This piece of work was aimed to understand synthesis of different zeotypes and isomorphous substitution of cobalt and manganese atom in the framework of various aluminophosphates (zeotypes). Further work was aimed to use these catalysts as green catalysts in various reactions. Synthesis of different zeotypes was carried out by hydrothermal method and isomorphous substitution which generates catalytic activity in these catalysts. Synthesized materials were characterized by different techniques such as X-ray Diffraction, Fourier Transform–Infrared Spectroscopy, Scanning Electron Microscopy, Energy Dispersive Spectroscopy, BET Surface area analysis etc. Catalytic studies were carried out to synthesize 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol, 6-nitro-2,3-diphenylquinoxaline and butyl acetate at various synthesis conditions such as effect of reaction time, weight of catalyst, reaction temperature and catalyst recycling. The synthesized products were characterized by NMR and FT-IR techniques. The study is divided into five chapters which are summarized as below.

Chapter-1

This chapter contains the general introduction about different aspect of the work and research problem. It introduces about research problem, solution and recent approaches in the field. It also provides general idea about catalysis and catalytic reactions including various catalysis reactions and catalysts. Green chemistry aspects and use of catalyst materials for various syntheses are covered in this chapter. In this chapter, use of zeotypes and their synthesized metal analogues as green recyclable solid acid heterogeneous catalysts has been reviewed in such a way that one can reproduce the work and use these catalysts in reactions where environmental issues are important. A brief review of the related work on different types of zeolites and reactions catalyzed by zeolites, has been included. It also includes scope, objective, advances and proposed methodology of the work. Application of these materials in various fields has been summarized. Basic concept about structure of zeolites and zeotypes, isomorphous substitution, metal incorporation and generation of acidity in the framework of aluminophosphate materials are explained in this chapter. Scope, objective, advances and proposed methodology of the work are also a part of this chapter. Various applications of zeolites and zeotypes materials have been mentioned in this chapter in addition to the application of these materials as a catalyst.

Chapter-2

This chapter includes materials and methods used in this work. In this chapter, different materials and methods are embedded with the explanation of other materials and methods which can also be utilized for the same study as per literature review. The source of different starting materials and their chemical properties are also mentioned in this chapter. A review about structure, occurrence, chemistry and other general information of zeotypes used in the present study (AlPO-5, SAPO-5 and SAPO-34), are also a part of this chapter. In this chapter, details of synthesis methods used in this study are explained in such a way that one can reproduce work. This chapter also includes the instrumentation part with their working principle used for the characterization of materials such as X-ray Diffraction, Fourier Transform–Infrared Spectroscopy, Scanning Electron Microscopy, Electron Dispersive Spectroscopy, BET Surface area analysis etc. This chapter explains the principle and basic concept of instrumentation techniques which were used for the characterization of the synthesis product of the reactions under study with standard parameters of instrumental operation.

Chapter-3

This chapter includes characterization of synthesized catalyst materials (AlPO-5, MnAPO-5, CoAPO-5, SAPO-5, MnSAPO-5, CoSAPO-5, SAPO-34, MnSAPO-34, CoSAPO-34). These synthesized materials were characterized by different techniques such as X-ray Diffraction, Fourier Transform–Infrared Spectroscopy, Scanning Electron Microscopy, Electron Dispersion Spectroscopy, DRS, BET Surface area analysis etc. For initial confirmation of successful synthesis of the materials, XRD technique was used and XRD patterns reveal that all the materials are crystalline in nature and obtained XRD phase is desired one. X-ray diffraction patterns of metal substituted forms and their corresponding parent zeotypes are similar which confirm that parent framework has not undergone any significant structural change during the incorporation of metal ion and the crystallinity of the materials was preserved, though, a slight change in the intensity of few XRD peaks was observed. FT-IR was used for evaluation of bonding in structure of the framework of zeotypes material and changes on metal incorporation in the framework of these materials. Result obtained shows that FT-IR spectrum are as expected. Metal incorporation causes some changes in lower region which confirms the metal incorporation. FTIR spectra of all materials show absorption band at around 450 cm^{-1} which was attributed to Si-O-Al bond and those at around 740 and 980 cm^{-1} were attributed to the asymmetric and symmetric stretching of materials respectively. These bands are characteristic band in the FTIR spectrum. Slight changes and shift of band at around 3540 cm^{-1} confirmed metal incorporation in the zeotype framework. From the SEM images, it is observed that all the nine synthesized materials have relatively non uniform surface, unique pore morphology and difference in the particle size. SEM images show that zeotype AlPO-5 and its metal substituted forms are like cauliflower in shape at low resolution. Shape of the crystals of SAPO-5 is not perfectly hexagonal but few crystals are looking to be hexagonal with size upto 2µm. Crystals of SAPO-34 are perfect cubical in shape and their size is upto 7 µm. However incorporation of metals in SAPO-34 causes variation in morphology of substituted crystals. Irregular shape of these crystals was attributed to the high amount of doped metals. The EDS study confirmed elemental composition of these synthesized materials. Elemental composition of materials (calcinated) shows that the ratio of Al/P is exactly one for most of the materials and elementals composition is in accordance which was taken during the preparation of gel precursor of these materials. However, few variations in the elemental composition are due to the presence of unburned carbon residue. To obtain surface area of materials, BET method was used which has been covered in this chapter. Surface area of materials is comparable to the standard one.

DRS technique was used in this study to calculate metal incorporation in the framework of zeotype materials. In case of the cobalt substituted materials, all DRS spectra show a triplet band at around 550nm which is characteristic of successful cobalt substitution in the framework of parent material. DRS spectra of Manganese substituted materials also show a characteristic band at around 250nm. Result obtained for this study, are listed in this chapter. Additionally NMR technique and the results obtained for the reaction products are also listed in this chapter.

Chapter-4

In this chapter, the results of the study are discussed and interpreted in order to find analytical relation, causes and factors. The results of catalytic activity of various zeotype catalysts (AlPO-5, MnApo-5, CoAPO-5, SAPO-5, MnSAPO-5, CoSAPO-5, SAPO-34, MnSAPO-34, CoSAPO-34) for the synthesis of organic compounds viz 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol, 6-nitro-2,3-diphenylquinoxaline and esterification reactions are listed with different synthesis variables and possible correlation to the factors causing these results. These results have been interpreted by carrying out the reactions under different experimental conditions:

- Reaction time
- Catalyst weight
- Reaction temperature
- Solvent
- Catalyst recycling

Chapter-5

It deals with summary & conclusion of the study undertaken. The catalytic efficiency of various synthesized forms of catalyst materials is concluded in this chapter. Few of the valuable points which may be useful in order to reproduce the work are also included in this chapter as a concluding remark.

Conclusion

The zeotype catalysts used in this study are good solid acid catalysts. These catalysts have several properties which make them valuable in order to use them as solid catalyst. These catalysts were synthesized by hydrothermal method. The isomorphous substitution of cobalt and manganese in these zeotype catalysts was carried out successfully. These synthesized materials were then subjected to the various characterizations after few post synthesis/crystallization treatments. All the obtained catalysts meet the requirement of XRD standards. XRD technique was employed in order to check phase of these catalysts which suggest that all the catalysts meet the pattern of standard XRD patterns, however VPI-5 shows a different pattern due to its conversion or thermal transformation at low temperature. After assurance of XRD phase, other characterizations were carried out. BET surface area measurement was carried out in order to measure the surface area which suggests that surface area is large. BET surface area of AlPO-5, SAPO-5 and SAPO-34 was found around 370 m^2/g, 390m^2/g and 450 m^2/g respectively.

DRS study suggests that metal atoms are in the framework structure thus has replaced framework atoms and metal atoms are not as adsorbed one on the surface of the catalysts. Excellent results were found for cobalt atom substitution which suggests successful incorporation of cobalt in the framework. Same results were obtained for manganese-substituted zeotypes.

Catalytic efficiency of the all three catalysts (SAPO-5, AlPO-5 and SAPO-34) is in the order as given below.

SAPO-5>AlPO-5> SAPO-34

Metal substituted (Cobalt and Manganese) forms of the above catalysts show different order of catalytic efficiency which is as given below.

Nonsubstituted or Parent catalysts > Cobalt substituted> Manganese substituted

Catalytic efficiency of these catalysts vary with reactants which is in the order as given below.

For Imidazole synthesis < For Quinoxaline synthesis < For esterification reaction

These obtained trends of catalytic efficiency are discussed in the fourth chapter. SAPO-5 shows the highest product yield for different reaction because its surface area is too large and pore size of SAPO-5 catalyst is also highest among all the synthesized catalysts. However metal ratio in metal substituted forms of this catalyst and crystal size and shape obtained by SEM-EDS study are not regular but due to large surface area and pore size, this zeotype has greater catalytic efficiency. AlPO-5 and its metal substituted form show lower efficiency than corresponding forms of SAPO-5 though they are from same framework type (AFI). It is assumed that due to absence of silicon in the framework of AlPO-5, its catalytic efficiency is low because corresponding metal analogues of SAPO-5 and AlPO-5 (CoSAPO-5, MnSAPO-5, CoAPO-5 and MnAPO-5) show difference in catalytic efficiency. Additionally surface area is also low for AlPO-5 catalyst which is also a factor leading to its lower catalytic efficiency. AlPO-5 shows the lowest catalytic efficiency among all the catalysts in this study. It is due to the fact that framework of AlPO-5 catalyst has no catalytic sites as there is no metal in its framework which are responsible for the generation of the catalytic sites. Whatever catalytic efficiency is shown by this catalyst, it is attributed to the framework defect and related Lewis acid sites present in the framework of AlPO-5. SAPO-34 shows the highest surface area among all the catalysts but its efficiency is least in this study. However efficiency of this catalyst is same as AlPO-5 catalyst. According to IZA commission, SAPO-34 belongs to Chabazite family or framework type (CHA) which has pore size of about 7-8 Å. This pore size is less than AlPO-5 AFI framework type (10Å). Due to this fact, SAPO-34 catalyst provides minimum access of catalytic sites to the reactant molecules in compare to AlPO-5. Larger surface area (as a major factor which affects product yield of reaction) of this zeotype (SAPO-34) was neglected here in making the above conclusion because surface area was measured by N_2-BET method in which nitrogen gas molecules were employed as adsorbate molecule. Nitrogen molecules have lower molecular dimension in comparison to all the reactant molecules used in all the three reactions in this study. Thus surface area that was obtained for SAPO-34 was based on the size of nitrogen-like smaller size molecules. Thus surface area of SAPO-34 is a measure of total access points or adsorption (catalytic) sites available at the surface of SAPO-34 for adsorption of N_2-like smaller size molecules.

As the molecules of reactants of all three reactions, are bigger in size than nitrogen molecules thus it can be argued that the total surface area provided by SAPO-34 for reactant molecules (to react and form product) will be equal for N_2 molecules and reactant molecules having bigger molecular dimension than N_2 molecules. Thus the above mentioned fact can be considered in case of SAPO-34 to understand why SAPO-34 shows lesser catalytic activity than that of other two zeotype catalysts (SAPO-5 and AlPO-5).

The yield of butyl acetate, the product of esterificaion reaction, was found to be the highest. Due to the small size of the product & reactant’s molecule of this esterification reaction, there is full possibility for maximum access of catalysts’surface area & catalytic sites of the catalysts including those which are in the narrow pores of zeotypes. Thus it is the reason for the highest yield of butyl acetate as a product of esterification reaction than the product yield of other two reactions (Quinoxalin and Imidazole). Same trend is followed by other products of other reactions of this study. Thus it can be concluded that surface area and pore size are main factors, regulating yield of product. In other words, access of catalytic sites should be maximum for reactants to get maximum yield of product.

This study was aimed to obtain green and better catalysts for various reactions. Catalysts used in this study are solid crystalline aluminophosphates. In concluding remark, it can be interpreted that these catalysts are good solid acids and sustainable catalysts because of the properties as given below.

Reusability

These catalysts can be recycled several times without any change in their catalytic activity. Conventional or solid supported catalysts have several drawbacks. For instance, decrease in their catalytic activity after successive recycling, leaching of catalytic sites, release of hazardous substances in the environment etc. In this regard, catalysts used in this study are good alternative because they are free from such problems. Reusability of these catalysts was tested in this study which shows that these catalysts are recyclable with no loss in their catalytic activity.

Separation of catalysts

This is a major problem encountered in case of liquid catalysts which are soluble in reaction mixture. In case of aluminophosphate catalysts, this problem was not encountered in course of study because these can be separated from reaction mixture very easily as these are solid catalysts with high thermal stability (1200°C).

Green chemistry use

These catalysts fulfill the demand of green chemistry mentioned in the Introduction (Chapter-1) due to their valuable properties. Thus they can be used as sustainable catalysts.

Chemical properties

In addition to the above mentioned properties of these catalysts, the chemical properties of these catalysts can be tuned according to the requirement. For example, shape selectivity of these catalysts may be useful in order to obtain selective product molecule. Moreover catalytic sites can also be regulated by changing metal molar composition thus catalytic efficiency is regulable. This property was studied in this work. This property can also be used in interpretation of host-guest interactions inside the framework of these catalysts.

Safe disposal

Most of the catalysts have the problem of their disposal. But aluminophosphate catalysts are safe to be disposed in the environment.