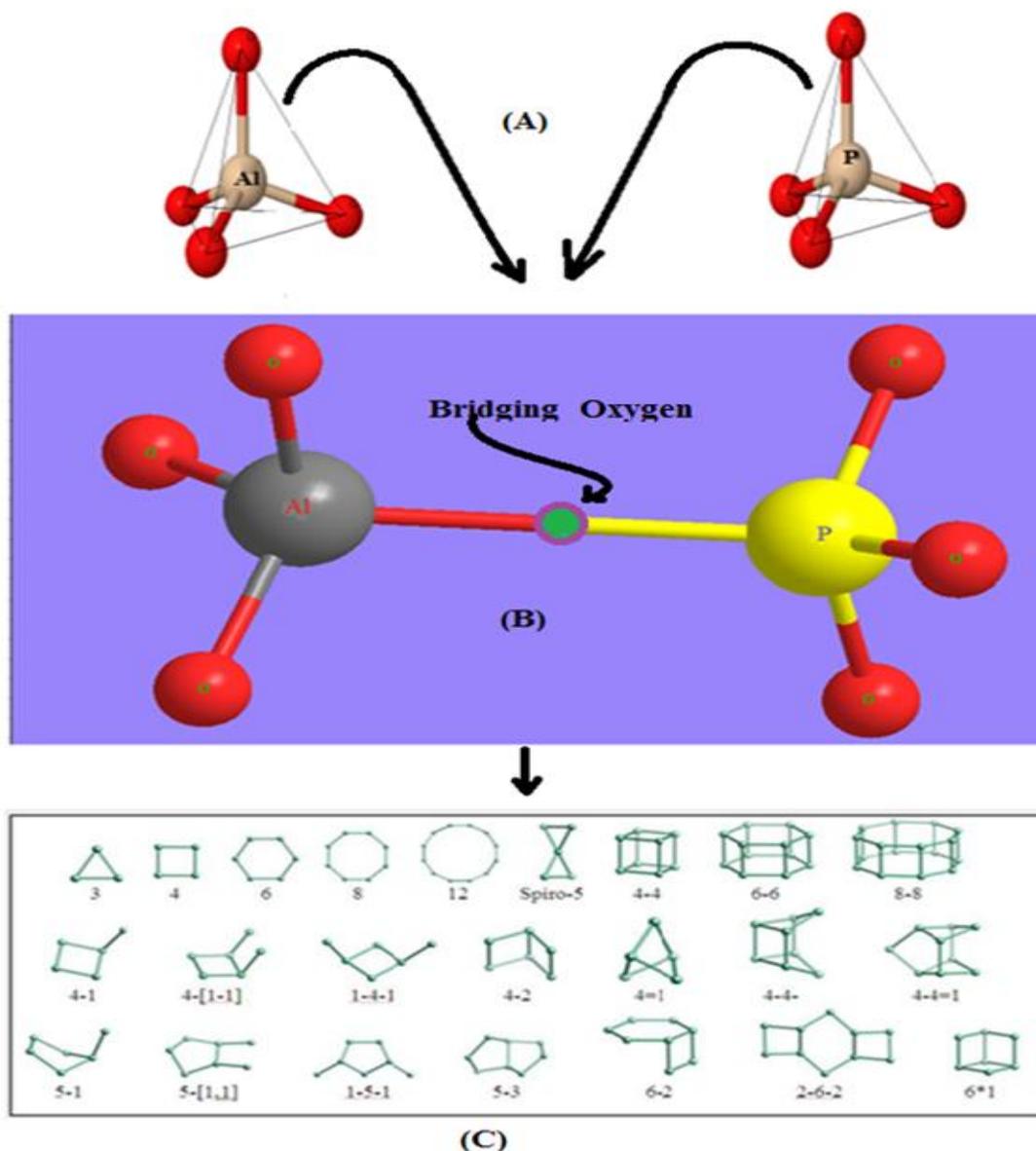


Fig.5. Construction of framework by the tetrahedral units. Single tetrahedra of aluminum and phosphorus (Primary Building Units) (A). Bonded tetrahedral units via oxygen (B). Different Secondary Building units (C) in which each corner-ball is showing a tetrahedral unit. Here bridging oxygen has not been shown for clarity.

Lowenstein has formulated that whenever two tetrahedra are linked by an oxygen bridge, the centre of only one of them can be occupied by Al; the other centre must be occupied by Si or other small ions having an electrovalence of four or more [23]. In simple words, Al-O-Al, P-O-P or Me-O-Me bonding is not possible in the framework of these materials. When the primary building units are combined, they produce simple ring like structure presented in Fig. 5C, which are known as secondary building units (SBU). A SBU is consisted of selected geometric groupings of primary tetrahedral units. There are nine such building units, which can be used to describe all of the known zeolite structures, although several other SBUs are also possible. These secondary building units consist of 4, 6 and 8-membered single rings, 4-4, 6-6 and 8-8 member double rings, and 4-1, 5-1 and 4-4-1 branched rings etc. The topologies of these units are shown in Fig. 5C. These SBUs combine to form more complex building polyhedral (Tertiary Units) presented in Fig. 6 (A, B).

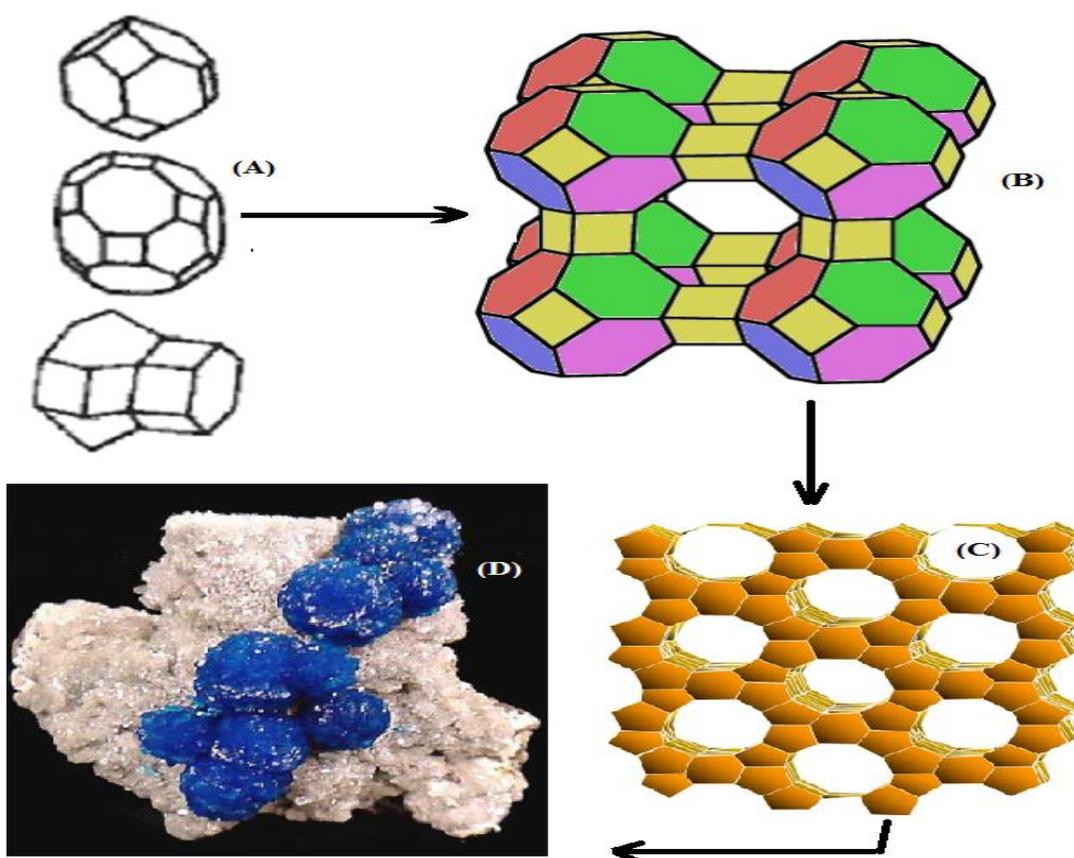


Fig. 6. Complex polyhedra formed by the joining of various SBUs in a regular pattern (A, B). An aluminophosphate framework with the unidirectional pore channels (C). Colourful crystal of aluminophosphate (D).

Finally, all these units form different framework structure-types (Fig. 6C) depending on the synthesis conditions e.g. temperature of crystallization, template used etc. The template acts as a structure directing agent and preserves the pore symmetry of framework. On calcination of the material, organic template gets burned from pore giving porous structure.

1.3.3 Isomorphous substitution

It has been clear in the last section that aluminophosphates are built from the strict alternation of AlO_4 and PO_4 tetrahedral units ^[25]. Thus composition of aluminophosphate framework should always has the ratio of aluminium to phosphorus equal to (Al/P) unity. Loeswentien rule is applied for the determination of distribution and arrangement of these tetrahedral units only which are tetra-coordinated ^[23]. However elemental composition of aluminophosphate may be changed depending on the several conditions for example presence of defected-framework centres ^[25]. When the aluminophosphates were first synthesised by Union Carbide Laboratories, the basic target was to develop a catalyst material with greater flexibility and efficiency and to prepare a material similar to zeolite which can be prepared by combination of other elements that are used in the synthesis of zeolites. Result was the discovery of aluminophosphate material ^[19]. Unfortunately this material is electrically neutral with either less or no catalytic efficiency. Now the research was directed to generate catalytic power in the framework of this material. In 1986, a successful attempt was done in this regard ^[19, 26-29] when elements of aluminophosphate framework were isomorphously substituted by the other metals. In the isomorphous substitution, an atom with about similar or crystallographically adjustable radius, replaces any of the atom of framework that are Al or P. However replacement is crystallographically controlled and is limited. Only those elements from periodic table can be replaced which are crystallographically favourable in the unit cell of crystal of aluminophosphate framework. Several transition metals and other earth metals have been reported to be incorporated in the framework of aluminophosphate ^[30]. Although it has been a matter of research that which atom of framework will be replaced by the third atom. Few of the reports, support only replacement of only aluminium atom and few reports claims for replacement of both Al or P atom ^[30].

Fig. 7 shows the replacement of an aluminium atom by cobalt in the framework of aluminophosphate.

Flanigen et al. [27] elucidated the bonding concepts in AIPO-n based molecular sieves. The linkages of Al–O–P, Si–O–Si, Si–O–Al, Me–O–P, Me–O–P–O–Me have been observed, while the linkages of P–O–P, P–O–Si, Al–O–Al, Me–O–Al, Me–O–Me appear to be unlikely. Martens and Jacobs further elaborated the types of isomorphic substitutions according to various substitution mechanisms [31].

1.3.4 Acidity of aluminophosphates and chemical behaviour of framework bonding

In the last subsection, explanation of the structure of aluminophosphate is given. Thus it is clear that one AlO_4 tetrahedral unit has one negative charge and similarly PO_4 tetrahedral unit has one positive charge. When these primary building units combine to form a zeotype framework, they cancel out the total charge on the framework. When other atom with different oxidation state ($\text{Me}^{2+,3+,4+}$ etc) replaces Al Or P atoms, a charge imbalance on the framework of parent aluminophosphate is caused which is shown in Fig. 7. In the Fig. 7b, total charge on the framework is zero but when one aluminium atom or one tetrahedral unit $[\text{AlO}_4]^-$ of framework is replaced by the cobalt tetrahedral unit $[\text{CoO}_4]^{2-}$, only single negative charge of cobalt tetrahedral unit is balanced by the phosphorus tetrahedra $[\text{PO}_4]^+$ and rest one negative charge remains unbalanced on the framework of aluminophosphate (Fig. 7c) which is balanced by a proton (Fig. 7d). This proton acts as the Brønsted acid sites in the framework. However, several reports also claim for Lewis acid sites in the framework of the aluminophosphate due to the presence of either unfilled orbital of framework atoms or due to the presence of defect centres in framework where few tetrahedra atoms are coordinatively unsaturated. In the literature review, several attempts were made to understand the chemical bonding of proton in the framework. Recently, DFT and quantum chemistry were also utilised to understand the actual bonding nature of these hydroxyl groups between two tetrahedra of framework [32-34]. Nature and behaviour of intrinsic acidity in aluminophosphate depends on the chemical properties of the substituting atom. A possible bonding structure has been proposed by Tielens et al. [35] (Fig. 8).

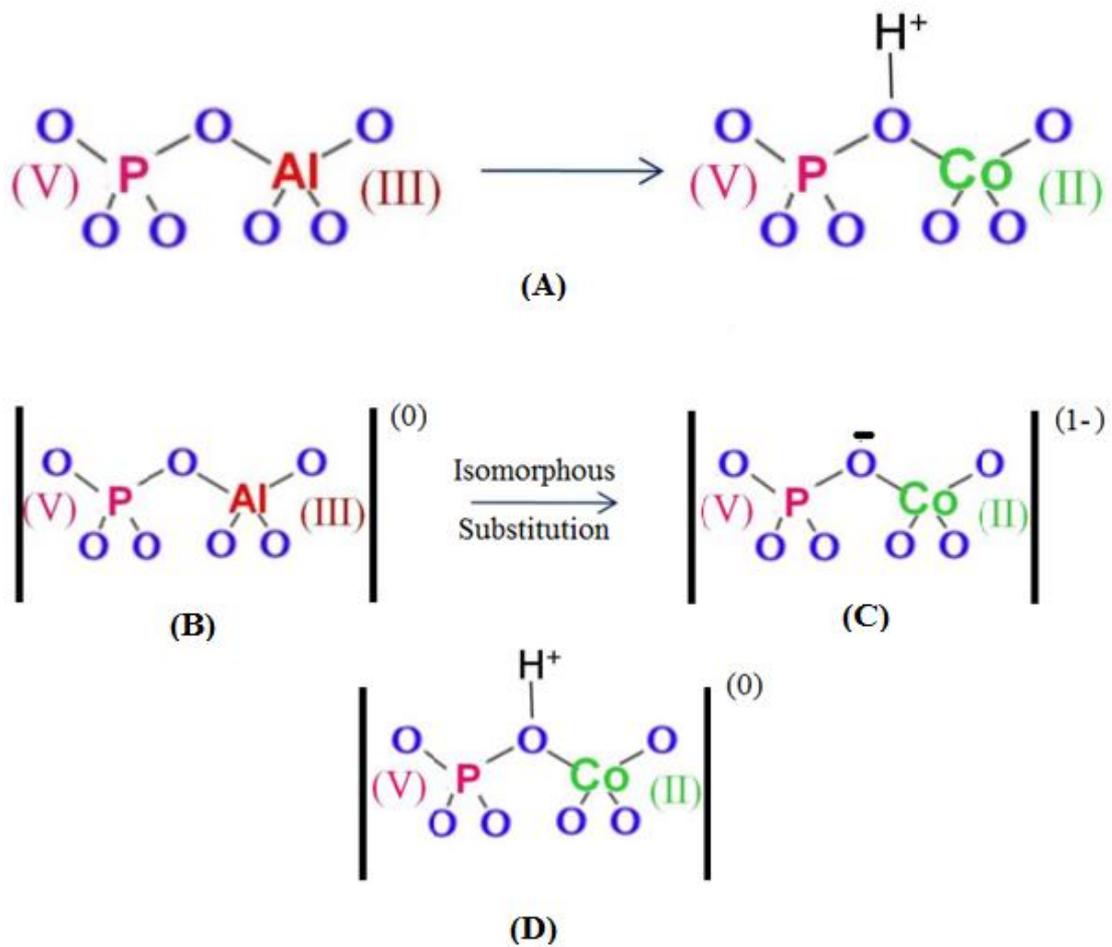


Fig. 7. Isomorphous metal substitution in aluminophosphate framework

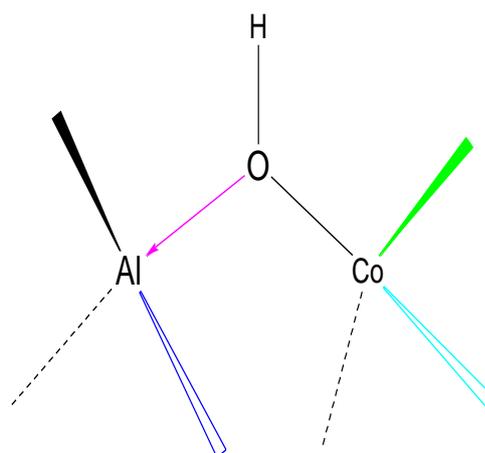


Fig. 8. Proposed structure of bonding in AlPO-n framework proposed by Tielens^[35].

1.4 Synthesis of aluminophosphate materials

1.4.1 Requirement of reagents

Zeolite synthesis is a subject of perturbations caused by impurities present in the source materials used for synthesis. Such contaminations may remain insoluble in the reaction mixture during crystallization of zeolite or aluminophosphate and may cause undesired species to nucleate. Thus it is required to use pure reagent for synthesis of zeolites. Few frequently used chemicals are discussed below:

(A) Source of aluminium

Generally aluminium isopropoxide or pseudoboehmite is used as the alumina source. Both these sources of alumina were used as the starting reagents for the synthesis. Alumina source has a great effect on the synthesis of aluminophosphate as it affects the pH of reaction gel that may alter the resultant product after crystallization. Role of alumina source for the synthesis of aluminophosphate is reviewed in our article ^[36].

(B) Silica source

Several silica sources can be used in various zeolite syntheses. For example silica sol, sodium silicate, colloidal silica (Ludox), precipitated silica etc.

(C) Source of phosphorus

Generally in the synthesis of aluminophosphate materials, aqueous phosphoric acid is used but polyphosphoric acids are also used.

(D) Template

It is needful to maintain a homogenous pore size and shape of aluminophosphate frameworks. Thus template (structure directing agent or SDA) material is used. Generally organic amines are used as a template but research is not limited up to the use of these amines. Now a days several specially designed templates are being used ^[37]. Surfactants ^[38] are also good alternative for the purpose. Sometimes seeding ^[39] by a small amount of the same material which is to be synthesised, is used in the reaction mixture to crystallize the material.

Organic amines or quaternary ammonium salts exhibit a critical structure directing role in the synthesis of aluminophosphate based molecular sieves. They exert both steric and electronic influence^[40] on the synthesis of aluminophosphate. In their absence, no crystalline porous aluminophosphate is produced. More than eighty amines and quaternary ammonium salts have been used as template species. Their structure directing specificity varies widely. For example, more than twenty templates lead to the formation of AlPO-5, which is a structure type with nearly a circular channel system having a diameter of ≈ 0.73 nm. On the other hand, several organic amines are known to produce different framework structures by slightly changing the synthesis variables. Thus, di-n-propylamine can be used in the synthesis of many aluminophosphate-based molecular sieves (AlPO-4-11, MAPO-39, CoAPO-43, CoAPO-50, SAPO-n (n = 5, 11, 31))^[41, 42].

(E) Water content

When the composition of the reaction mixture for the aluminophosphate synthesis is established, water content of the reagents has to be taken into account [IZA].

(F) Metal sources

When the metal substituted aluminophosphate materials are to be synthesised, metal salts are used. In this study, acetates or nitrates of cobalt and manganese were used. Here only theoretical aspects about reagent sources are considered. Detailed explanation of reagent used in the study, are given in the next chapter.

1.4.2 General synthesis procedure for the synthesis of zeolite/zeotype

In typical synthesis procedure, source of alumina is mixed to a solution of phosphoric acid solution in water. Alumina is either mixed directly to phosphoric acid solution or slurry of alumina prepared in water, is mixed to acid solution. Acid may also be mixed to the alumina source drop wise. This mixture is then stirred for proper homogenization. To this mixture, metal salt is mixed for doping purpose although metal salt may also be mixed with phosphoric acid which can be mixed to the alumina source directly. Stirring is mandatory in synthesis. Now template is mixed to this mixture and stirring is continued. This mixture is then transferred to autoclave for

crystallization. After crystallization, the autoclave was cooled, the material was washed, dried in air and calcinated for using as catalyst.

1.4.3 Mechanism of crystallization and role of variables

This particular energetic is very important in the rational synthesis of such materials which may regulate/control the synthesis-chemistry and all physical properties of aluminophosphate materials.

The mechanism of zeolite and aluminophosphate synthesis is same in general terms but few variations are in both the types e.g. aluminophosphates are generally crystallized in acidic solution but the condition is reversed in case of zeolites. pH is the main variable in both types, because nucleation and crystal growth are typically governed by a driven force related to the super saturation which is also controlled by pH. Temperature, role of template or SDA ^[43], molar composition of gel, time and procedure of synthesis are the issues which also affect the mechanism of synthesis. The basic knowledge of crystallization and synthesis can be obtained in the verified synthesis of zeolites from IZA commission. The mechanism and role of variables in case of aluminophosphates are listed in reference ^[36].

The diverse coordination and connection of Al and P, has created a diverse structure and composition of aluminophosphate materials with the aid of various templates. Due to their immense importance, rational synthesis of these aluminophosphates is required to fulfil the desired need of particular interest in material science applications. For rational synthesis of AIPO-n, a proper understanding of the structural construction or crystallization mechanism is needed and is a challenging task too. The use of several In-situ and Ex-situ instrumental techniques have made easy the hurdle of complex conditions in the way of hydrothermal synthesis to understand crystallization. Researchers ^[44-49] tried to explain crystallization from the first laboratory synthesis of aluminosilicate and aluminophosphate molecular sieves. Li and Davis ^[50] initially indicated about the important role of water in crystallization of VPI-5. This indication probably was utilized by Oliver et al. ^[51] and they proposed the crystallization mechanism for aluminophosphates. Instead of less clear initial step, this can be taken as the general pathway for the synthesis of VPI-5 and related hydrates and dense phases in the current knowledge of different approaches of corresponding crystallization

mechanisms. According to the model of Oliver et al. ^[51] linear chain aluminophosphates are the building blocks (which are primary structure to be crystallized) for synthesis system and water acts as a catalyst here. Other complex aluminophosphate chains are formed through hydrolysis, condensation and self-assembly pathway of this linear chain aluminophosphate, under a particular set of conditions (nature of template, gel composition, pH , temperature etc.) which in turn may produce porous layer or 3D open framework type structures.

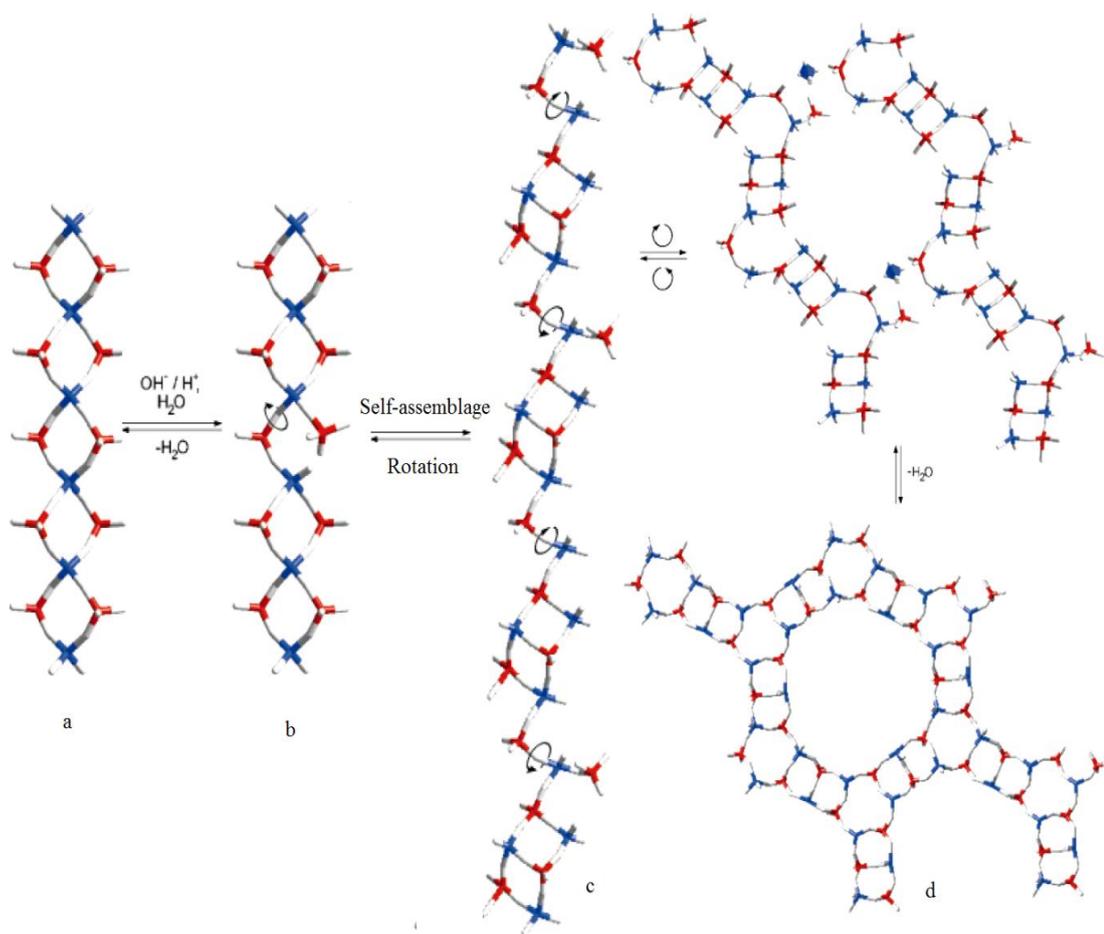


Fig. 10. Crystallization mechanism of aluminophosphate (VPI-5 as a model) proposed by S. Oliver

Oliver et al. ^[51] stated that in the initial gel, phosphoric acid mineralizes alumina and phosphate ions break the Al-O-Al linkage followed by the formation of Al-O-P covalent bond. In the next step an aggregation polymers exists for the metal phosphate which is stable in the lower pH and precipitates as pH increases. In this

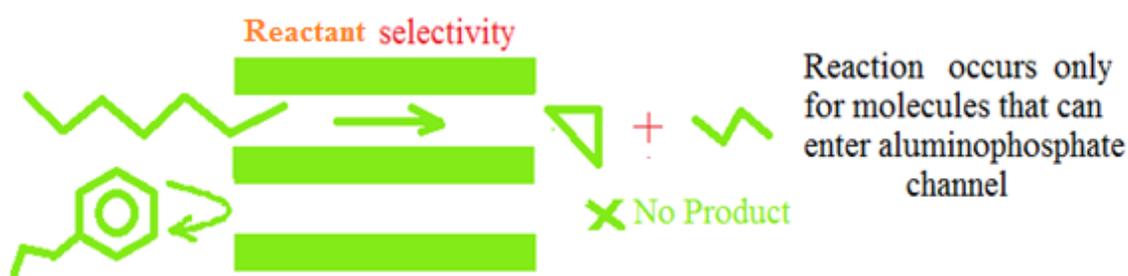
order he supposed that higher molecular weight species (aggregation polymers) exist as a chain aluminophosphate prior to precipitation. These chains act as primary building blocks or precursor and self-assemble to produce various structures via hydrolysis, rotation and condensation.

These chain (metastable) structures (Fig. 10a) are consisting of aluminium corner sharing four-rings ($\text{Al}_2\text{P}_2\text{O}_4$). AlO_4 tetrahedral units are linked to (via oxygen) four phosphorus atoms which are only connected at two points to the chain and also involve one P-OH and one P=O group to complete their four coordination. Upon hydrolysis in reaction mixture, Al-O-P bonds are broken and Al-OH and P-OH groups are formed (Fig. 10b). Rotation about the other (remaining) Al-O-P linkage brings Al-OH and P-OH groups close together which allow intra chain condensation (Fig. 10c). In this way different types of complex-chains are formed on progressive hydrolysis, rotation and condensation. Inter complex-chain condensation leads to final framework structure (Fig.10d).

1.5 Properties and application of aluminophosphates

1.5.1 Shape selectivity

Aluminophosphate materials are selective catalysts which show selectivity for reactants, products and transition states in a reaction ^[52].



1.5.2 Adsorption

These materials are good adsorbers thus widely used as the water softener, separation of gases, separation of toxic elements and radioactive waste treatment etc ^[53, 54]. They can remove water to very low partial pressure and are very effective desiccants, with a capacity of up to more than 25% of their weight in water. They can remove volatile organic chemicals from air stream and separate isomers and mixture of gases. A widely used property of zeolites is that of gas separation ^[55]. The porous

structure of zeolites can be used to “sieve” molecules having certain dimensions and allow them to enter the pores. They are used to purify natural gases through the removal of impurities such as carbon dioxide, sulphur dioxide and water. In addition to the upgrading natural gas, zeolites are used to separate oxygen and nitrogen in pressure swing adsorption columns. Domestic uses relate primarily to the odour and liquid adsorbing characteristics of zeolite. A range of gases including formaldehyde, hydrogen sulphide has been shown to be adsorbed by zeolites.

In the USA, zeolite is routinely added to small air filters to adsorb such gases and reduce allergy problems. Zeolites can adsorb or exclude many materials. They are thus widely used in the environmental applications^[56], odour control, water adsorption & desorption, desiccation, gas adsorption and industrial gas separation^[57].

1.5.3 Catalysis

Aluminophosphates and their metal substituted forms are used as catalyst and several applications have been reported^[58] in the open literature with excellent yield of the product. In this thesis main focus is on the application of substituted aluminophosphate as a catalyst in various ecofriendly reactions.

Aluminophosphates have the following inherent advantages over catalysis initiated by homogeneous catalysts:

- ❖ It is non-corrosive.
- ❖ The catalyst can be easily removed from the reaction mixture by decantation or filtration.
- ❖ The product selectivity can be achieved to a certain extent due to shape-selective nature of zeolite structure.
- ❖ These are environmentally benign, can be reused and are thermally stable.
- ❖ Acylation, alkylation, condensation, cyclization, esterification, etherification, nitration and transesterification are the most important reactions which involve the production of pharmaceutically important intermediates and other biologically active compounds can be synthesised using aluminophosphate catalysts.

Zeolites exhibit exceptional properties comparatively to other catalysts with respect to both activity and selectivity because of their ability to absorb and transform molecules in their inner pore volume. Shape selective catalysis and use of chirality for enantioselective catalysis^[59] is a great importance of these materials. An important

class of reactions performed by zeolites is the acid catalyzed reactions ^[58]. This is exploited in many organic reactions, including crude oil cracking ^[60-63], isomerisation and fuel synthesis ^[42, 61, 63, 64]. The shape and size of a particular pore system exerts a steric influence on the reaction, and thus controls the adsorption of reactants and desorption of products. A breakthrough herein was the industrial application of man-made zeolites X and Y in the cracking of heavy crude oil into lighter highly valuable products ^{[65] [66]} which resulted in a major increase in the yield of gasoline ^[67]. Nowadays, synthetic zeolites are being applied in industry, catalyzing numerous reactions mainly in the field of oil refining and basic petro chemistry. At present the hydro-isomerization of light alkanes over mordenite catalysts plays a key role as an environmental friendly way to enhance the octane quality of gasoline. Altogether, zeolite catalysts have become a most important sub-field of heterogeneous catalysts ^[15, 17]. Typical homogeneous acid catalysts such as AlCl_3 , BF_3 , H_2SO_4 , HF , H_3PO_4 , etc. are still commonly employed in industrial processes but these catalysts are not environment friendly. Therefore, considerable attention has been devoted in last years for the development of solid acid catalysts in petrochemistry and organic synthesis which are environmentally more acceptable. The use of solid acids such as zeolite, is convenient and also effective for acid-catalyzed reactions. There are two important aspects of zeolite catalysts i.e. activity and selectivity. The activity of the catalyst depends on the strength of chemisorptions whereas the selectivity of a catalyst is the ability to make a reaction in a particular direction to yield a particular product.

1.5.4 Other uses

Natural zeolites can be used to prepare lightweight concrete for construction. Its porous silicate structure makes it much lighter than sand with an increased volume per ton but with similar hardness and strength. Zeolite is free from clay which reduces the overall strength of concrete and its porous structure holds moisture which facilitates more rapid curing of concrete. When added to Portland cement as a Pozzolan, it can reduce chloride permeability and improve workability. Natural zeolite has high ion exchange capacity and a particular affinity for heavy metal cations. Zeolites are known to be slow release fertilizers ^[68]. Plant nutrients such as nitrogen and potassium are held by the negatively charged clinoptilolite structure and released on demand.

Zeolites are used as fillers in the manufacture of papers. These filler grades of zeolite have a large potential for utilization in paint and plastic industries. Zeolites can reduce ammonium and hydrogen sulphide levels in fish/prawn ponds, resulting in increased fish/prawn growth rates and population densities. Zeolite is an efficient ammonia remover and also provides a large surface area for nitrifying bacteria in recirculation systems. Zeolites not only provide optical clearness of water but also keep it biologically clean. Desalination is a process that removes dissolved minerals from seawater, brackish water or treated waste water.

On-Board Oxygen Generating Systems (OBOGS) also use zeolites in conjunction with pressure swing adsorption to remove nitrogen from compressed air in order to supply oxygen for aircrews at high altitudes.

In the aftermath of the Fukushima Daiichi nuclear disaster, sandbags of zeolite were dropped into the seawater near the power plant to adsorb radioactive cesium which was present in high levels. Hygroscopic property coupled with an inherent exothermic (energy releasing) reaction when transitioning from a dehydrated to a hydrated form makes natural zeolite useful in harvesting waste heat and solar heat energy. Zeolites are also used as a molecular sieve in cryosorption style vacuum pumps.

1.6 Review of literature

1.6.1 AIPO-5

At the onset of 1980's, the Union Carbide Laboratories reported ^[69] a new family of molecular sieves based on aluminophosphates (AIPO-n). Barrer and Marshall ^[70-72] were the first researchers who explored the incorporation of phosphorus into aluminosilicate structure with little success. Flanigen and Grose also reported synthesis of aluminosilicates, containing substituted phosphate ^[73]. Aluminophosphate molecular sieves exhibit well known enhanced structural diversity. Among all structural types of aluminophosphates, structures of AIPO-n and SAPO-n (silicoaluminophosphate) molecular sieves cover a wide range of different structural types in which some are analogous to zeolites e.g. SAPO-42 and SAPO-34. These SAPO-n (SAPO-42 and SAPO-34) have structure similar to zeolite A and chabazite structure respectively but there are also some unique structures such as AIPO-5 or VPI-5 ^[36]. Apart from their structural similarity, the crystal chemistry of AIPO-n

molecular sieves and aluminosilicate molecular sieves differ considerably as aluminophosphate frameworks are neutral in contrast to the negatively charged aluminosilicate. Aluminophosphate based molecular sieves can be synthesized hydrothermally at 100-250°C. Generally, MeAPO-n (metal ion substituted aluminophosphates) materials crystallize at lower temperature than other compositional variants (e.g. SAPO-n) for a same structure type ^[74] although this speculation is dependent on the method and conditions of synthesis and also the type of structure formed, depends on the variability of a number of factors.

About more than 20 structure types of aluminophosphates were reported by the Union Carbide Laboratories in 1982. AlPO-5 was one of them with one dimensional pore channel of about 10 Å. IZA has given the MFI structure code for this framework type. It is the most widely used aluminophosphate in various applications till date due to its simple procedure of synthesis and high thermal stability. Several catalytic reactions have been catalysed over this zeotype.

1.6.2 VPI-5

After the first synthesis of substituted aluminosilicate (1982), Davis et al. ^[75] reported first molecular sieve that was consisted of rings with greater than 12 T atoms (T is tetrahedrally coordinated atoms) and pores ≥ 12 Å i.e. VPI-5 (Virginia Polytechnic Institute Number 5) which belongs to the noble family of aluminophosphate based molecular sieve. VPI-5 is the largest pore size aluminophosphate framework and IZA has VFI code for this framework type. This framework contains rings consisting of 18 T atoms and pores ≥ 12 Å, although hypothetical molecular sieve with 18 or 24 T membered rings with one dimensional pore, had also been proposed ^[76] before the first synthesis of VPI-5. Element substituted VPI-5 have also been reported ^[36] with a variety of elements and checked for catalytic activity. This large pore aluminophosphate has tremendous properties such as thermal sensitivity and transformation to AlPO-8 ^[77] framework at low temperature and atmospheric pressure ^[36]. A triple helix of water molecules stay, inside the pores of the framework in place of template which does not remain inside the pores and surprising thermal stability of VPI-5 framework in controlled atmosphere. It has been reported that this transformation is reversible ^[78] although it

was not confirmed in beginning ^[79]. Few researchers ^[57] noticed on the basis of their work that VPI-5 can be synthesized by complete inorganic system.

McCusker et al. ^[80] have shown that in the hydrated VPI-5 structure (Fig.1) Al atoms between the fused four rings, are octahedrally coordinated with two water molecules and four framework oxygen atoms and remaining all Al atoms are tetrahedrally coordinated. These water molecules create triple helices in the 18 T ring channels of framework and fill the pore acting as an inorganic template. It was the beginning when d'Yvoire ^[81] separated VPI-5 together with AIPO-8 and other hydrated aluminophosphates (variscite, metavariscite, AIPO-H1, AIPO-H2, AIPO-H3, and AIPO-H4). A common feature of aluminophosphate hydrates is that, Al atoms are octahedrally coordinated in case of variscite and metavariscite and in rest of the cases (AIPO-H1, AIPO-H2, AIPO-H3, and AIPO-H4), it is coordinated in both forms i.e. tetrahedral and octahedral. These materials were prepared from dilute aqueous solution of alumina and phosphoric acid with a $P_2O_5:Al_2O_3$ ratio of 2.7 ^[81]. All the dramatic properties and synthesis variables have been covered in my article ^[36].

Due to very large pore size of this zeotype it has been used in several reactions as a catalyst ^[36] however poor thermal stability and its thermal transformation to the AIPO-8 structure has led to low scope of this thermally unstable framework (as catalyst) in catalysis which are performed in high temperature range.

1.6.3 SAPO-34

This is a silicon derivative ^[20] of aluminophosphate and IZA has given CHA framework type code for this zeotype because framework structure of SAPO-34 is analogous to that of the natural zeolite Chabazite (CHA). Effective pore openings (4.5 Å) of these materials are such that they can only adsorb straight chain molecules such as primary alcohols, linear paraffins and olefins. As a consequence, diffusion of larger molecules such as aromatics is largely restricted, leading to a high yield of lower olefins in the C_2 to C_4 range. Among the various metal modified small pore molecular sieves, NiSAPO-34 has received most attention since this catalyst exhibits high selectivity towards ethylene ^[82]. Many elements have been incorporated into SAPO-34 framework by isomorphous substitution to form MeSAPOs molecular sieves (Me=Be, B, Mg, Ti, Mn, Fe, Co, Ni, etc.) ^[7, 83]. And have been reported as useful catalysts for a variety of chemical reactions ^[60, 84, 85].

1.6.4 SAPO-5

Similar to the SAPO-34, SAPO-5 is also a silicoaluminophosphate type of the parent framework AlPO-5. Framework structure and symmetry is same as to the AlPO-5. This material catalyst has also been used in several organic reactions as a catalyst^[61]. Metal incorporation and generation of acid sites have been studied for this zeotype^[86, 87]. SAPO-5 molecular sieve structure is composed of 4 T ring, 6 T ring, and 12 T ring straight channels, which are interconnected by 6-ring windows.

Various reactions over the SAPO-n, AlPO-5^[2] and AlPO-11^[88] structure have been reported. These materials are able to catalyze various reactions such as cracking of hydro-carbons^[62], isomerization of olefins^[89], oligomerization^[64], hydroisomerization and alkylation^[90]. The acid properties have also been applied in polymerization or cyclization^[91]. The redox properties of CoSAPO-5 were applied for the selective oxidation of hydrocarbons^[92] or phenol^[17].

1.6.5 Nomenclature and abbreviations

Nomenclature of these zeotypes material (catalyst) is given according to the IZA commission. In this thesis, all substituted forms of zeotypes (AlPO-5, MnAPO-5, CoAPO-5, SAPO-5, MnSAPO-5, CoSAPO-5, SAPO-34, MnSAPO-34, CoSAPO-34) are abbreviated according to S.T. Wilson^[93]. Zeotype materials, which were not substituted by metals (SAPO-5, SAPO-34 and AlPO-5) are termed as parent materials. Generally these materials are abbreviated as MeAPO-n. Here “Me” refers to metal atoms which were used for isomorphous substitution (cobalt and manganese in this study). Here “n” represents characteristic number of a particular framework of zeotype which is either decided by IZA commission or inventor of that zeotype e.g. SAPO-5, SAPO-34. “A” is referred to aluminum and “P” represents for phosphorus atom. “S” represents for silicon atom. Representation of AlPO-5 is only different in which “Al” represents for aluminum atom. In this study, representation of Wilson et al.^[93] are followed.

1.6.6 6-nitro-2,3-diphenylquinoxaline (Quinoxaline)

Quinoxaline structure is a part of several heterocyclic compounds and is used as an intermediate in organic synthesis of biologically active compounds^[94], possessing a wide and diverse spectrum of pharmacological properties^[95]. Several

medicinal uses of quinoxaline structure containing compounds have been reported ^[96]. Particularly quinoxaline containing compounds have been used as anti malarial agent ^[97], anticancer ^[98] and in anti-inflammatory activities ^[88, 99]. Quinoxaline nucleus is also associated with applications in dyes ^[100], dehydroannulenes ^[101], and cavitands ^[102, 103]. The quinoxaline nucleus is a part of several antibiotics, such as echinomycin, levo-mycin, and actinomycin that inhibit the growth of Gram-positive bacteria and are active against various transplantable tumours ^[104]. Optical properties have also been reported for polymer composites of quinoxaline ^[14]. Quinoxaline derivatives have been used as D–A polymer units due to the electron-withdrawing property of two amine nitrogens. In addition, quinoxaline derivatives exhibit electronic properties that can be changed with various substituents ^[105-110].

Quinoxaline compounds have been synthesized using various catalysts such as ceric (IV) ammonium nitrate ^[111], iodine in DMSO ^[112], sulfamic acid ^[113], Yb(OTf)₃ ^[114], H₆P₂W₁₈O₆₂.24H₂O ^[115], CuSO₄.5H₂O ^[116], Rice husk ^[117] etc. Lewis acids and many other catalysts including sulfamic acid ^[113], montmorillonite K-10 ^[118], polyaniline-sulfate salt ^[119], InCl₃ ^[120], have also been used. Cellulose/sulphuric acid has also been utilised ^[121, 122] as a catalyst. In this work several metal substituted aluminophosphates were used as a catalyst to synthesize quinoxaline derivative.

1.6.7 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol (Imidazole)

Imidazole ring has drawn great interest among the chemists because Imidazole and its derivatives cover very important and wide aspects of pharmacological and biological activities ^[123, 124] and it can be used as a versatile building block for synthesizing natural products and therapeutic agents ^[125, 126]. In particular, 2,4,5-trisubstituted imidazole occurs as an anti-inflammatory ^[127], analgesic ^[128] and glucagon & CB1 cannabinoid receptor antagonist ^[129-131]. Imidazole also plays an important role in metabolic and enzymatic actions inside the body ^[132-136]. Anti-tumour activity has also been reported ^[137]. Application in agriculture and plant physiology has also been reported ^[138]. Imidazole also occurs in the hypnotic agent Etomidate ^[139]. In addition, imidazole has been reported for potential applications ^[140] in molecular photonics and sensing due to its piezochromism, photochromism and thermochromism properties with several other optical applications ^[141].

Various synthesis methods with different catalysts have been reported for the synthesis of Imidazole such as silica gel or zeolite-HY ^[142], silica gel/NaHSO₄ ^[143], molecular Iodine ^[144], K₅CoW₁₂O₄₀.3H₂O ^[145], heteropolyacids ^[146], HClO₄-SiO₂ ^[147], Yb[OTf]₃ ^[148], l-Proline ^[149], BF₃-SiO₂ ^[150], and silica-supported Wells-Dawson acid ^[151]. Microwave irradiation ^[152-154] and refluxing in acetic acid ^[155] has also been utilized successfully. Silica sulphuric acid ^[156], NiCl₂.6H₂O/Al₂O₃ ^[157], ZrCl₄ ^[158], ionic liquids ^[159, 160], ceric ammonium nitrate ^[161] and Cu(NO₃)₂/zeolite ^[162] has also been reported. Tetrafluoroborates and solid supported tetrafluoroborates with other derivative forms have also been utilised ^[163]. However, all the above methods have their own importance in a particular aspect with considerable potential but they also suffer from one or more disadvantages such as the use of costly moisture sensitive metallic reagents, specific reaction time and conditions, extra separation procedures, huge amount of metal wastes into the environment due to large amount of catalyst loadings, release of solvent and toxic substances in the environment. It is unfortunate that all these types of supported catalysts have a major drawback of leaching of catalytic centres in reaction mixture in highly extreme conditions of temperature.

1.6.8 Esterification

Esters, which include a wide category of organic compounds ranging from aliphatic to aromatic, are generally used as plasticizers, solvents, perfumery, and flavour chemicals, and also as precursors for a gamut of pharmaceuticals, agrochemicals and other fine chemicals ^[164]. The conventional homogenous catalysts which are widely used in industries for esterification include H₂SO₄, HCl, HF, H₃PO₄, and ClSO₂OH ^[165, 166]. But they suffer from several drawbacks, such as their corrosive nature, the existence of side reactions and the fact that the catalyst cannot be easily separated from the reaction mixture. Due to stringent and growing environmental regulations, the chemical industry needs the development of more eco-compatible synthetic methodologies ^[167]. The use of heterogeneous acid catalysts offer an alternative and has received a lot of attention in the past years in esterification reactions ^[168].

Some commercially available plasticizers such as dibutylphthalate (DBP), dioctylphthalate (DOP), dioctyladipate, di-*iso*-entylphthalate (DIPP), and di-*iso*-heptyl phthalate (DIHP) are usually prepared via esterification reaction between

corresponding acids/anhydrides and alcohols in the presence of acidic catalysts. Use of heteropolyacids ^[169], silicoaluminophosphate molecular sieves ^[170, 171] and sulfated zirconia ^[172] as heterogeneous catalysts for esterification and/or transesterification reactions have been reported earlier. The use of these catalysts cause some problems such as corrosion, loss of catalyst, and many other environmental problems. Therefore, development of more efficient catalysts will be interesting and useful. It is well known that the use of heterogeneous catalysts for liquid phase organic synthesis reactions can give a lot of benefits, for example, a clean reaction product solution can be obtained after simple filtration, the catalyst is easy to be recovered and reused, avoidance of corrosion etc. Hence, attention has been paid to the use of heterogeneous catalysts in the esterification reactions.

Proposed Work

The proposed work involves synthesis of metal substituted forms of zeotypes or aluminophosphates viz AIPO-5, SAPO-5 and SAPO-34 by hydrothermal method and their characterization by XRD, TEM, and FTIR techniques. These synthesized materials will be used as catalysts to synthesize organic compounds. Transition metal doped forms of these aluminophosphates may be used as an efficient catalyst in various ecofriendly reactions. The various forms of these materials will be synthesized by the isomorphous substitution of transition metals in the framework of these zeotypes. Zeolites are having uniform pore sizes with molecular dimensions, good stability, selectivity and activity due to their crystallinity. The possibility of incorporating heteroelements into the framework and their ion exchange capacities make them unique materials in several processes. The main advantage of using zeolites in comparison to a non-zeolitic catalyst is that they are environmentally benign, can be reused and are thermally stable.

The proposed work involves:

1. Synthesis of transition metal doped analogues of aluminophosphates namely AIPO-5, SAPO-5 and SAPO-34.
2. Characterization of these analogues of aluminophosphates by X-ray diffraction (XRD), Transmission Electron Microscope (TEM) and FT-IR spectroscopy analysis.
3. Synthesis of imidazoles using synthesized analogues of zeotypes as catalyst.
4. Use of synthesized metal doped analogues of zeotypes as effective and reusable heterogeneous catalyst for the synthesis of Quinoxaline derivative.
5. Study of catalytic efficiency of synthesized metal doped zeotype analogues for esterification reaction.

Proposed Methodology

- Synthesis of Zeolites by hydrothermal method.
- Separation of the material from suspension with the help of high speed centrifuge.
- Synthesis of organic compounds using zeolite as a catalyst.
- Separation of by-products by column chromatography.
- Product characterization by suitable analytical techniques and correlation of the results for better scientific approach.