One of the greatest challenges before synthetic chemist and material scientist is to develop material from cheap natural resources and produce chemicals by adopting greener technologies. Among the viable alternatives available for green synthetic methods, clays and clay-based catalysts in particular have attracted significant attention due to their high abundance and low cost. The sorptive, swelling, ion exchange, acidic and textural properties make clays attractive for various applications like adsorption and catalysis. As aluminosilicates of layer structure, the interlayer space can be effectively used for hosting guest molecule for various applications. The interest level in clays among the scientific community has increased dramatically in recent years due to their intercalation chemistry and various modification possibilities. This chapter includes a brief introduction to clay minerals, their structure, different modification procedures such as pillaring, template assisted modifications process like porous clay heterostructures etc. A brief review of modified clays and catalytic applications of modified clays for various organic transformations are presented. Scope and objectives of present work are also given in this chapter.
1.1 Introduction

Geologists, mineralogists, chemists and soil scientists all approach the term “clay” in a quite different manner. Historically the term clay has been referred to the small inorganic particles with less than 2μ size of a soil fraction without regard to composition or crystallinity and clay minerals has been referred to the specific phyllosilicates of layered, hydrous magnesium or aluminium silicates in such a soil fraction. In 1995 Joint Nomenclature Committie of AIPEA (Association Internationale Pour l'Etude Des Argiles) defined clays as a “Material composed primarily of fine-grained particles which is generally plastic at appropriate water contents and will harden when dried or fired ” [1-2]. The term clay generally refers to aluminosilicates with layer structure where the particle size is in the micron range and exhibit cation exchange capacity. This broad term encompasses zeolites but the term is normally used in connection with sheet silicate only. Clays and zeolites both are aluminosilicates, but in zeolites both silicon and aluminium forms tetrahedra and zeolites have well defined three dimensional structures. Clay minerals are produced as a result of weathering, hydrothermal alteration or diagenesis. Two broad class of clays are identified, cationic clays (clay minerals) which are wide spread in nature and anionic clays (LDHs materials) which are rare in nature and usually synthesized in laboratories and industries in an easy and inexpensive way.

Clays have been used from the very beginning of civilization for making cooking pots, potteries, bricks and drainage pipe. Ancient people realized the plastic nature of clay i.e., when mixed with sufficient amount of water it is plastic and can be molded in to any desired shape and when it is heated it changed in to dry solid mass. Fireclays are used for more refractory purposes
such as heat-resistant tiles or bricks. The major use of clay is for the manufacture of cement. Hundred million tons of clays find commercial applications in fields as diverse as ceramics, building materials, paper coatings, fillers, drilling muds, foundry molds, pharmaceuticals, skin care products, kitty litter and laundry detergents. Organoclay gels are added to paints to improve its rheological properties. The performance of cosmetics is enhanced by the use of organo clays and they allow good colour retention and coverage.

1.1.1 Structure of Clays

Clays have two structural units, silica tetrahedra and alumina or magnesia octahedra, both form layer structure, silica tetrahedra by corner sharing alumina octahedra by edge sharing. By sharing three oxygen atoms silica tetrahedra are polymerized to form a hexagonal mesh in one dimension and the fourth oxygen (apical) lie perpendicular to it and it is cornerly shared with aluminium or magnesium octahedral sheets [3].

![Figure 1.1. structural units of clays](image)

Different combination of tetrahedral and octahedral sheets forms different clay minerals. In 1:1 clay mineral such as in kaolinite, one tetrahedral sheet combines with one octahedral sheet.
In 2:1 clays such as in montmorillonite the octahedral sheet is sandwiched between two tetrahedral sheets facing to each other to form a three sheet complex called a lamella (1nm thickness). The interlayer and the T-O-T layers
are bound together by both electrostatic and hydrogen-bonding force. Octahedral aluminium may sometimes isomorphously substituted by low valence Mg\(^{2+}\) or Fe\(^{2+}\) creating -ve charge [4]. The tetrahedral silicon may also be substituted by low valance Al creating -ve charges and the net negative charge is balanced by cations like H\(^+\), Na\(^+\), K\(^+\), Ca\(^{2+}\) etc or water between the layers. Thus naturally occurring clays have -vely charged layer structures balanced by exchangeable interlayer cations and they are usually called cationic clays since they have cation exchange capacity. Thus, the primary structure of clay is lamellar with parallel layers of tetrahedral silicate and octahedral aluminate sheets. Secondary structure stems from valence deficiencies in primary structure. The tertiary structure is a consequence of secondary structure in which interstitial cations that are trapped as freely moving ions between negatively charged layers [5]. If the trivalent aluminium is the dominant cation in the octahedral layer, then only 2/3 of the octahedral sites are occupied. Such a structure is described as "dioctahedral", since there are two octahedral cations per unit cell. When a divalent cation such as Mg\(^{2+}\) is dominant in the octahedral layer, all the available sites are filled. They have three octahedral cations per half unit cell and the structure is described as "trioctahedral".

According to AIPEA recommendation, clays can be classified in to different types based on their layer type, layer charge and chemical composition. Their classification is summarized in Table 1.1 [2].
<table>
<thead>
<tr>
<th>Structure Type</th>
<th>Layer charge</th>
<th>Group</th>
<th>Composition</th>
<th>Examples</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1 (TO)</td>
<td>0</td>
<td>Kaolin-Serpentine</td>
<td>(\text{Al}_2\text{Si}<em>4\text{O}</em>{10}(\text{OH})_8)</td>
<td>Kaolinite, dickite, nacrite</td>
<td>Kaolin subgroup, dioctahedral, nonswelling</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al_2Si_3O_10(OH)_8 \cdot 4H_2O</td>
<td>(\text{Al}_2\text{Si}<em>3\text{O}</em>{10}(\text{OH})_8 \cdot 4\text{H}_2\text{O})</td>
<td>Halloysite,</td>
<td>Kaolin subgroup, dioctahedral, swelling</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mg_6Si_2O_10(OH)_8</td>
<td>(\text{Mg}_6\text{Si}<em>2\text{O}</em>{10}(\text{OH})_8)</td>
<td>Chrysotile, antigorite, lizardite</td>
<td>Serpentine subgroup, triotahedral, nonswelling</td>
</tr>
<tr>
<td>2:1 (TOT)</td>
<td>0</td>
<td>Pyrophyllite-Talc</td>
<td>(\text{Al}_2\text{Si}<em>3\text{O}</em>{10}(\text{OH})_8)</td>
<td>Pyrophyllite</td>
<td>Dioctahedral, nonswelling</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mg_6Si_2O_10(OH)_8</td>
<td>(\text{Mg}_6\text{Si}<em>2\text{O}</em>{10}(\text{OH})_8)</td>
<td>Tale</td>
<td>Tale, Triotahedral, nonswelling</td>
</tr>
<tr>
<td>2:1 (TOT)</td>
<td>0.5–1.2</td>
<td>Smectite</td>
<td>((\text{Al}<em>2\text{Si}</em>{2.5}\text{O}_{10}(\text{OH})<em>8\times</em>{0.5-1.2}))</td>
<td>Beidellite</td>
<td>Dioctahedral, swelling</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>((\text{Al}<em>{0.5-2.5}\text{Mg}</em>{0.5-1.2}(\text{Si}<em>{2.5}\text{O}</em>{10}(\text{OH})<em>8\times</em>{0.5-1.2}))</td>
<td>Montmorillonite</td>
<td>Dioctahedral, swelling</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>((\text{Fe}<em>{0.5}\text{Si}</em>{7.5}\text{Al}<em>{0.5-1.2}\text{O}</em>{10}(\text{OH})<em>8\times</em>{0.5-1.2}))</td>
<td>Nontronite</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>((\text{Mg}<em>{0.5}\text{Si}</em>{7.5}\text{Al}<em>{0.5-1.2}\text{O}</em>{10}(\text{OH})<em>8\times</em>{0.5-1.2}))</td>
<td>Saponite</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>((\text{Mg}<em>{0.5}\text{Si}</em>{7.5}\text{Al}<em>{0.5-1.2}\text{O}</em>{10}(\text{OH})<em>8\times</em>{0.5-1.2}))</td>
<td>Hectorite</td>
<td>Triotahedral, swelling</td>
</tr>
<tr>
<td>2:1 (TOT)</td>
<td>1.2–1.8</td>
<td>Vermiculite</td>
<td>((\text{Al}<em>2\text{Si}</em>{2.5}\text{O}_{10}(\text{OH})<em>8\times</em>{0.5-1.2}))</td>
<td>Vermiculite</td>
<td>Dioctahedral, swelling</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>((\text{Mg}<em>2\text{Si}</em>{2.5}\text{Al}<em>{0.5-1.2}\text{O}</em>{10}(\text{OH})<em>8\times</em>{0.5-1.2}))</td>
<td>Vermiculite</td>
<td>Triotahedral, swelling</td>
</tr>
<tr>
<td>2:1 (TOT)</td>
<td>2</td>
<td>Illite</td>
<td>((\text{Al}<em>2\text{Si}</em>{2.5}\text{O}_{10}(\text{OH})<em>8\times</em>{0.5-1.2}))</td>
<td>Illite</td>
<td>Dioctahedral, nonswelling</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>((\text{Al}<em>2\text{Si}</em>{2.5}\text{O}_{10}(\text{OH})<em>8\times</em>{0.5-1.2}))</td>
<td>Illite rih in Fe</td>
<td></td>
</tr>
<tr>
<td>2:1</td>
<td>2</td>
<td>Mica</td>
<td>((\text{Al}<em>2\text{Si}</em>{2.5}\text{O}_{10}(\text{OH})<em>8\times</em>{0.5-1.2}))</td>
<td>Muscovite</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>((\text{Fe}<em>{2}\text{Mg}</em>{2}\text{Si}<em>{2.5-7.5}\text{O}</em>{10}(\text{OH})<em>8\times</em>{0.5-1.2}))</td>
<td>Celadonite</td>
<td>Dioctahedral, nonswelling</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>((\text{Mg}<em>{0.5}\text{Si}</em>{2.5}\text{Al}<em>{0.5-1.2}\text{O}</em>{10}(\text{OH})<em>8\times</em>{0.5-1.2}))</td>
<td>Phlogopite</td>
<td>Triotahedral, nonswelling</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>((\text{Li}<em>{2}\text{Mg}</em>{2}\text{Si}<em>{2.5}\text{O}</em>{10}(\text{OH})<em>8\times</em>{0.5-1.2}))</td>
<td>Taenolite</td>
<td>Triotahedral, lithium mica</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>((\text{Al}<em>2\text{Si}</em>{2.5}\text{O}_{10}(\text{OH})<em>8\times</em>{0.5-1.2}))</td>
<td>Margarite</td>
<td>Dioctahedral, nonswelling</td>
</tr>
<tr>
<td>2:1 channels</td>
<td>Variable</td>
<td>Palygorskite</td>
<td>((\text{Mg}<em>2\text{Al}<em>2\text{Si}</em>{2.5}\text{O}</em>{10}(\text{OH})<em>8\times</em>{0.5-1.2}))</td>
<td>Palygorskite</td>
<td>Dioctahedral, nonswelling</td>
</tr>
<tr>
<td>or inverted</td>
<td></td>
<td></td>
<td>((\text{Mg}<em>2\text{Al}<em>2\text{Si}</em>{2.5}\text{O}</em>{10}(\text{OH})<em>8\times</em>{0.5-1.2}))</td>
<td>Palygorskite</td>
<td>Dioctahedral, nonswelling</td>
</tr>
<tr>
<td>ribbons</td>
<td></td>
<td></td>
<td>((\text{Mg}<em>2\text{Al}<em>2\text{Si}</em>{2.5}\text{O}</em>{10}(\text{OH})<em>8\times</em>{0.5-1.2}))</td>
<td>Palygorskite</td>
<td>Dioctahedral, nonswelling</td>
</tr>
<tr>
<td>2:1:1 Variable</td>
<td></td>
<td>Clinohlorite</td>
<td>([\text{TOT}])</td>
<td>[TOT]</td>
<td>[TOT]</td>
</tr>
</tbody>
</table>
The interest level in clays among the scientific community has increased dramatically in recent years due to their intercalation chemistry and various modification possibilities. The interlayer gallery can be effectively used for hosting guest molecule for various applications. The sorptive, swelling, ion exchange, acidic and textural properties make clays attractive for various applications like adsorption and catalysis [6-7]. Clay based sensors were reported in literature owing to its large surface area and layer structure [8]. These cheap natural materials can be used as support for the immobilization of enzymes [9]. These natural nanomaterials can be successfully used as template for the synthesis of nano materials and the properties of the nano materials depend on nature, basal spacing and cation exchange capacity of the clays [10]. S. J George et al. prepared an aminoclay which can act as scaffold for dangling donor and acceptor dye molecules on clay by a non covalent interaction and at a particular composition of clay to dye, a gel is formed which can be used as light harvesting material in solar cell [11]. Graphene oxide and polymer dendrimer intercalated clays can be used for the storage of hydrogen owing to its high storage efficiency [12]. High surface area and biocompatibility make clays suitable candidate as drug carrier for the controlled release of drugs [13]. Because of high aspect ratio, in-plane strength and low cost, clays are added to polymers as a fillers and the clay polymer nanocomposites have enhanced mechanical strength, thermal stability, barrier properties and flame retardance [14].

1.2 Properties of clays
1.2.1 Swelling capacity

The smectite clays have the capacity to expand beyond a single molecular layer of intercalant. Swelling is a reversible processes that occur
essentially from extra hydration of interlamellar cations. The extent of swelling depends on layer charge, location of charge and nature of swelling agent [2]. Talc and phyllophyllite have very low capacity to swell as they have nearly zero charge. Clays with very large charges such as mica swell most readily with divalent, trivalent and polyvalent cations and swelling decreases according to that order. Thus Li and Na exchanged form of minerals are particularly susceptible to swelling by water [15]. Several models were recommended for explaining swelling mechanism of smectites [16]. A macroscopic energy balance model for crystalline swelling of 2:1 phyllosilicates was suggested by Laird [17].

1.2.2 Cation Exchange Capacity

Cation exchange capacity (CEC) is defined as the amount of exchangeable cations that a clay mineral can absorb at a specific pH. This is a measurement of the net negative charge of clay layers. The negative charges are produced in clay layers as a result of the following process [2].

(a) Isomorphous substitution within the lattice,
(b) Broken bonds at edges and external surfaces,
(c) The dissociation of assessable hydroxyl groups

Since exchangeable cations compensate the unbalanced charge in the interior of layer due to isomorpous substitution, CEC is a measure of the degree of substitution [18].

1.2.3 Acidity of clays

Clays have both Lewis and Bronsted acidity. Protons and polarizing cations in the interlayer contribute to Bronsted acidity. H3O+ ions associated with negatively charged clay layers contribute to Bronsted acidity. Brosted
acidity also arises from terminal hydroxyl groups and from bridging oxygen atoms. The strong dependence of Bronsted acidity on structural OH groups has been evidenced from many reports [19]. Al$^{3+}$ occurring at edge or arising from Si-O-Al bond rupturing contributes to Lewis acidity. Dehydroxylation of Bronsted site would also lead to Lewis acidity. Obviously water will convert the Lewis sites in to Bronsted sites, a fact that limits the study of Lewis sites to relatively anhydrous systems [20].

1.2.4 Clays as catalyst

In 1865, Von Leibeg noticed the unusual property of china clay that could catalyze the formation of water from oxygen and hydrogen at temperature and pressure they were usually unreactive. It was one of the earliest catalysts used for cracking petroleum. Eugenehoundry found that acid modified smectite gave gasoline in high yield when used as petroleum cracking catalysts [21] and were used extensively as commercial catalysts until the mid 60s. There is theory that prebiotic life is originated with the formation of biomolecules catalyzed by natural clay minerals[22]. Experimental results suggested that certain montmorillonite minerals have a tendency to bind and catalyze small molecules to form larger molecules and oligomers like RNA [23] and they could facilitate the transformation of RNA into vesicles [24]. Although “life-from-clay” is still under debate, it is obvious that raw clay minerals inherently possess super-selective adsorption [25] and excellent catalytic activity. The catalytic role of clays have been recognized in several natural process like chemical transformation in soils [26] petroleum forming reactions [27] and the reactions related to evolution [28].
1.3 Modification in clays

Natural clays may not be efficient for acid catalyzed reactions especially if the unit cell composition is neutral or balanced with alkali or alkaline earth metals. Further strategic modifications are needed with the clear objective of improving the acidity, porosity, thermal stability, mechanical strength etc for variety of applications. Among the various clay minerals smectites are usually modified for catalytic purpose as they have layer charge and have swelling capacity. Among smectites, montmorillonite is most studied because of its high abundance, cation exchange capacity, swelling capacity, intrinsic acidity and relatively high surface area. Montmorillonite is commercially available in two forms as Montmorillonite KSF and K10, having different surface area but almost same acidity. Their Hammett acidity ($H_0$) is -8 which is similar to that of Conc. HNO$_3$. The important modification strategies include acid activation, ion exchange, intercalation, pillaring, grafting etc.

1.3.1 Acid activation

In this modification procedure, clays are treated with mineral acid like HCl, H$_2$SO$_4$ etc which replaces the inter lamellar cations with protons. Acid activation causes little damage to the silicate layer where the structures for the centre of platelet remain intact. However there may be dissolution of some Al$^{3+}$ and Mg$^{2+}$ of octahedral layer leading to more broken edge M-O$^-$ bonds and those ions then occupy the interlayer sites. The rate of dissolution increases with the concentration of acid, temperature, contact time and increasing Mg content in the octahedral sheets [29]. Surface area may increase due to the dealumination which contributes to mesoporosity. The acidity may be enhanced due to exchanged protons in the interlayer and leached hydrated
alumina occupying the cation exchange sites. However prolonged acid activation may result complete de-alumination which will lead to the collapse of clay layer. Among acid activated clays K-10 is representative of a commodity product that has immense applications in organic synthesis [30]. The use of concentrated inorganic acids, however leads to environmental issues owing to the generation of a great deal of acidic wastewater, in addition to equipment corrosion and operational dangers. Instead of inorganic acids organic acids such as carboxylic acids and sulfonic acids, can provide an alternative route to activate clay minerals. In addition, organic acid could lead to different degrees of changes in the layer, interlayer, and the edges compared with those attacked by mineral acids [31].

1.3.2 Cation exchange

In this method interlamellar cations are exchanged with cations by treatment with metal salt solution. Such a principle affords a facile way to prepare a clay based catalyst with the desired ions as catalytically active species. The monovalent (Na\(^+\)) and divalent (Ca\(^{2+}\)) cations which commonly occupy the interlayer region in natural clay can be readily replaced by other ions. In this way, either homoionic or heteroionic montmorillonite in principle can be produced. Furthermore, hydrophilic clays can be changed into hydrophobic clays by exchange with organic cations such as quaternary ammonium cations NR\(_4^+\) [32].

1.3.3 Intercalation

Intercalation is the insertion of guest molecules in interlamellar space of the clays with the preservation of layer structure. Organic compounds or inorganic complexes can be intercalated in to the interlamellar region. On the
basis of CEC of clay more than 95 % of guest ions can be incorporated in to
the clay layers [33-34]. Non ionic guests with large dipole moments such as
ketones and nitriles can be adsorbed in to the exchangeable metallic ions
within the layer according to their coordination with ionic sites in the
interlayers. A large variety of organic molecules are intercalated by so called
displacement method [35]. The intercalation of polymers in to the clay layer is
an important growing area of research. Hybridization with polymer molecule
may result material with high mechanical and flame retardant properties.
Intercalation of bulky metal organic compounds or chiral complexes into clay
minerals gives an alternative pathway to biomimetic catalyst systems [36]. The
immobilizations of complex catalyst in clay structure makes it possible to
conduct reactions in heterogeneous way to minimize many of the technical and
economical barriers associated with the use of homogeneous catalysts. The
advantages of catalyst intercalation go beyond mere immobilization as the
chemical and physical forces acting interlayers, can affect catalytic specificity
relative to homogeneous solution [37].

1.3.4 Grafting

Organic molecules can be covalently bonded to silanol (Si-OH) or
aluminol (Al-OH) group of clay layers. An example for such modification is
given in Figure1.4. A fluorescent dye dansyl was grafted in to kaolinite clay
by two step process. The authors claim that this is the first example for
grafting of a fluorescent dye which will have tremendous application in future
[38]. Functionalization with APTES is another example for grafting.
1.4 Pillared clays

The concept of using intercalation chemistry to transform the lamellar solid into a porous structure by inserting molecular props between the layers of clays was introduced by Barrer and Macleod in 1965 [39]. They used organic compound tetra alkyl ammonium ions to open up lamellae and develop porosity. However, the organic pillaring agent collapsed at relatively modest temperature. Oil price hike in the mid seventies spurred research for materials having large surface area than that of zeolites and could be used as cracking catalyst and having good thermal stability led to the development of material called “Pillared Inter Layered Clays (PILCs)” or simply pillared clays [40]. The term “Pillaring and Pillared” originates from the work of Brindley, Semples [41] and Vaughan, Lussier in 1973 [42]. They found that thermally stable robust inorganic metal oxide species could be intercalated between the clay layers.
Chapter 1

Pillaring is the process in which metal oxide pillars are inserted between the clay layers to prop apart the natural clay layers. They are prepared by the intercalation of bulky inorganic poly oxo-hydroxo cationic species followed by calcination. The robust metal oxide pillars formed between the clay layers prevent the collapse of the expanded layers and lead to the formation of large pores depending upon the extent of pillaring. Consequently, a bi-dimensional zeolite-like material with high thermal stability and high surface area was produced. The micropore structure is tailored by the nature of the host material and nature of the pillaring species and the resulting material may have pore sizes larger than those of zeolites and zeolite-related materials. Furthermore, intrinsic catalytic activity is induced in the pillared interlayered solids according to the nature of the pillar. Thus, the pillared derivatives have received widespread interest as a new type of microporous solid that can serve as shape selective catalysts, separating agents, supports, sorbents, etc. By varying the size, charge and shape of entering ion, a homogenous network of micropores obtained with pore opening ranging from 16-30 Å.

Figure 1.5. Scheme of pillaring process
Pillaring mechanism consists of the exchange reaction between interlamellar charge balancing cations (preferably Na\(^+\)) by cationic oligomers/polymers (Pn\(^{v+}\)) of pillaring solution. If M is the symbol representing clay, then pillaring process can be represented as

\[
MNa_v + P_n^{v+} \rightarrow MP_n + vNa^+
\]

The gallery height or spacing increases by a length somewhat lower than the radius of oligomer. The oligomer itself is produced from condensation reaction such as

\[
nP^{z+} \rightarrow Pn^{v+} + n(Z-v)H^+ + XH_2O
\]

The careful processing of the intercalated solid transforms the clay structure into a thermally stable porous structure. Dehydration and dehydroxylation of the polycation occurs in calcinations step to get stable oxide cluster as a pillar between the layers. Calcination shifts the bonding between interlayer species and clay layers from ionic to covalent. The nature and extent of crosslinking action of Pn\(^{V+}\) on adjacent microcrystals depends on the nature of surface of clay and that of pillar. Since the pillaring oligomers are cationic, they will be distributed on the surface as far as possible to reduce mutual electrostatic repulsion. The microporous structures of pillared clays are characterized by the distance between intercalated metal oxide pillars (inter pillar distance) and interlayer distances. The interlayer spacing depends on the chemical nature and height of intercalating species and the inter pillar distance is related to the density of pillars which in turn depends on the extent of distribution of charge density on clay layers and also on size of pillars.
1.4.1 Pillaring agents

In general, preparation of porous pillared materials consists of a direct exchange of the interlayer cations of smectite clays by cationic precursors to form intercalated clays. In the preparation of intercalated clays, the preparation of metal precursors is a crucial step. Cationic precursors can be categorized into four different groups, such as

1) polynuclear metal oxo or hydroxo cations,
2) metal chelate complex ions,
3) metal cluster complex ions
4) positively charged colloidal sols

On heating, these intercalated species are converted to metal oxide pillars, expanding the smectite layers.

1.4.2 Polynuclear metal oxo–hydroxo cations

These are the most commonly used pillaring agents that are usually obtained by the partial hydrolysis of metal salts at specific pH. Mostly the M$_{13}$ oligomeric species formed by the base hydrolysis at specific OH/M ratio proved to be the better pillaring species. The formation of poly nuclear cations was first recognized by Bjerrum [43] in his study on the hydrolysis of Cr$^{3+}$ and later for metal ions such as Al$^{3+}$, Be$^{2+}$, Zr$^{4+}$, Hf$^{4+}$, Ti$^{4+}$, Fe$^{3+}$, Ga$^{3+}$ and Ce$^{4+}$ by other workers [44-61].

Until now most of the research on pillared clays has been focused on the Al$_{13}$ polyoxocation as a pillaring agent since the solution chemistry of aluminium was well known. Solutions containing this complex are prepared through forced partial hydrolysis by the addition of a base (hydroxide,
carbonate, etc.) to AlCl\textsubscript{3} or Al(NO\textsubscript{3})\textsubscript{3} solutions up to an OH/Al molar ratio of 2.5. From \textsuperscript{27}Al NMR and small angle X-ray scattering it has been proven that the pillaring species is most probably the tridecamer [AlO\textsubscript{4}Al\textsubscript{12}(OH)\textsubscript{24}(H\textsubscript{2}O)\textsubscript{12}]\textsuperscript{7+} with a Keggin structure composed of one aluminium tetrahedron surrounded by 12 aluminium octahedra [62]. Upon calcination the Al\textsubscript{13} polycation yield Al\textsubscript{2}O\textsubscript{3} pillars.

\[
[\text{Al}_{13}\text{O}_{4}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+} \rightarrow 6.5\text{Al}_2\text{O}_3 + 7\text{H}^+ + 20.5\text{H}_2\text{O}
\]

This equation only suffices the idea of what is actually happening in the solid during heating. This is a very simple approximation because the pillars are not simple metal oxides and during the calcination process the cross-linking reaction can also take place, which involves the formation of true bonds between the pillars and clay mineral layers [31].

Figure 1.6. Keggin structure of aluminium pillaring species

Plee et al. used \textsuperscript{27}Al and \textsuperscript{29}Si solid state nuclear magnetic resonance (MAS NMR) techniques to study the thermal transformation of the pillars and
their linkage with the clay sheets [63]. Their $^{27}$Al MAS NMR spectra of beidellite (which have Al/Si substitution in tetrahedral layers) revealed two separate Al (IV) resonances, one due to the tetrahedral Al present in the clay structure and the other one in the center of the Al$_{13}$ pillar. They proposed a model in which linking of the pillar to the tetrahedral sheet induced an inversion of an Al tetrahedron of the tetrahedral sheet. This would lead to new Si-O- Al linkages, in which the negative charge is exposed in the interlayer space. Such a linkage should induce a larger number of stronger, Bronsted acid sites, observed for pillared beidellite. Alternative linkages between the pillar and the tetrahedral sheet can be formed by the inversion of a Si tetrahedron of the tetrahedral sheet or by inversion of the Si-O-Al bond in a tetrahedron.

1.4.3 Zirconium pillaring agent

In the case of Zr pillaring species the solution chemistry is fairly complex and zirconyl ion is mainly found as tetramer. Zirconium poly oxo-hydroxo cations of the type $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$ or $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}(\text{Cl,Br})_x](8-x)^+$ can be used to prepare zirconium pillared clays [64-65]. Zirconium poly oxocation can be prepared by dissolution and aging of zirconyl chloride ZrOCl$_2$H$_2$O. In zirconium tetramer, four zirconium ions are located in the four corners of slightly distorted square linked OH bridges placed above and below the plane of that square [66]. Controlled polymerization offers the possibility to prepare pillared clays with different interlayer distances and surface areas [67]. The degree of polymerization depends on the concentration of pillaring species, pH and aging of intercalated clay suspension. Depending on exact preparation method a rather variation in basal spacing and surface area were observed.
Addition of bases like NaOH accelerates the polymerization and increases the stability of the Zr pillared clays due to a higher pillar density [67].

Ohtsuka et al. observed two different phases in intercalated clays [69]. Clays pillared with a solution containing less than 1 M zirconyl chloride exhibited a basal spacing of 23.3 Å, whereas pillaring with a solution containing a higher zirconyl chloride concentration had a basal spacing of 21.3 Å. Insertion of single zirconium tetramers parallel to the clay layers surface form the low basal spacing of approximately 13–14 Å [70]. This is in contrast to observations of Yamanaka and Brindley. They observed a basal spacing around 19.6 Å which was interpreted as formed by either the same tetramers standing perpendicular to the clay layer surface or by stacking of two tetramers on top of each other [71]. However, there is no clear evidence for this type of pillar positioning. The larger basal spacing between 19 and 24 Å in some of the zirconium pillared clays are interpreted as being due to either the formation of larger polymeric cations or by overlap due to mismatch between cations adsorbed on opposite clay layers [72]. FT-IR studies on pyridine adsorption on Zr pillared clays showed that the Lewis acid sites were
only located on the pillars, while the Bronsted acid sites were associated with the exposed clay surface and the pillar clay bonding [73].

1.4.5 Cationic metal complexes as pillaring agent

Incorporation of metal chelate cations \([\text{M(cheIl)}_3]^{3+}\) in to smectite clays and subsequent calcination provide metal oxide pillared materials. The first successful preparation of Mn pillared clay was by the intercalation of trimeric \([\text{Mn}_3\text{O(COOCH}_3\text{)}_6(\text{H}_2\text{O})_3]\text{CH}_3\text{COO}\) complexes [74]. Similarly chromium pillared clays were reported in the literature by the intercalation of trimeric chromium oxyformate \([\text{Cr}_3\text{O(HCO}_2\text{)}_6(\text{H}_2\text{O})_3]\) as pillaring agent [75]. Similarly magnetic iron oxide pillared clays were prepared by the intercalation of \([\text{Fe}_3\text{O(OCOCH}_3\text{)}_6. \text{CH}_3\text{COOH. 2H}_2\text{O}]^+\) as pillaring agent [76].

![Figure 1.7 Structure of cationic complex pillaring species](image)

1.4.6 From positively charged sol

Positively charged metal oxide sols can be intercalated into the interlayer of clays by cation-exchange reactions, providing pillared materials after calcinations. Although pillared materials with super galleries were made, the pore structure is not homogeneous and the pore size distribution occurs over a
broad range because the interlamellar region is stuffed with flocculated sol particles of different sizes. Titanium pillared clays can be prepared by this approach. Titanium sol prepared by the hydrolysis of titanium alkoxide by HCl can be used as pillaring agent for the preparation of titanium pillared clays [77].

![Figure 1.8 Structure of titanium pillaring species](image)

1.4.7 From metal cluster cations

This is a new approach of intercalating rare transition metal oxide pillars inside the clay layer. Pillaring of smectite with niobium and tantalum oxides was achieved with the cation exchange and subsequent oxidation of niobium and tantalum cluster cations of the type $M_6\text{Cl}_{12}^{n+}$ ($n = 2, 3; M = \text{Nb, Ta, Mo}$). The niobium oxide and tantalum pillared clays after calcination at 325 $^\circ$C exhibited an interlayer spacing around 9 Å and BET surface area of 60–70 m$^2$/g only [78].

1.4.8 Factors affecting the pillaring process

The structural textural and acidic properties of pillared clays depend on recipe of preparation process. The various factors influencing are

- The source and type of clay
Several host clays which have appreciable layer charge and swelling capacity can be used as parent materials. The intercalation of montmorillonite is, by far, the most documented process. The pillaring of saponite, beidellite, vermiculite, hectorite, mica, laponite and synthetic clays were also been reported [79–93]. The effects of the reaction time and other conditions (temperature, shaking/stirring speed) have been also studied by several authors [94-95]. The washing, drying, and calcination processes have a great influence on the properties of the final solids, especially in the development of the porosity.

Figure 1.9 Aggregation of layers in pillared clays
Drying have dramatic influence as air drying predominantly leads to face-face association while freeze drying leads edge to face or edge to edge aggregation leading to structure referred as “house of cards” [96]. Finally, calcination of the solids can also be carried out in different ways (in air or in inert atmosphere) in order to best stabilize the metallic polycations. The effect of calcination temperatures and heating rates were also reported by many researchers. In conclusion, the final properties of the pillared clays strongly depend on the thermal history of each sample.

1.4.9 Characteristics of Pillared Clays

A broad spectrum of pillared clays can be formed by control of experimental variables prior to the addition of clay, during clay addition and post pillaring reactions. The structural evolution of pillars does not involve clay lattice reconstruction, i.e., the basic structure of clay remain intact. Comparison of model isotherms based on cylindrical pore geometry with the help of DFT and experimentally observed pore volume distribution showed that nature of clay surface was nearly unaffected by pillaring reaction [97-98]. It has been proved that thermal stability of clays is improved after the pillaring process. Up on dehydroxylation during calcination step, the bond between the pillar and clay is thought to shift from ionic to near covalent which results in stabilization of porous network.

1.4.10 Acidity of pillared clays

Pillaring the clay will modify the surface acidity in at least two ways. 1) the polycationic pillars displaces the cation originally present on the surface of clay. 2) Pillar’s own acidity may create Si-OH-Al bridges in smectites with aluminium substitution in the tetrahedral layer. These OH may provide an
anchoring point to the pillar. There is a general agreement on the presence of higher proportion of Lewis sites than Bronsted sites in pillared clays [99-100]. In calcined forms the pillar being usually metal oxide clusters contribute mainly to Lewis acidity. However unavoidable contribution to Bronsted acidity by pillar has also been evidenced [101,102]. The structural hydroxyl groups are major source of Bronsted acidity in dried samples which slowly disappear during thermal activation due to the migration of protons in to clay lattice sites where the –ve charge originates.

1.4.11 Advantages of pillaring

The main advantage of pillaring process includes

- Increase in basal spacing of clay
- Increase in pore size and surface area
- Enhancement of acidity
- Enhancement of thermal stability
- The active species are immobilized as “pillars” which do not leach in liquid reactions in polar solvents in comparison with ion exchanged clay catalysts.
- Enhancement in catalytic activity

1.4.12 Mixed pillaring

The thermal stability, surface area, surface acidity, porosity etc of single oxide PILCS can be improved by incorporating a second component to pillars. Various metals have been reported in combination with the Al polyoxocation, the most important of them being Fe, Ga, Si, and Zr. A large number of mixed pillared clays such as Ga-Al, Al-Fe, Al-Zr, Al-Cr, Fe-Cr, Fe-Zr etc. were reported in literature [105-111]. The second pillaring species may form
discrete or mixed pillars depending on metal combination and preparation conditions. For example Ga forms mixed pillars in which the pillaring species $[\text{GaO}_4\text{Al}_{12}(\text{OH})_2\text{H}_2\text{O}_{12}]^{7+}$ is a tridecamer with central gallium tetrahedron surrounded by twelve aluminium octahedra.

![Figure 1.10 Structure of Mixed Al-Ga pillaring species](image)

Bradley et al. [105] carried out a complete study on Ga–Al-pillared solids, by hydrolysis of GaCl$_3$ or a mixture of GaCl$_3$ and AlCl$_3$ respectively. They compared the thermal stability of montmorillonite pillared with Al$_{13}$, Ga$_{13}$, and GaAl$_{12}$ oligomers. The study of the changes in basal spacing upon calcination showed that the stability increased in the order Ga$_{13}$ < Al$_{13}$ < GaAl$_{12}$. Lewis acid site concentration was very high in the Ga-Al pillared clays and the Bronsted acidity decreased in the order GaAl$_{12}$ > Al$_{13}$ > Ga$_{13}$.

In Fe- Al mixed Pillared clays both mixed and discrete species were reported in literature. Lee et al. presented a detailed study of Fe –Al mixed pillared clays and their intercalating solutions [112]. These materials were studied by Mossbauer spectroscopy. It was found that iron preferentially decorated the surface of the alumina pillars and at least one monolayer of Fe(III) was accommodated at the surface of the pillars. Even though the
formation of $[\text{Al}_{12.5}\text{Fe}_{0.5}\text{O}_4\text{(OH)}_{24}]^{7+}$ polycations was postulated, the authors did not find any evidence of mixed species containing iron and aluminum in the same complex, but rather with discrete alumina and iron oxide pillars. Bergaya et al. proposed the formation of mixed $\text{Al}_{13-x}\text{Fe}_x$ pillars in Al-Fe pillared laponite, based on the Fe content of the pillared solids [93]. Chemical analysis and $\text{H}_2$ TPR experiments showed the presence of two iron species, in the mixed pillars and discrete iron pillars. Al–Fe pillars in alumina rich samples were particularly active for a syngas conversion reaction, showing high selectivity to light olefins probably due to the presence of $\text{FeAl}_6\text{O}_7$ mixed oxides.

1.4.13 Post pillaring modifications

The sulfate or phosphate groups can be anchored in to the metal oxide pillars by adsorption method to improve the acidity. Phosphoric acid anchored on the metal oxide pillars of aluminium exhibit an increased Bronsted acidity which was ascribed to the formation of monodentate or bidentate complexes [113]. The pillared clays can be used as suitable support for dispersing transition metals whose presence may help as catalysts in reactions that requires redox nature or multifunctionality.

![Figure 1.11 Anchoring of phosphate group on metal oxide pillars](image)

**Figure 1.11 Anchoring of phosphate group on metal oxide pillars**
Applications of pillared clays

The relevance of PILCs is evident from the extensive reviews [7,98] of scientific literature and books [6,21] being published in last few years. An important aspect of their relevance is that PILCs can be prepared in large scale without much cost and can provide commercial PILCs with low price. Many natural clays from the different part of the world is often evaluated to develop PILCs. Thus natural resources of the country can be valorized to get value added products. The major interests of pillared clays are related to heterogeneous catalysis but other uses are also reported in the field of environmental uses, thermal insulators, pigments, electrodes and membranes.

1.5 Porous clay heterostructures (PCHs)

Since the discovery of Mobil Catalytic Material (MCM) in 1992 [114], a lot of research has been conducted on mesoporous materials. In 1995 Galarneau et al. [115] applied the MCM technology on natural fluorohectorite clay, obtaining a large pore clay derivative, designated as Porous Clay Heterostructures (PCHs). PCH materials are relatively new class of modified clays in which mesoporous silica network is incorporated between the gallery of smectite clays by a template assisted route. These new derivatives are formed by surfactant-directed assembly of open-framework silica in the galleries of smectite clays with high charge density. In the synthesis of a PCH material, clay is firstly opened up by the introduction of an ionic surfactant via a cation exchange reaction (usually by long chain alkyl ammonium cations). Neutral amine co-surfactant molecules are then intercalated along with silica precursor (such as TEOS) and its insitu hydrolysis and polymerization around micellar template of surfactant and co-surfactant give rise to a templated
heterostructure. After calcination for the removal of organic surfactants the porous network of silica within interlayer region is being formed [115-108].

Figure 1.12. Mechanism of PCH formation

PCHs attracted particular attention due to its high surface area (250-1000 m²/g), ion exchange capacity, surface acidity, mesoporosity with narrow pore size distribution, good thermal stability and mechanical strength. In contrast to pillared clays whose pore sizes are typically in the microporous range with wide pore size distribution, PCH materials exhibit regular porosity in the super micropore to mesoporous range. In that sense porous clay heterostructures transcend the pore size limitation of pillared clays [115]. PCH materials have properties inherent to both components, the properties of clays (e.g; CEC and acidity) and properties of silica network (e.g; ability to be functionalized).

In fact PCH materials are pillared clays with silica pillars inserted between clay layers. The difference in the preparation process and the difference in mechanism of process lead to the new terminology called porous clay heterostructures. In some respects the approach is similar to conventional pillaring process, where pillared clays are formed by the insertion of dense nanoscale aggregates in to the galleries of layered host. The pillaring process is mostly governed by CEC of clay, nature of pillaring species and recipe of pillaring process, where as in PCH materials intergallery templating process
involves the insitu assembly of surfactants and inorganic precursor nanostructures, the morphology of which will be determined by the collective energetic of inorganic organic species as they assemble together. The choice of surfactant, its alkyl chain length and surfactant to precursor ratio all plays a crucial role in preparation process [115-116].

The preparation process of PCH materials has some analogy with the preparation of MCM type materials. Synthesis makes use of the micellar ordering of silicate species and the supra molecular ordering of surfactants as in the synthesis of mesoporous MCM-41 molecular sieves. However PCH assembly differs from MCM-41 chemistry in so far as framework organization occurs in the restricted two-dimensional gallery region of the clay rather than in the three-dimensional bulk phase [115]. Since PCH design combines the open framework structure of the gallery silica with the chemistry of the clay layer, new properties for selective heterogeneous catalysis may be anticipated. Surfactant removal from synthesized PCHs by calcination results in the formation of protons which migrate in to interlayers to balance clay layer charges. Consequently silica in interlayer PCHs are intrinsically acidic, where pure silica meso structures possess little or no acidity. In PCH materials new Bronsted acid sites are created along with the retention of intrinsic acidity of clays. More over PCH materials are stable indefinitely while it has been reported that MCM-41 material degrades after two months of preparation at ambient conditions [118].

The major acidic sites related to PCH material are Bronsted acid sites. This is due to the formation of protons during the calcination step by the decomposition of surfactants [118]. The silanol group of newly formed silica pillars also contributes to Bronsted acidity. In addition, the silicate layers can undergo local restructuring upon calcination at elevated temperatures, giving
rise to Lewis acid sites in the gallery region [119-120]. Lewis acidity of PCHs materials can be improved by addition of transition metals. Metals can be incorporated in to intragallery silica frame work of porous clay heterostructures by the addition of corresponding metal alkoxide along with silica source in preparation process by the direct synthesis approach.

The preparation procedure was extended by various researchers to prepare PCHs materials involving species other than silica which introduce novel synthetic aims. Thus Ti or Zr can be incorporated in to the wall of intragallery silica by the addition of precursor of titanium alkoxides or zirconium alkoxide along with silica source in preparation process [121-122]. But huge amount of metals could not be added in this fashion as that will lead to structural collapse. The generation of alumina/silica PCHs has been achieved by Ahenach et al. using a molecular designed dispersion method [123]. The irreversible adsorption of the aluminium acetylacetonate complex followed by its thermal decomposition yielded aluminium oxide PCHs. In this way, AlO₅ species can be grafted on to the surface of previously formed PCHs leading to the formation of Si-(OH)-Al bonds by anchoring with surface silanol of PCHs. Zhou et al. prepared Al/SiPCHs by the in situ assembly of TEOS and aluminium isopropoxide precursors. Although aluminium was incorporated with in pillars by Si-O-Al bonds providing lewis acid sites, textural properties are not improved so much compared to other Al incorporation methods [124]. Recently F. Kooli et al. prepared aluminium incorporated PCH materials by the use of aluminium intercalated clay, aluminium pillared clay, dodecylamine and a silica source [125]. This method allowed them to reduce the use of the organic template and to incorporate the aluminum species directly into the silica framework intercalated between the
clay sheets in one step. The PCH material prepared from the Al\textsubscript{13}-intercalated clay exhibited higher surface area, mesopore volume, Bronsted and Lewis acid sites. However, the use of pillared clays did not lead to the formation of PCH material due to the strong interaction between the alumina species and the clay sheets, which hindered their exchange with dodecylamine, as indicated by XRD and \textsuperscript{29}Si and \textsuperscript{27}Al solid-state NMR results.

Aminopropylsilane has been employed to functionalise PCHs material for further immobilisation of copper and vanadium complexes creating effective catalyst for epoxidation reactions [126]. In the same way PCH modified with APTES were used for immobilizing Mn(III) salen complexes to develop heterogeneous catalysts for asymmetric epoxidation of alkenes [127].

![Figure 1.13. Mn salen complex immobilised on PCHs](image)

PCHs modified with APTES can be used as adsorbing substrate for carbon dioxide. 3-mercaptop propyltrimethoxysilane functionalized PCHs were used as heavy metal absorbent (Cd, Cu, Mn, Ni, Pb and Hg) useful for water treatment and modified electrodes [126-127]. Recent advances in PCH material include the development of more efficient and functional materials exploring different
type of clays, modifying the synthetic methodology described by Pinnavaia et al. and using the known precursors. For example PCHs prepared from several smectites such as saponite, montmorillonite and vermiculite have been modified by ion exchange method to incorporate metal active phases (Fe, Cu etc.) to develop optimum catalyst for DeNO\textsubscript{X} reactions with ammonia [130-131].

Another new type of porous material related to clay is delaminated porous clay heterostructures (DPCHs). Letaief and R.Hitzky described a controlled route for the formation of delaminated silica porous clay heterostructures [132]. Pre swelled organoclay in polar solvent such as alcohols is treated with alkoxide followed by the addition of water give rise to hetero coagulation of expanded organoclay suspension with alkoxide being hydrolyzed to give nano particles assembled to the clay derivative network.

1.6 Catalysis by modified pillared clays

The use of metal exchanged /supported and intercalated clay based materials in organic synthesis has a rather extensive history. The pillaring of clays increases the accessibility of the reactant molecules to the interlayer catalytic sites, resulting in a possibly high catalytic activity. Simultaneously, the interlayer and interpillar distances exert shape selective effect, which control diffusion rates of reactant, reaction intermediates and products. Most catalytic reactions using pillared clays as catalysts are based on the acidic properties of the catalyst. PILCs have been investigated as acid catalysts for various reactions like alkylation, acylation, isomerisation, cracking, dispropanation and methanol conversion [6,133,134].
The suitability of pillared clays as a catalyst support has been explored because of their textural acidic properties. Transition metal can be deposited into pillared clays by ion exchange or wet impregnation methods. Potential application of pillared clays in catalytic process of redox or bifunctional nature would require pillared clays to accommodate transition metals as active species. Literature reviews show that copper and vanadium have been vastly explored as active species and to lesser extent nickel, cobalt and other elements. Aluminium pillared clay is greatly explored as catalytic support compared to other pillared clays. Since the present work mainly focus on catalysis by metal supported pillared clays, catalytic application of those materials for various organic transformations is summarized in Table 1.2.

Table 1.2. Transition metal supported pillared clays for various organic transformations

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Al Pillared clay</td>
<td>Xylene and toluene oxidation</td>
<td>135</td>
</tr>
<tr>
<td>Cu/ Al Pillared clay</td>
<td>Hydroxylation of benzene</td>
<td>136</td>
</tr>
<tr>
<td>Cu/Al Pillared clay</td>
<td>Oxidation of phenol</td>
<td>137</td>
</tr>
<tr>
<td>Cu or Ce /Al Pillared clay</td>
<td>Preferential oxidation Of CO</td>
<td>138</td>
</tr>
<tr>
<td>Cu/Fe-Al Pillared Clay (FAZA)</td>
<td>SCR of NO with C\textsubscript{3}H\textsubscript{8}</td>
<td>139</td>
</tr>
<tr>
<td>Rh/Ni/Pd ce/ALPC</td>
<td>Dry reforming of methane</td>
<td>140</td>
</tr>
<tr>
<td>Pd or Ce/ Al Pillared clay</td>
<td>Deep oxidation of benzene</td>
<td>141</td>
</tr>
<tr>
<td>CoMo/ Al Pillared clay</td>
<td>Ethyl benzene to styrene</td>
<td>142</td>
</tr>
<tr>
<td>NiMo/ Al Pillared clay</td>
<td>Hydrotreating of crude oil</td>
<td>143</td>
</tr>
<tr>
<td>Ce/Zr or Al pillared clay</td>
<td>Cyclohexanone transformation</td>
<td>144</td>
</tr>
<tr>
<td>Cu/Pd Aluminium pillared clay</td>
<td>Nitrate Reduction</td>
<td>145</td>
</tr>
<tr>
<td>Ce or Fe/Al pillared clay</td>
<td>2 propanol oxidation</td>
<td>146</td>
</tr>
<tr>
<td>Co/ Al Pillared clay</td>
<td>Ethyl benzene to Styrene</td>
<td>147</td>
</tr>
<tr>
<td>Fe, Ce, or Ag/Ti Pillared clay</td>
<td>SCR Of NO</td>
<td>148</td>
</tr>
<tr>
<td>Cu/Ti pillared clay</td>
<td>Catalytic combustion of methane</td>
<td>149</td>
</tr>
<tr>
<td>Neobium /Al pillared clay</td>
<td>Synthesis of β hydroxyl ether</td>
<td>150</td>
</tr>
<tr>
<td>V/ZrPC</td>
<td>Oxidative dehydrogenation of propane</td>
<td>151</td>
</tr>
<tr>
<td>V/FePILC</td>
<td>Catalytic oxidation of H\textsubscript{2}S</td>
<td>152</td>
</tr>
<tr>
<td>V/TiPILC</td>
<td>Selective catalytic reduction of NO</td>
<td>153</td>
</tr>
</tbody>
</table>
1.7 Objectives of the present work

Transition metals can be deposited in to pillared clays and porous clay heterostructures by ion exchange or impregnation method. Acidic properties of pillared clay together with the redox properties of transition metals make them interesting material for organic transformations. In Pillared clays transition metals mainly reside on pillars rather than on silicate layers, uniformly distributed when loaded in small quantities showing promising catalytic activities. The hydrophobicity of porous clay heterostructures may be reduced by incorporating metals like Ti or Zr by direct method which may also contribute to overall acidity. However huge amount of metal cannot be added in that fashion as it leads to the structural collapse. The hydrophilicity, acidity, redox property etc may be improved by incorporating transition metals by ion exchange or wet impregnation methods.

Catalysis by heteropoly acids (HPAs) has attracted increasing attention in both academic and industrial fields because of their unique strong Bronsted acidity and structure alterability. The bulk heteropoly acids have some disadvantages like extremely small surface area and high solubility in polar solvents. Hence, to improve catalytic applications of HPAs, it has to be dispersed on high surface area of carriers such as silica, active carbon, molecular sieves, Al₂O₃ and so on. Owing to relatively large pore size and surface area of PCHS, heteropoly acids can be successfully anchored on the mesoporous channels of silicon pillars of PCHs.
The main objectives of the work are

- Prepare single and mixed pillared clays like zirconium, iron-aluminium pillared clays by ion exchange method.
- Prepare porous clay heterostructures like silicon and zirconium silicon PCHs by template assisted method.
- Modify PILCs and PCHs by loading transition metals like Cu, Ni, Co, V etc. by wet impregnation method.
- Characterize the prepared catalysts using different physico chemical techniques like X-ray Diffraction, Surface area measurement, FTIR, UV-Vis DRS, ICP-AES, $^{29}$Si NMR, TPR, XPS, Acidity measurements using TPD of ammonia, SEM, TEM etc.
- Evaluate the catalytic activity of the prepared catalysts for organic transformations like liquid phase oxidation of phenol, hydroxylation benzene, oxidation of benzyl alcohol and vapour phase tertiary butylation of phenol.
- Immobilize heteropoly acid dodeca tungstophosphoric acid on porous clay heterostructures and characterize the supported catalysts using different characterization techniques and evaluate the catalytic activity for acetalization of cyclohexanone reaction.
References

Introduction and literature survey


Introduction and literature survey


Introduction and literature survey


Chapter 1


