PHOSPHOMOLYBDIC ACID NANOCLUSTERS DISPERSED IN THE MICROPORES OF ZrO_2-PILLARED CLAY AS AN EFFICIENT CATALYST FOR SYNTHESIS OF SOME BIOLOGICALLY IMPORTANT MOLECULES

A **Dissertation**
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NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

By

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Under the Guidance of

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CERTIFICATE

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Associate Professor
Dept. of Chemistry

This is to certify that the dissertation entitled “**PHOSPHOMOLYBDIC ACID NANOCLUSTERS DISPERSED IN THE MICROPORES OF ZrO_2-PILLARED CLAY AS AN EFFICIENT CATALYST FOR SYNTHESIS OF SOME BIOLOGICALLY IMPORTANT MOLECULES**” being submitted by **Sudhir Kumar Sahoo** to the Department of Chemistry, National Institute of Technology, Rourkela, Orissa, for the award of the degree of Master of Science is a record of bonafide research carried out by him under my supervision and guidance. I am satisfied that the dissertation report has reached the standard fulfilling the requirements of the regulations relating to the nature of the degree.

N.I.T. Rourkela. Dr. Braja Gopal Mishra
Date: **Supervisor**

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Sudhir Kumar Sahoo

CHAPTER 1

INTRODUCTION TO CLAY MATERIALS

1.1 GENERAL INTRODUCTION

Clays are the most common minerals on earth's surface. Clays are used in many area of application such as building ceramics, paper coating and filling, drilling muds, foundry moulds, and pharmaceuticals. These materials are also the most primitive materials to be used as adsorbents and catalysts for various industrial applications [1]. The high surface area and polarity of the clay structures help in retaining the ionic species such as K^+, NH_4^+ and Ca^{2+} which are vital for the plant growth [2]. Clay minerals are also known to be very good adsorbents for toxic organic chemicals such as chlorinated compounds, heavy metal ions (eg. Pb^{2+}, Hg^{2+}) and nuclear waste [3, 4]. Salt loaded, acid-treated and ion exchanged clays are the different modified form of clay materials evaluated as efficient catalysts for many organic reactions [1,5, 6]. Clays are divided into two main groups: cationic and anionic clays [6]. The cationic clays are widely available in nature and contain negatively charged alumino-silicate layers. The negative charge in the layer is balanced by the presence of cations in the interlayer of these materials. These materials exhibit surface acidic properties due to the presence of structural hydroxyl groups. The work described in the thesis mainly concerned with the structural modification and catalytic application of the cationic clays.

1.2 STRUCTURE AND CLASSIFICATION OF CLAY MATERIALS

Clays are two dimensional hydrous layer silicates belonging to the phyllosillicate family [7]. The basic framework of clay consists of silicate layers formed from the condensation of the extremely stable SiO_4 tetrahedral units. The SiO_4 tetrahedra share three basal oxygen atoms by corner sharing to from the silicate layer. The structure of a typical silicate layer of a clay mineral are shown in the Fig.1.1.

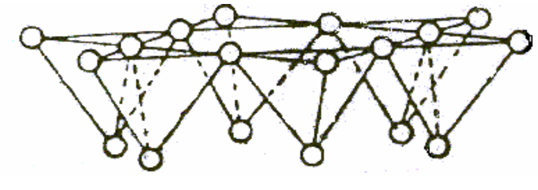


Fig. 1.1 Silicate sheet of a clay mineral formed by corner sharing of SiO_4 unit

These silicate planes condense with different octahedral planar units through the unshared oxygen atoms to from different classes of clay materials. The octahedral layer is formed form the edge sharing of the MO_6 (M= Al, Mg etc.). The MO_6 octahedra are polymerized in the plane by sharing four of its edges to form the octahedral layer [7]. The structure of an alumina layer is shown in the Fig. 1.2.

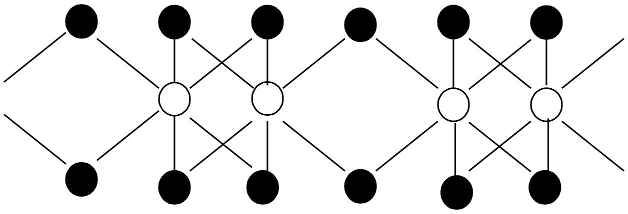


Fig. 1.2 Alumina octahedral sheets in clay mineral

The most widely used clay material in catalysis is montmorillonite. The structure of montmorillonite consists of an alumina layer sandwiched between two-silicate layers. The clay sheets are then stacked in the z-direction to form the structure of montmorillonite. The structure of montmorillonite clay is shown in Fig. 1.3.

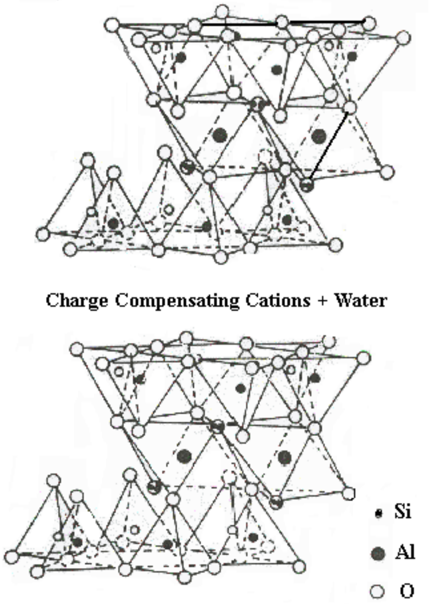


Fig. 1.3 Structure of 2:1 clay mineral montmorillonite

The space between each sheet of clay is called the interlayer spacing. Isomorphous substitution of Al^{3+} ion by lower valent ions such as Fe^{2+}, Mg^{2+} in the octahedral layer of clay sheet is a common phenomenon in clay minerals. This results in the development of negative charge in the clay sheet, which is usually satisfied by cations of alkali and alkaline earth metals. These charge-compensating cations are found in the interlayer and are easily exchangeable with other cationic species. The total amount of negative charge originated as a result of isomorphous substitutions is called the cation exchange capacity (CEC) of the clay material [8].

1.3 ACIDIC PROPERTIES OF CLAY MATERIALS

Cationic clays are used as solid catalysts for several acid catalyzed reactions. The acidity observed in the clay materials is mostly BrØnsted in nature. However, it is possible to generate Lewis acidity by suitable thermal treatment. The Lewis acidity is mainly associated with the exposed Al^{3+} ions at the broken crystallite edges. Such sites can be created by heat treatment of the clay materials at higher temperatures. The origin and nature of Brønsted acidity in clay have been studied by several authors [9, 10]. The most important source of Brønsted acidity in case of clay materials is due to the dissociation of water molecules in the hydration sphere of the interlayer exchangeable cations. The other source of acidity of the clay materials is the structural hydroxyl groups present in the octahedral layers. Several varieties of hydroxyl groups have been identified on the clay layers by FTIR spectroscopy [11]. These hydroxyl groups differ in the chemical environment around them and consequently exhibit acidic property of different strength.

1.4 DISADVANTAGES OF CLAY MATERIALS AS CATALYSTS

Although clay materials are used as solid acid catalysts for variety of organic reactions, they possess certain inherent disadvantages, which limit their application in heterogeneous catalysis [12]. Extensive dehydration of the clay sheets takes place at high temperatures leading to the loss in Brønsted acidity. The interlayer dimension of the clay materials are typically between 3-5 Å, which is smaller than the kinetic diameter of most of the bulky reactant molecules. This result in diffusional constraints and most of the interlayer catalytically active sites remain unutilized during catalysis.

1.5 MODIFICATION OF CLAY MATERIALS

In last two decades, different types of surface as well as interlayer modifications have been done to increase the thermal stability, acidity and catalytic properties of clay materials. The most important modifications reported in literature are the exchange of interlayer cations by inorganic and organic cationic species [1], acid treatment [6], supporting active species on clay surface for catalysis [13] pillaring by inorganic polycations [1, 6, 12] and clay-polymer nanocomposites [14]. While the first three processes essentially increase the acidity and catalytic activity, the pillaring of clay by inorganic polycations provides a multitude of advantages in terms of increasing surface area, microporosity, thermal stability, acidity and catalytic activity.

1.6 PILLARING OF CLAY BY INORGANIC POLYCATIONS

The pillared clay materials are prepared by exchanging the interlayer cations of the clay materials by inorganic polyoxocationic nanoclusters [8,12,15]. The intercalated polycations increase the basal spacing of the clays and upon heat treatment they are converted to stable metal oxide clusters. These oxide clusters called pillars hold the individual clay sheets and prevent them from collapsing during high temperature applications. Clay pillared with a variety of inorganic polycations of Al [16], Zr [17], Ti [18], Cr[19], Fe [20], Si [21] etc. are reported in literature. These polycations are generally prepared by controlled hydrolysis of the corresponding metal cations in solutions [8].

The process of pillaring is shown schematically in Fig. 1.7.

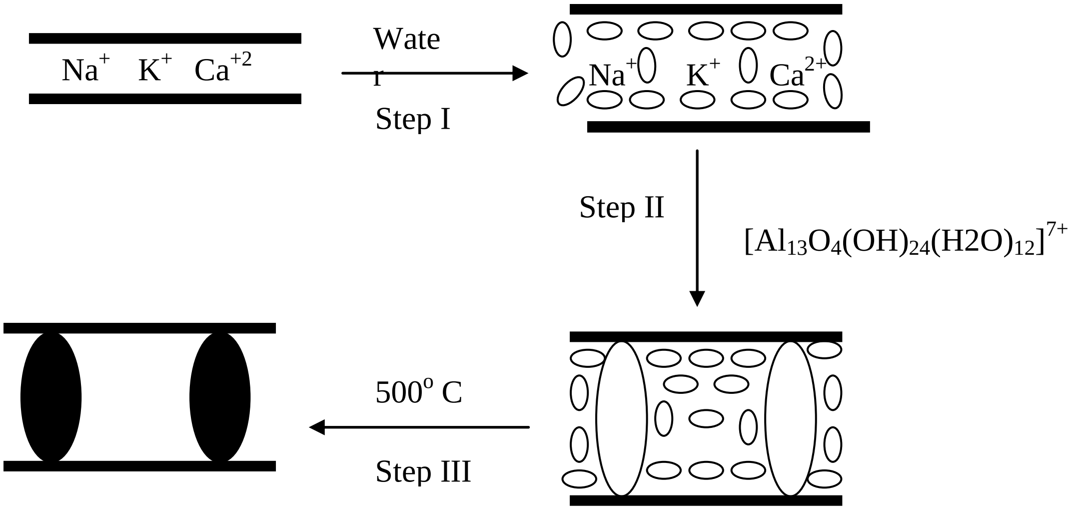


Fig. 1.7 Schematic representation of the process of pillaring of the clay sheets

The characteristic changes that occur as a result of pillaring include increase in the higher thermal stability, microporosity, surface area and acidic properties of the parent clay.

1.7 HETEROPOLY ACID

Heteropoly acids (HPAs) are a class of polyoxometallates with interesting tunable acidic and redox properties [22]. Among various hetropoly acids, Keggin type heteropoly acids have been extensively investigated for industrially important chemical reactions because of their higher structural stability, Bronsted acidity, oxidation potential and resistance to deactivation by hydrolysis [23]. The chemical formula of a Keggin type heteroply acid is generally presented as $X^{n+}M_{12}O_{40}^{(8-n)-}$ where X is a heteroatom from 1st row transition elements and main group. The metal cation M such as Mo^{+6}, W^{+6}, V^{+5} have the characteristics of high charge and smaller size.

The structure of Keggin anion can be described as composed of a central tetrahedron XO_4 surrounded by 12 edge- and corner-sharing metal-oxygen octahedron MO_6. The octahedronl are arranged in four M_3O_{13} groups. Each group is formed by three octahedra sharing edges and having a common oxygen atom, which is also shared with the central tetrahedron XO_4 [23]. The Brønsted acidity of HPAs in solid and liquid state has been studied using several analytical techniques such as indicator titration, TPD, FT-IR study of adsorbed probe molecules, microcalorimetry and NMR spectroscopy [22, 23]. These studies revealed that the Bronsted acidity of HPAs are stronger than most of the conventional solid acids such as SiO_2-Al_2O_3, H_3PO_4/SiO_2, and HX and HY zeolites. Moreover, due to discrete and mobile ionic structure, HPAs in many respects behave like solutions.

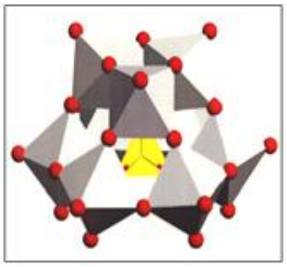


Figure 1.8. Structure of Keggin anions

In recent years, there have been extensive efforts to utilize the potential of the HPAs in synthetic organic chemistry such as deprotection of t-butyldimethylsilane [24], regioselective aerobic oxygenation of nitrobenzene to 2-nitrophenol [25] and oxidation of aliphatic, benzylic and allylic alcohols using dimethyl sulfoxides as oxygen transfer agents [26]

1.9 OBJECTIVE OF THE PRESENT STUDY

The main objectives of the present study is to

1. Prepare surface and interlayer modified Zirconia pillared clay by various post treatment steps such as sulfate grafting and using as a support for phosphomolybdic acid and explore its potential as a heterogeneous catalyst for synthesis of fine chemicals.
2. characterize the synthesized modified Zr-Pillared caly materials by various analytical techniques such as XRD, SEM and UV-Vis to obtain complete information on the physicochemical characteristics of these materials
3. To synthesize coumarins by condensation of phenols with ethylacetoacetate in presence of the pillared clay materials under solvent free conditions.

CHAPTER 2

MATERIALS AND METHODS

2.1 PREPARATION OF CATALYST

2.1.1 PREPARATION OF PILLARED CLAY

The montmorillonite clay (Kunipia-F, Kunimine industries, Japan) was used as such without any purification. The structural formula of the clay is $(Na_{0.35}K_{0.01}Ca_{0.02})$ $(Si_{3.89}Al_{0.11})^{tet}$ $(Al_{1.60}Fe_{0.08}Mg_{0.32})^{oct}$ $O_{10}(OH)_2.nH_2O$. The cation exchange capacity of the clay is 120 mequiv (100g clay)$^{-1}$. The 0.1 M $ZrOCl_2.8H_2O$ solution was prepared by dissolving the required amount of salt in double distilled water. The solution was then subjected to heating at 70^{o}C for 24 h to prepare the pillaring solutions. The pillaring process was performed with 2 wt% clay slurry in 200 ml of water. The pillaring solutions were added drop wise to the clay aqueous suspension under constant stirring conditions at a ratio of 10 mmol Zr per g of clay. The slurry was kept under stirring for 24 h at room temperature and then filtered, washed repeatedly in distilled water till free from chloride ions, dried in a hot air oven and calcined at 450^{o}C for 2 h to prepare Zr-Pillared clay (Zr-P).

2.1.2 SULPHATE TREATMENT OF PLLARED CLAY

The sulphate treated Zirconia pillared clay (SZr-P) was prepared by suspending the Zirconia pillared material in 0.5M sulphuric acid for 24h followed by washing with 0.05M sulphuric acid and heat treatment at 400˚ C for 1h.

2.1.3 PHOSPHOMOLYBDIC ACID GRAFTING

The dispersion of the phosphomolybdic acid in the micropores of sulphated Zirconia pillared clay was done by wet impregnation method. Required amount of PMA was dissolved in 50 ml of double distilled water and to this solution added 1 gm of the sulphated Zirconia pillared clay. The aqueous suspension was stirred for 12 h at room temperature and then heated with continuous stirring till complete removal of water. The resulting material was dried overnight in a hot air oven and calcined at 200oC for 1h to prepare PMA grafted sulfated Zr-Pillared clay (PMA/SZr-P).

2.2 CHARACTERIZATION OF CATALYST MATERIALS

2.2.1 X-RAY DIFFRACTION: The X-ray diffraction patterns of the Zr-pillared clay, Sulphate treated Zr-pillared clay and Phosphomolybdic acid grafted sulphated Zr-pillared clay samples were recorded on a Siemens D-500 diffractometer using Ni-filtered CuK_{α} radiation. The

XRD measurements were carried out in the 2θ range of 4-20° with a scan speed of 2 degrees per minute using Bragg-Brantano configuration.

2.2.2 **UV-VIS SPECTROSCOPY:**

UV-Vis Spectra of pure clay, Zr-P, SZr-P, PMA/SZr-P were recorded taken using Barium Sulphate as reference on a Shimadzu spectrophotometer (UV-2450) in the range of 200-900nm.

2.2.3 INFRARED SPECTROSCOPY:

The IR spectra of different clay samples (as KBr pellets) were recorded using a Perkin-Elmer infrared spectrometer with a resolution of 4 cm^{-1}, in the range of 400 cm^{-1} to 4000 cm^{-1}. Nearly 3-4 mg of the sample was mixed thoroughly with 30 mg of oven dried KBr and made into pallets. The pallets were stored in vacuum desiccators and exposed to IR lamp for 1 minute prior to the IR measurement.

2.3 CATALYTIC STUDIES

2.3.1 SYNTHESIS OF COUMARIN

A neat mixture of resorcinol(1 mmol), ethyl acetoacetate (1 mmol), and 100 mg of PMA/SZr-P clay was heated at 110° C for required amount of time. The progress of the reaction was monitored by TLC. After completion of the reaction the crude product from the reaction mixture was dissolved in 10 mL of hot ethanol and the catalyst was separated by filtration. The filtrate containing crude product was heated under reduced pressure to remove the ethanol and recrystallized. The catalyst was regenerated by washing three times with 10 mL portion of methanol followed by heat treatment at 400°C for 1h. The final products were identified by comparing their physical and spectral properties with those reported in literature.

CHAPTER 3

RESULTS AND DISCUSSIONS

3.1 XRD study

The XRD patterns of the Parent clay, along with the as synthesized Zr-Pillared clay and Zr-Pillared clay clacined at 500^{o}C is presented in figure 3.1. The parent clay shows relatively broader and intense reflections at 2θ = 6.8^{o} with basal spacing of 12.9 Å. This peak corresponds to the reflection from the (001) plane of the layered material. After the intercalation of the Zr-oxyhydroxy cluster into the clay layer the (001) peak has shifted to lower 2θ value indicating indicating an expansion in the layer structure as a result of pillaring.

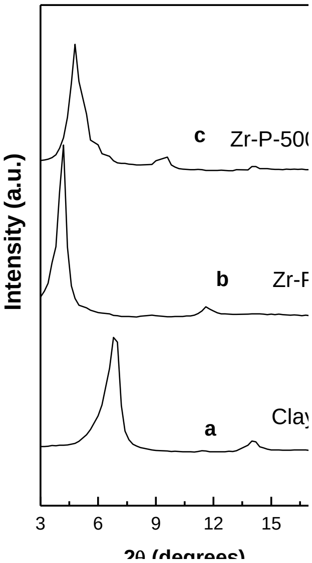


Figure 3.1. X-ray diffraction patterns of (a) clay, (b) Zr-P and (c) Zr-P calcined at 500^{o}C

The air dried Zr-pillared clay shows a basal spacing of 21Å corresponding to a interlayer spacing of 11.4 Å. Heat treatment of the air dried Zr-P shows a slight decrease in basal spacing due to the conversion of the oxyhydroxy cluster to stable oxide nanocluster. The calcined Zr-P shows a basal spacing of 19.2 Å with an interlayer spacing of ~ 9 .5 Å (Fig. 3.11c). The XRD study clearly indicate that the clay material gain thermal and structural stability as a result of pillaring.

3.3 FTIR study

The IR spectra of the parent clay, Zr-P, SZr-P and PMA-SZr-P materials are shown in figure 3.2. At the O-H stretching frequency region, all the pillared clay materials show two intense IR band at 3630 cm^{-1} and 3425 cm^{-1} (Fig. 3.2, Panel I). These two bands are assigned, respectively, to the O-H stretching vibration of the structural hydroxyl groups in the clay sheets and the water molecules present in the interlayer [27]. In addition to these bands, in case of PMA-SZr-P an additional band is observed at 3250 cm^{-1} which is assigned to the water molecules coordinated to the cationic cluster of phosphotungstic acid. The IR band observed at 1630 cm^{-1} (Fig. 3.2, Panel II) is attributed to the bending vibration mode of OH groups. Montmorillonite clay is known to contain two types of water molecules [28].

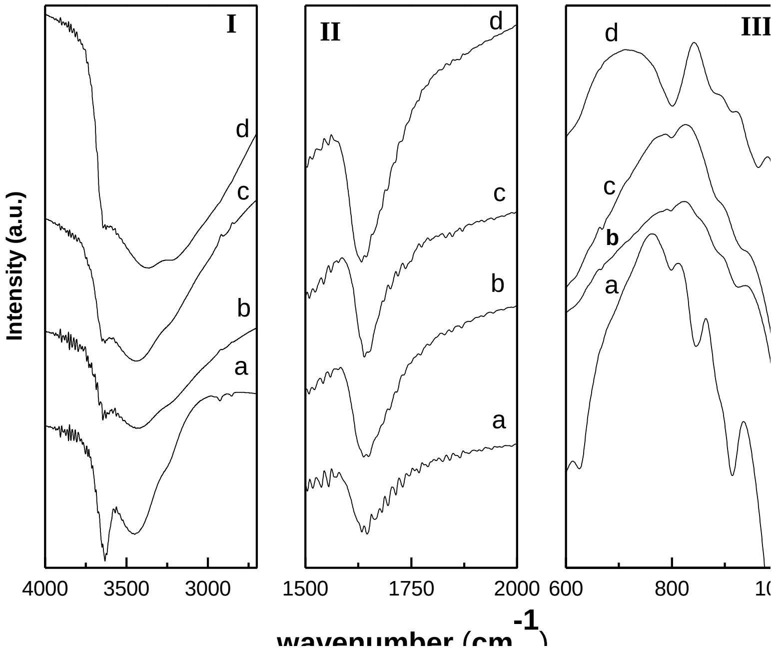


Figure 3.2. IR spectra of (a) parent clay, (b) Zr-P, (c) SZr-P and (d) PMA-SZr-P (panel I, II and III represent different regions of the spectrum).

One of them is more labile with IR absorption pattern similar to that of liquid water present in the outer coordination spheres of the interlayer cations and pillars. The other type of water molecules are those which are firmly held and coordinated directly to the interlayer cations in the first coordination sphere. Both type of water molecules contribute to the broad O-H vibrational band observed at 3425 cm^{-1}. However, the water molecules coordinated to interlayer cations contribute significantly to the absorption band at 1630 cm^{-1} [28]. Since the water molecules present in the 1st coordination sphere dissociate and contributes to the acidity of the clay, this peak can indirectly be correlated to the acidic nature. This peak is most intense in case of PMA-SZr-P material indicating the possibility of more acidic sites in this material compared to others. The structural OH-bending mode in montmorillonite absorbs IR radiation between 700 and 950 cm^{-1} and shows a series of discrete peaks depending upon the cation composition in the octahedral sheet [28]. In case of all the clay, three bands were observed at 915, 845 and 805 cm^{-1} which bands have been assigned to the bending vibration modes of Al-Al-OH, Al-Mg-OH and Mg-Mg-OH groups, respectively, in the octahedral layer of the clay. In case of the PMA-SZr-P material however, in addition of these bands distinct bands are observed at 800, 878 and 962 cm^{-1} which are characteristics of the phosphomolybdic acid clusters [29]. The PMA clusters are thus intact in the PMA-SZr-P material.

3.4 UV-Vis Study

The UV-Visible spectra of the parent clay along with Zr-P, SZr-P and PMA-SZr-P are shown in figure 3.3. The parent Montmorillonite clay displays a characteristic broad band centered at 247 nm (Fig. 3.3a). This band is assigned to ($Fe^{3+} \leftarrow O^{2-}$, OH^- or OH_2) charge transfer band for the structural iron present in the octahedral layer of the clay mineral [28]..

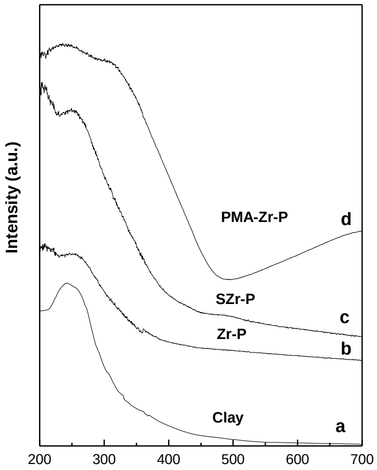


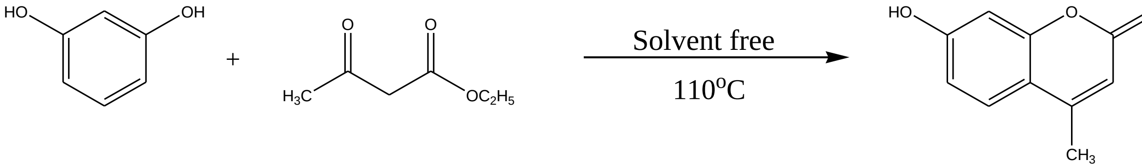
Figure 3.3. UV-Vuis spectra of different clay materials.

Intercalation of the zirconium pillars into the clay structure results in a change in the absorption pattern and a new band appeared at 212 nm (Fig 3.3b). This band has been assigned to the $Zr^{4+} \leftarrow O^{2-}$ charge transfer transition of the nanosized zirconia cluster intercalated into the clay interlayer. There is no significant change in the absorption pattern upon grafting of the sulphate species onto Zr-P (Fig. 3.3c). However, addition of PMA to the SZr-P results in significant change in the absorption pattern. Two prominent and broad bands are observed at 236 and 306 nm. These bands corresponds to various oxygen to metal charge transfer transitions in the PMA structure and indicate the structural integrity of the phosphomolybdic acid in the PMA-SZr-P catalyst [29]

3.5 Catalytic studies

3.5.1 Synthesis of coumarins

Coumarins are an important class of natural products with interesting biological and therapeutic properties. Coumarins are extensively used in the cosmetics, perfume, pharmaceuticals industries, for preparation of optical brightners and laser dyes [30]. The Pechmann reaction is widely used for the synthesis of Coumarins. The Pechmann reaction involves the condensation of phenols with β-keto esters in presence of acid catalysts to yield coumarins (Scheme 1). Several homogeneous catalyst such as H_2SO_4, P_2O_5, $FeCl_3$, HCl, $TiCl_4$, $ZnCl_2$, and Trifluoroacetic acid have been used as catalysts for the preparation of coumarins using Pechmann reaction [31]. The main disadvantages of the processes using these catalysts are, they require high temperature often in the range of 100-150^{o}C, longer reaction time, large amount of the catalysts and tedious purification process after completion of the reaction. Recently there are reports on the use of cation exchange resins, zeolites and clays as catalysts for the preparation of coumarins [32]. In this investigation, we have synthesized coumarins by Pechmann condensation reaction of a variety of phenols and ethylacetoacetate in presence of the PMA-SZr-P catalyst. Initially, the reaction of resorcinol and ethyacetoacetate was taken as a model reaction (Scheme 3.1) and the activity of the various clay materials were tested under solventfree conditions at 110^{0}C. The results obtained from this study are presented in Table 3.2.



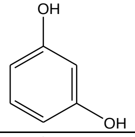
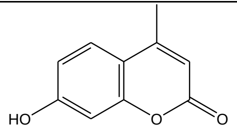
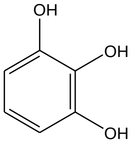
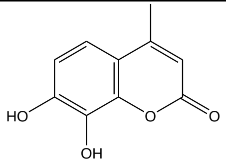
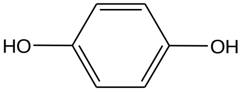
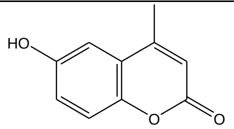
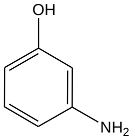
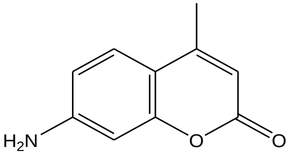
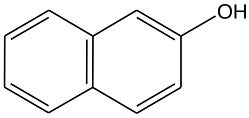
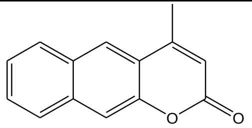
Scheme 3.1. Synthesis of coumarins by Pechmann condensation reaction

Table 3.2 Catalytic activity of different clay materials for synthesis of coumarins

Catalyst	Reaction time (min)	Yield (%)
Parent clay	720	No reaction
Zr-P	240	9.8
SZr-P	120	68
PMA-SZr-P	90	75

From Table 3.2 it is clear that the post treatment steps performed on the Zr-pillared clay such as sulfate and PMA grafting has a profound influence on the activity of the Zr-Pillared clay. The parent clay under the reaction condition does not yield any product. The PMA-SZr-P catalyst was choosen for further study. By varing different reaction parameter it was observed that for 1 mmol reactants 100 mg of the catalyst at 110°C under solvent free condition gives good yield of the product (Table 3.3).

Table 3.3. PMA-SZr-P catalyzed synthesis of Coumarins

Sl. No	Reactant	Product	Time (min)	Yield (%)
1			90	75
2			90	77
3			120	72
4			240	65
5			240	69

Under the optimized condition different phenols such as pyrogallol, hydroquinone, aminophenol and β-naphhol was used for the reaction. It was observed that the reaction proceeds faster in case of polyhydric phenols with excellent yield of the product where as for substituted phenols and naphthols the reaction requires longer time (Table 3.3). Overall, using different type of phenol it was demonstrated that PMA-SZr-P catalyst is an efficient catalyst for Pechmann condensation reaction.

CHAPTER 4

CONCLUSION

In this thesis we have performed certain structural and interlayer modification of the clay materials to generate efficient heterogeneous catalytic materials for application in the field of organic synthesis. The Zr-pillared clays were prepared by intercalation of the Zr-oligomeric clusters into clay interlayer and subsequent thermal activation. In order to further enhance the catalytic efficiency of the Zr-Pillared clay, the materials were treated with sulfuric acid to graft sulfate ions onto the zirconia nanopillars. The sulfate grafted Zr-pillared materials were used as a effective carrier for the phosphomolybdic acid to generate PMA-SZr-P composite materials. The XRD study of the materials indicates the expansion of the interlayer structure as a result of pillaring. The retention of the interlayer space after calcinations of the Zr-Pillared materials at 500^{o}C indicate enhancement of the thermal stability of the pillared clay materials. UV/Vis and FTIR study indicate the structurally integrity of PMA clusters in pillared clay inter layer. All the characteristic spectral features of PMA was observed in the FTIR as well as UV-Vis study. The PMA- SZr-P material was used as a efficient catalyst for the synthesis of coumarins under solventfree condition by condensation of phenols with ethylacetoacetate. The post treatment of Zr-Pillared clay was found to have a profound influence on the activity of these materials. The PMA- SZr-P material was found to give good yield and purity of the products for a variety of monohydric as well as polyhydric phenols. Overall, the reaction protocol developed in the present study was found to be advantageous in terms of simple experimentation, use of heterogeneous catalysts, and preclusion of toxic solvent, use of water as green reaction media and high yield and purity of the products.

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