ORGANIC REACTIONS CATALYSED BY MODIFIED CLAYS

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By

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August 2008

DECLARATION

I hereby declare that the thesis entitled "**ORGANIC REACTIONS CATALYSED BY MODIFIED CLAYS**" submitted for the award of Ph.D. Degree, is based on the original research work done by me under the guidance of Dr. K. Sreekumar, Reader, Department of Applied Chemistry, Cochin University of Science and Technology and further that it has not previously formed the basis for the award of any other degree.

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This is to certify that the thesis entitled **"ORGANIC REACTIONS CATALYSED BY MODIFIED CLAYS"** submitted for the award of the Degree of Doctor of Philosophy of the Cochin University of Science and Technology, is a record of original research work carried out by Mr. Suresh. S. under my supervision and guidance in the Department of Applied Chemistry, and further that it has not formed the part of any other thesis previously.

14/10/08

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PREFACE

'Sustainability' has emerged as one of the keywords in discussions in the fields of politics, society and science within the past 20 years. The need for the production of high-quality products with minimum waste and energy demands is a key challenge in today's environment. This is even more salient when the increase in the world population and the decrease in fossil fuel resources are considered. In the field of chemistry, the concept of sustainability is clearly defined by the use of low-waste chemical transformations plus the use of catalysts in order to decrease the amount of energy needed for a process. Although most catalytic reactions fulfill the criteria for a sustainable transformation on the macroscopic scale, often the high price of catalysts, which are mostly transition metal based and their ligands paired with an inherent toxicity contradict these criteria on a microscopic scale. This contradiction has spurred interest in developing transformations that make use of sustainable catalysis. Organocatalysis and biocatalysis both fulfill the criteria of sustainable catalysis: the catalysts are cheap, readily accessible and non-toxic. In the field of sustainable metal catalysis, iron-catalyzed transformations have evolved as powerful tools for performing organic synthesis.

Natural clays are highly heterogeneous in composition and, almost invariably, contain 'impurities' in the form of associated minerals and X-ray amorphous materials. The mineralogical composition of clays is also influenced by particle size, the smaller the size, the larger the contribution of X-ray amorphous material. The fineness of clays predetermines both their vulnerability and reactivity. By the same token, clay particles are sensitive to mechanical and chemical treatments. A variety of spectroscopic and instrumental techniques have been used to analyse and characterize clays and clay minerals. Improvements in sensitivity, selectivity, and accuracy are constantly being sought. The development of new techniques and the refinement of old ones create a complex, multidimensional problem. Verification of the reproducibility of results, obtained in different laboratories, is not an option, but a necessity. The chemical and mineral composition of clays is more difficult to quantify than other hard rocks. Differences in clay mineral populations, structural imperfections, variations in crystallinity, and the presence of impurities are problems that are specifically associated with the identification and quantitative analysis of clays.

The present thesis is concerned with organic reactions mediated by clay minerals, specifically of kaolinite in nature which are the most abundant in our localities. Large number of reactions and studies have been conducted in recent years. Kaolin based studies are comparatively low in literature though much have been devoted to montmorillonite type of clays.

First chapter deals with the various aspects on the clay mineralogical studies, which include structure of clays, comparison and identification of various types of clays etc. A brief account on characterization studies of clay minerals including, chemical composition, acidity measurements, Fourier-Transform Infrared spectroscopy, Thermogravimetric studies, X-ray diffraction, surface area measurements, are explained. The properties of clays such as ion exchange, swelling of clay layers, intercalation and cation exchange, pillaring of clays and the acidic nature of clays are well demonstrated. Brief accounts of organic reactions including dehydration, addition, oligomerization, isomerization and rearrangement, aromatic electrophilic substitution, Diels-Alder, Heck, Suzuki, esterification reactions, oxidation and reduction reactions based on clay catalysts are discussed. Reactions based on basic clay catalyst like Knoevenagel type, sonochemical nucleophilic substitution are explained with examples.

Second chapter starts with the collection of clays from various sources and from different localities. Detailed chemical analysis of the clay minerals are included. Based on these analysis suitable clay was selected. Selected clay was made into seven catalysts. Four acid activated catalysts using different acid concentrations of two acid types (HCl and H_2SO_4 of 2M and 5M respectively), and one type each of 10% $CuSO_4$ and 10% $FeCl_3$ impregnated and one type is taken as raw type to assess the various modifications. The prepared catalysts are characterized by determining chemical composition, FT-IR spectroscopy, X-Ray diffraction patterns, Thermogravimetry, Surface area measurements, Acidity measurements.

From chemical composition data, the percentage ion variation, and the Silica/Alumina molar ratio is ascertained. From the FT-IR measurements, the various bond nature and the difference in the strengthening and weakening of various bound groups based on the intensities are found. From the X-ray patterns, the extent of crystallinity could be assessed by comparing the intensities of major peaks. From the thermogravimetry data the extent of thermal stability is ascertained. Surface area measurements give details of the active surface sites and the extent of catalytic activity. Acidity measurements could be used for the strength of weak and strong acid sites determination. The results are compared with standard clays such as KSF and K10.

Third chapter deals with the experiments conducted using the prepared catalysts. Diazotisation and coupling reactions are discussed in this chapter. Methyl orange was taken as the reference reaction to study the activity of the catalysts. Based on the results iron impregnated catalyst was selected as the better one. Five azodye derivatives such as methyl orange, orange II, Orange IV, Sudan I, and butter yellow were prepared. The recycling ability was studied.

Preparation of 4,4'-diaminodiphenylmethane, an important raw material for polyurethane foams is discussed in the fourth chapter. The yield of the products is compared with standard catalysts such as KSF and K10. Five derivatives, such as 4,4'-Diaminodiphenylmethane, 4,4'diamino-3,3'-dicarboxyldiphenylmethane, 4,4'-N,N,N'N'-tetramethyldiaminodiphenylmethane, 3,3'dimethoxy-4,4'-diaminodiphenylmethane 3,3'-dimethyl-4,4'-diaminodiphenylmethane were prepared using the iron impregnated catalyst. Recyclability of the catalysts is also studied.

One of the method for introducing alkyl substituents into the aromatic system is through Friedel-Crafts alkylation. Homogeneous acidic catalysts were used for the reaction. This introduces several problems such as tedious work up, use of corrosive chemicals, moisture sensitivity, decreasing regioselectivity and so on. To overcome the drawbacks replacement of soluble Lewis acids is achieved by solid acids which facilitates improved procedures. In the fifth chapter, attempts are made to achieve Friedel-Crafts alkylation reaction under vapour-phase conditions. The preparation of *t*-butylphenol was attempted to optimize the reaction conditions. All the catalysts were tested for the tertiary butylation of phenol. The results are compared with standard catalysts. The catalyst with highest activity is further utilized for different substrates. Five derivatives such as *p*-tertiarybutyl phenol, Isopropylbenzene, Ethylbenzene, and *p*-Cresol and toluene are prepared and the products are isolated in good yield. Characterization studies are conducted with physical constants, Gas chromatographic methods, and spectral data. The recyclability of the catalysts is studied.

Vapour-phase esterification reaction has also been carried out using the same methods and procedures. The esterification reaction of benzoic acid with ethyl alcohol is taken as the standard reaction and is studied in detail for the activity of the prepared catalysts. Five products such as ethyl benzoate, methyl benzoate, ethyl salicylate, methyl salicylate and cyclohexyl benzoate with highly active catalyst are prepared and characterized using standard methods. Recycling study is conducted for the esterification reaction with the highly active catalyst. The yields of the product can be controlled by adjusting the flow of the reactant into the reactor. Since the reaction is in vapour phase condition, monitoring the progress of the reaction is easier. Catalyst removal and thereby the regeneration of the catalysts is made easy. The easy method of preparing the alkylation and esterifcation products and relatively low amount of by-products and easier method of purification, relatively low amount of supported reactants and conditions render the reaction more advantageous.

Microwaves, a nonionizing radiation incapable of breaking bonds, are a form of energy. and are manifested as heat through their interaction with the medium or materials wherein they can be reflected (metals), transmitted (good insulators that will not get heated) or absorbed (decreasing the available microwave energy and rapidly heating the sample). Microwave (MW) irradiation, an unconventional energy source, has been used for a variety of applications including organic synthesis wherein chemical reactions are accelerated because of selective absorption of MW energy by polar molecules, nonpolar molecules being inert to the MW dielectric loss. Sixth chapter deals with attempts to use alternate energy source such as microwave in organic reactions. In this chapter microwave mediated organic reactions such as esterification and oxidation of alcohols to carbonyl compounds using the clay catalysts are discussed.

In this study, the catalysts were used for esterification reaction. The efficiency of the catalysts in both conventional heating and microwave heating is compared. The conventional heating involved heating the reaction mixture with the refluxing vessel. The microwave heating is employed using the house hold microwave oven. The esterification reaction of benzoic acid using ethyl alcohol is carried out using the catalysts and the yields are compared. Using the high yielding catalyst, further esterifications are performed using different substrates to prepare five esters such as ethylbenzoate, methylbenzoate, ethylsalicylate, methylsalicylate and cyclohexylbenzoate were done. The products are characterized using standard procedures. Recyclability studies are also conducted and found to be comparable with the standard clays.

The oxidation of alcohols to carbonyl compounds is an important transformation in organic chemistry which is attracting much current interest. Although a large number of reagents are known in the literature for such a transformation, there still appears a need either to improve the existing oxidation methods or to introduce newer reagents to permit better selectivity under mild conditions and with easy work up procedures. The oxidation of benzyl alcohol to benzaldehyde has been taken as a reference reaction. The high yielding catalyst was utilized for further study of oxidation. Oxidation of four alcohols such as benzyl alcohol, cyclohexanol, benzoin and 4,4'-dimethoxybenzoin are considered. The products are well characterized using physical constants and spectral data. The recyclability of the high yielding catalyst was checked. The microwave assisted reactions are characterized with low time and higher yield. The product separation is much easier than conventional reactions. The products obtained are found to be of comparatively high pureity. Works of this kind may be much easier when we apply suitable modification to the microwave oven setup.

Polyaniline (PANI) is one of the most important conducting polymers. It is commonly prepared by the oxidation of aniline with ammonium peroxydisulfate in an acidic aqueous medium. Polyaniline and polyaniline derivatives can be synthesized both chemically and electrochemically by using suitable protonation media. Seventh chapter describes the preparation of polyaniline by template assisted polymerization using clays. Four types of polyaniline derivatives have been prepared using the acid activated clay catalyst. The polyaniline derivatives prepared are Polyaniline/kaolin, Poly(*o*-Toluidine)/kaolin, Poly(*o*-Methoxyaniline)/kaolin, Poly(*m*-Chloroaniline)/ kaolin which are characterized using IR Spectroscopy, UV Spectroscopy, SEM, Conductivity measurements and XRD techniques.

The last chapter gives a brief summary of the work done and provides scope for further improvements in the study of catalysis using acid treated and metal impregnated clay catalysts. References are given at the end of each chapter.

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CHAPTER I

ORGANIC REACTIONS USING CLAY CATALYSTS

Conspectus

This chapter deals with the salient features of clay minerals, their types and classification. The structure and characterization techniques such as chemical composition, FT-IR, XRD, surface area analysis, acidity measurements etc., are explained. Their properties including ion exchange, swelling, acidic nature are mentioned. A discussion on reactions catalyzed by clay materials in the preparation of fine chemicals is presented.

1. 1 Clay minerals as catalysts

In petrochemical processes such as cracking, solid catalysts were used for decades. Originally, the catalysts were based on acid-treated clays, but, for many years now, framework silicates (zeolites) have proved more effective and selective. Established manufacturing processes for other organic chemicals are, however, still largely based on stirred tank reactors and out-dated methods, employing volatile solvents, stoichiometric reagents and hazardous chemicals[1]. The processes are often inefficient and produce large volumes of waste (commonly 10–50 times the product). Heterogenisation is one among the recent and important of the new clean technologies, which is being developed to reduce waste in liquid phase organic reactions. If the catalyst or reagent stays in a separate solid phase, then water quench phase (the source of much of the waste) is unnecessary. Additional benefits of this approach include avoiding solvent (a heterogeneous catalyst or reagent can act as a solid solvent) and enhancing selectivity (due to pore constraints). In order to exploit this exciting, greener technology in organic chemical manufacturing, we need to produce highly effective catalysts in flexible physical forms to suit a multitude of chemical process technologies. Zeolites have advantages, but are limited in the size of molecules they can accommodate in their limited-size pores. Mesoporous silicas, on the other hand, have suitable pore sizes, but lack chemical activity.

Recent years have witnessed a phenomenal growth in the use of inorganic solids as reaction media for organic transformations[2-6]. The future of organic chemistry rests with heterogeneous media rather than the currently predominant homogeneous systems due to certain specific advantages of using solid surfaces. Clay minerals constitute one such medium.

Clay minerals have a different and interesting set of properties. They are very effective catalysts for a wide variety of organic reactions, often displaying highly sought product, regio- or shape-selectivity. In addition, however, ''soft'' dimensional constraints are often displayed. They have significant potential in organic chemical processing. Their potential was not realized, because:

(1) The variability of natural clays, the wide variety of clay mineral types and the range of possible treatments meant that a reliable set of data on which predictive capability can be based was not generated: there have been too many restricted studies which did not link together.

(2) Not enough attention was given to the engineering of the clays into catalyst articles, pellets, membranes, etc. so that they can survive the rigorous conditions in a range of reactor types. The changes in interlayer spacing, which occur with exposure to reactants/solvents/products make engineering of the clays into catalyst articles, a challenging task.[7-11]

Early works with clays have concentrated either on acid treatment or on cation exchange to increase Brønsted or Lewis acidity. However, in the last few years, the reaction portfolio has widened so that clay minerals are now recognized as effective catalyst for a range of other types of reactions including redox reactions, reactions involving reactive intermediates and cycloadditions (such as Diels–Alder reactions).[12] The high surface area of clays also means that they can act as effective supports for (usually inorganic) reagents bringing the benefits of heterogeneous catalysis to several important reactions.

1.2 Structure of clays

The atomic structure of clay minerals consists of two types of structural units. These are the SiO_4 tetrahedron and $Al(OH)_3$ gibbsite or $Mg(OH)_2$ brucite octahedral unit, both of which form sheet or layer structure. Tetrahedral layers consist of continuous sheets of silica tetrahedra linked via three corners to form a hexagonal mesh and the fourth corner of each tetrahedron is shared with adjacent octahedral layers. Octahedral layer consists of flat layers of edge-sharing octahedra containing cations at its center[13,14]. The general scheme of clay minerals is generated by the combination of sheets of tetrahedral and octahedral units. The basic building units were found to be layers of linked tetrahedra articulated, by sharing oxygens, with layers of octahedra. The individual tetrahedra consists of four oxygens disposed around a central cation, usually Si^{4+}, which can be replaced by other ions of suitable size, such as Al^{3+}. The octahedra consist of six oxygens surrounding larger cations such as Mg^{2+} and Fe^{2+} [15-18] as shown in the figure (Figure 1-3).

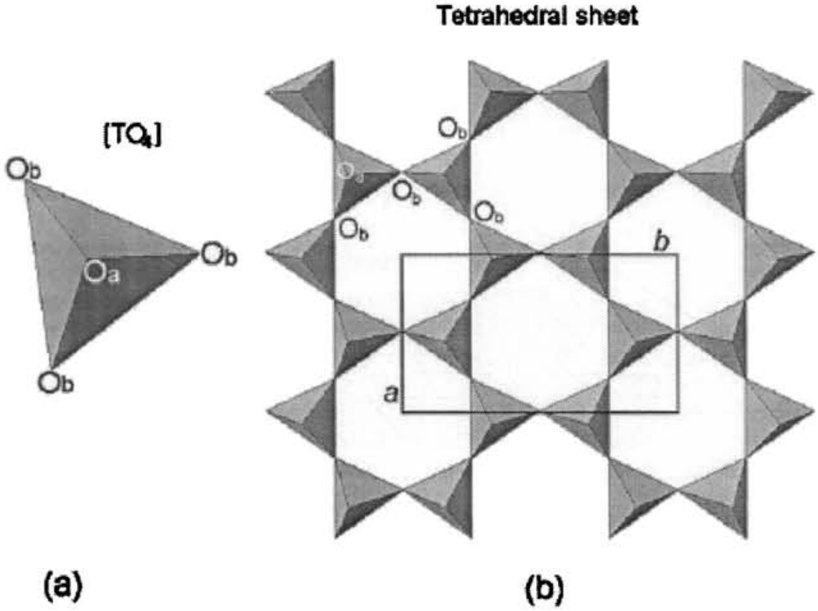


Figure 1: a. Tetrahedron (TO_4). b. Tetrahedral sheet. O_a, O_b –apical ,basal oxygens

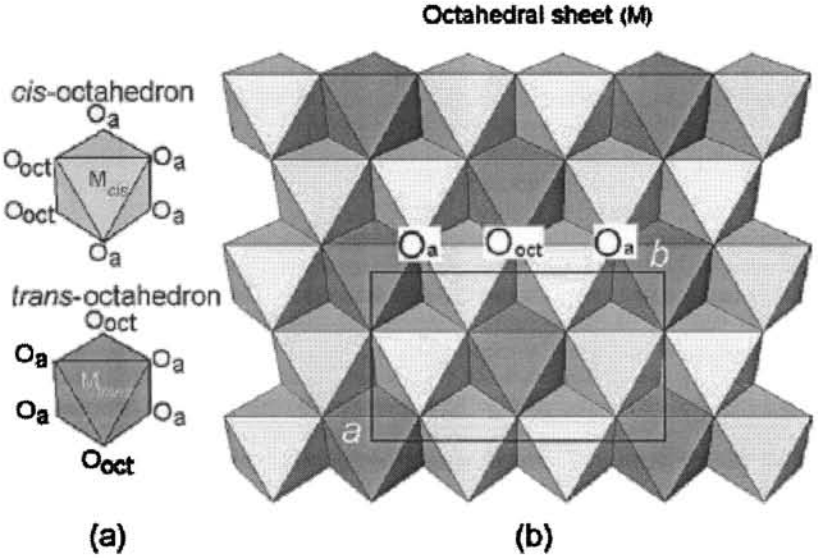


Figure 2: a. O_{oct} (OH, F, Cl) orientation in cis and trans octahedron; b. location of cis- and trans- sites in the octahedral sheet. O_a, O_b –apical, basal oxygens

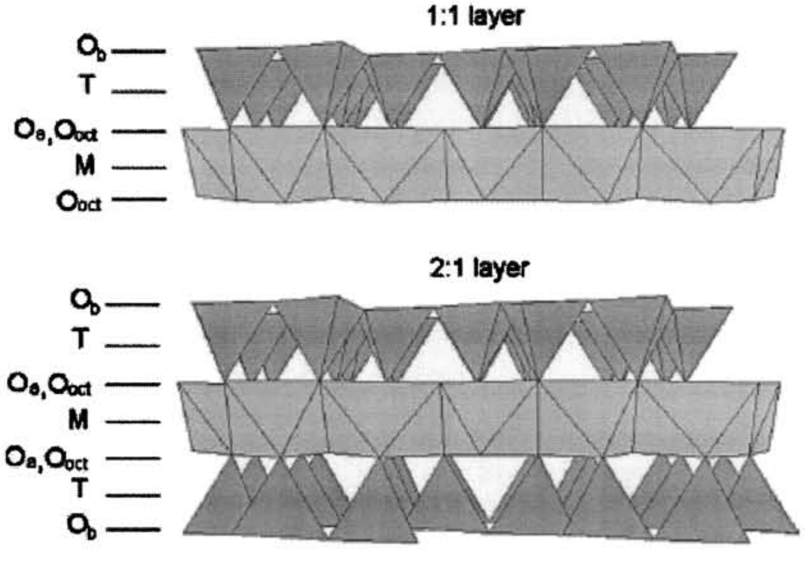


Figure 3: Models of 1:1 and 2:1 layer structure. O_a, O_b and O_{oct} apical, basal and octahedral anionic position respectively

1.2.1 Kaolin Minerals

Kaolinite consists structurally of the following layers (Figure 4). Kaolinite is having the structure of 1:1 dioctahedral. Some of the representing species are Kaolinite[19], Nacrite[20, 21], Dickite[22, 23], Anauxite[24-26], Halloysite[27] (Figure 5) etc.

$$\left.\begin{array}{c} O_3 \\ Si_2 \\ O_2.\,OH \end{array}\right\} \text{Tetrahedral arrangement}$$

$$\text{Octahedral arrangement} \left\{\begin{array}{c} O_2.\,OH \\ Al_2 \\ (OH)_3 \end{array}\right.$$

Figure 4: Layer arrangement of kaolinite

1.2.2 Halloysite

$$\left.\begin{array}{c} O_3 \\ Si_2 \\ (OH)_2 \end{array}\right\} \text{Tetrahedral arrangement}$$

$$\text{Octahedral arrangement} \left\{\begin{array}{c} (OH)_3 \\ Al_2 \\ (OH)_3 \end{array}\right.$$

Figure 5: Layer arrangement of Halloysite

1.2.3 Pyrophyllite

$$\left.\begin{array}{c} O_3 \\ Si_2 \\ O_2,(OH) \end{array}\right\} \text{Tetrahedral arrangement}$$

$$\text{Octahedral arrangement} \left\{\begin{array}{c} O_2,(OH) \\ Al_2 \\ O_2,\ (OH) \end{array}\right.$$

$$\left.\begin{array}{c} O_2,\ (OH) \\ Si_2 \\ O_3 \end{array}\right\} \text{Tetrahedral arrangement}$$

Figure 6: Layer arrangement of pyrophyllite

1.2.4 Montmorillonite

Montmorillonite is having the layer arrangements of 2:1 dioctahedral or trioctahedral. Some of the representing species are Beidellite, Nontronite, Hectorite, Saponite etc [28-30].

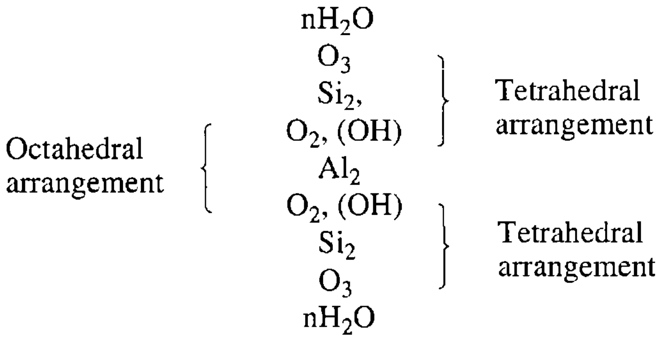


Figure 7: Layer arrangement of montmorillonite

1.2.5 Micaceous Clays

Micaceous clays are having the structure of 2:1 dioctahedral or trioctahedral, and having the species: Muscovite, Paragonite, Phylogopite, Lepidolite, etc [31-39].

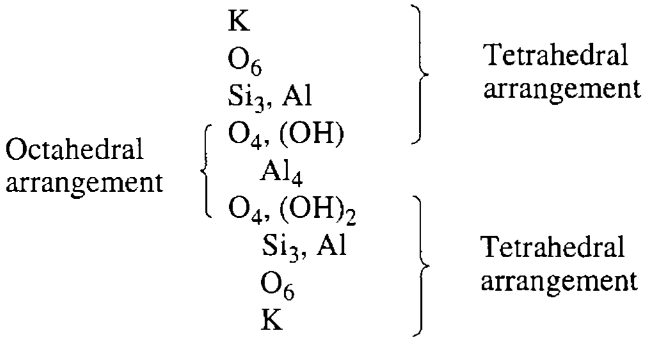


Figure 8: Layer arrangement of micaceous clay

1.2.6 Talc (soapstone, steatite)[40]

O_3 } Tetrahedral arrangement
Si_2
O_2, (OH)

Octahedral arrangement { O_2, (OH)
Mg_3
O_2, (OH)

O_2, (OH) } Tetrahedral arrangement
Si_2
O_3

Figure 9: Layer arrangement of Talc

1.3 Characterization techniques used for structural identification of clays

1.3.1 Chemical composition

Stoichiometric determination of various ions present in the clays can be ascertained by AAS, AES, UV-Visible spectroscopy etc. to find the concentration of cations of elements like Al, Si, Fe, Ti, Ca, Mg, and alkali metal ions like Na^+; K^+, etc. Silica/Alumina Ratio is calculated by,

$$\text{Si/Al ratio} = \frac{\%\text{ of } SiO_2 \text{ x Mol.wt of } Al_2O_3}{\%\text{ of } Al_2O_3 \text{ x Mol.wt. of } SiO_2}$$

This has influence on the extent of catalytic activity due to the presence of the ions. So long as the aluminium content is low enough to allow its distribution in octahedra linked with four silica tetrahedra, the charge in the clay network increases with the aluminum content. Silanols are thermally more stable than hydroxyls bound to aluminium. Hydroxyls bound to aluminium are "acid" and to silicon, are "neutral" and so on.[41] The neutrality of a crystalline structure or structural unit of smectite is obtained by adsorption of exchangeable cations (either anhydrous or hydrated) in the interlayered space, generating its cation-exchange capacity (capacity of reversible exchange of cations). [16]

1.3.2 Acidity measurements

Acid sites in clays are generated either by filling of hydrogen atoms in the unsaturated bonds of the networked oxygen atoms (Bronsted sites) or by the effect of the substitution by metal ions in the unbonded oxygen network (Lewis sites). (Figure 10). The higher the electronegativity of M^+, the stronger are the acidic sites generated. Clay minerals have layer surface and edge defects, which would result in weaker Bronsted and/or Lewis acidity, generally at lower concentrations. The acid strength is usually expressed by the Hammett scale. On this scale, the acidity of clay minerals can be comparable to that of concentrated sulfuric acid. The surface acidity of natural clays with Na^+ or NH_4^+ as interstitial cations ranges from +1.5 to -3. Washing of the clay with mineral acid, such as HCl, brings down the Hammett (H_o) function from -6 to -8, which is between conc. HNO_3 (-5) and H_2SO_4 (-12).

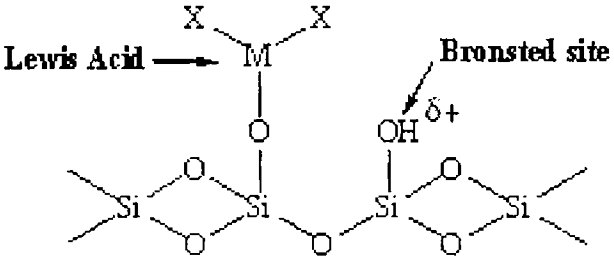


Figure 10. Schematic representation of generation of Lewis and Bronsted acid sites

Temperature programmed desorption technique is used to find weak and strong acidic sites. Acidity measurements are used to characterize clay minerals in the following manner. (1) To ascertain the extent of acidic sites to prepare acidity with the desired value. (2) To compare various types of catalysts and their activity in a reaction. (3) To find the Hammett acidity function. [42]

1.3.3 Infra Red and Raman spectroscopy

Infra Red (IR) spectroscopy is a technique based on vibrations of atoms in a molecule. The IR spectrum of a clay mineral is sensitive to its chemical composition, isomorphous substitution and layer stacking order. This makes Fourier Transform Infrared (FTIR) spectroscopy, the most informative single technique for assessing the mineralogy and crystal-chemistry of a clay mineral sample.

FTIR spectroscopy is a rapid, economical and non-destructive technique used more widely in clay mineral investigations. The developments in FTIR spectrometers have greatly enhanced the field of applications. Modern instruments have high sensitivity, speedy data collection, enhanced spectral precision and reproducibility. Efficient computers enable routine transmission methods to be improved. They also allow the use of different reflectance techniques that are difficult to be implemented with classical dispersive instruments.

FTIR spectroscopy can be used for studying intermolecular bonding features like distortion of molecular units at various lattice sites, the structure of molecular units in solids, the coordination polyhedra of metal ions, etc.

The vibrations of the OH groups are the most fully understood and studied because they are very sensitive indicators of their environment. The absorption coefficients of the OH stretching vibration bands are assumed to be constant, whatever the local chemistry around OH groups within dioctahedral [43-46] and trioctahedral clay minerals [47,48]. The absorbance of each OH band is then proportional to the number of absorbing centres of each type. When all the OH vibration bands occurring in the FTIR spectra are correctly assigned, the FTIR spectra can be quantitatively used.[49] It is found that the molar absorptivity of the OH bending vibrations varies with the water content. The OH vibrations are affected by the octahedral cations to which the OH group is coordinated, and to a lesser degree, by the tetrahedral, and interlayer environments. [50-55].

In natural clay minerals, the major changes in tetrahedral environment are due to multivalent substitutions of Al^{3+} and Fe^{3+} for Si^{4+}. Even if the sensitivity is less than for the octahedral environment, several features in the IR spectra are observed that are related to the degree of tetrahedral substitution such as the appearance of the Si-O-Al band and the shift of hydroxyl bands [56]. Vibrational modes of the interlayer cation are typically very low in frequency and occur in the far IR region (50–150 cm^{-1}). This region is suitable for studying the interlayer environment of clay minerals, using the interlayer cations as probes. However, only cations with low hydration energies in anhydrous clay minerals can be studied [57-61].

1.3.4 Thermogravimetry

In general terms, thermal analysis embraces any technique where a physical property of the material in question is assessed as a function of temperature. Thermogravimetry has the principle of change in properties with respect to temperature. The hydroxyl groups attached with the aluminium ions get dehydroxylated. This phenomenon is diagrammaticlly shown in the figure (figure.11). It could be observed that only the hydroxyl groups attached with the aluminium ions get dehydroxylated. The role of alumina in the process of ion formation is thus established. [62-67]

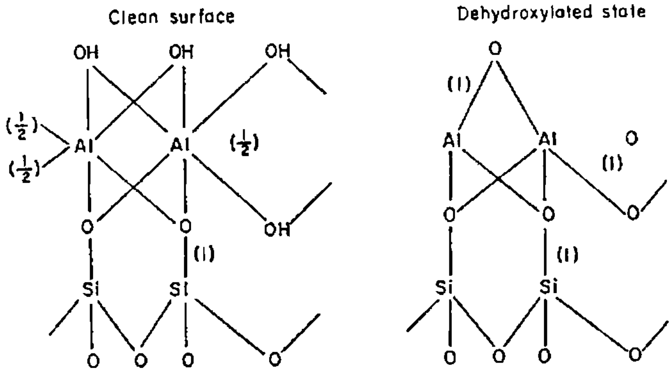


Figure 11: Representation of clean and dehydroxylated states of clay minerals

Mullite ($3Al_2O_3 \times 2SiO_2$) forms are important in structural application of clays. Mullite form possesses remarkable stability, low thermal conductivity, excellent creep resistance and strength at high temperatures. Crystallinity is changed after the loss of the adsorbed water and of hydroxyls during the mullite formation. This is one of the characteristic nature of kaolin which have strong exothermic peak observed around 1200-1250°C. The crystalline nature of kaolin changes due to quartz structure deformation around 550°C.

1.3.5 X-Ray Diffraction

X-Ray diffraction studies are used to characterize following aspects of structural features of clays, viz, identification of unknown phases, determination of phase purity, determination of lattice parameters, investigation of phase changes, structure refinement, determination of crystallite size, etc. Based on intensity of the peaks, extent of crystallinity can be observed[68]. The use of X-rays for structure determination is rather simple in concept, though complicated in its fine details. Monochromatic X-rays (like Cu Kα or Mo Kα source) are reflected by planes in the polycrystalline material when the Bragg equation, $2d \sin\theta = n\lambda$, is fulfilled, where d is the interplanar spacing, θ is the angle between planes and X-ray beam (Bragg angle), λ is X-ray wavelength and n, order of reflection[23]. Every crystalline structure has a unique X-ray powder pattern, since line positions depend on size, and line intensity depends on the type of atoms present and their arrangement in the crystal. Materials are identified from these values in conjunction with 'Joint Committee on Powder Diffraction Standards' (JCPDS) Powder Diffraction file. JCPDS contains cards of X-ray data for known crystalline phases that include d spacing and relative intensity values, Miller indices, unit cell dimensions etc. The experimental data, especially those of the highly intense peaks are matched with standard values using appropriate card[69].

1.3.6 Surface Area measurement

In the case of non-swelling clay minerals, the most widely used technique for determining specific surface area is based on gas adsorption, notably of nitrogen gas at 77 K. Adsorption isotherms, describing the amount of gas adsorbed as a function of relative pressure (P/P_0) can exhibit different features depending on the size of particles, the presence of organized pores (between 0.5 and 50nm), and the energetic properties of the mineral surface [70].

Different methods of data analysis are used to derive quantitative information from experimental adsorption curves of which the Brunauer Emmett and Teller (BET) analysis is the most common. This is based on the equation proposed by describing multilayer adsorption.[71] In the linearised form of the equation, it is possible to derive the amount of gas required to cover the surface of the particles by a single statistical layer, Q_{mono} by the expression shown below.[72]

$$\frac{x}{Q_{ads}(1-x)} = \frac{C-1}{Q_{mono}\,C}\,x + \frac{1}{Q_{mono}\cdot C}$$

Here x is the relative pressure (P/P_0), Q_{ads}, the adsorbed amount at P/P_0, and C, a constant related to the interaction between the adsorbed species and the surface. The surface area, also called the 'BET surface area', can be derived from the monolayer capacity (Q_{mono}.) and the cross-sectional area of the gas used. In the case of microporous materials, the measured BET surface area describes the combination of surface phenomena such as adsorption on external particle surfaces, and spatial phenomena such as condensation into micropores. A different method should then be used to derive the external surface area and micropore volume, based on comparing the experimental adsorption isotherm with a reference isotherm obtained on a non-porous sample. In the case of nitrogen, the most commonly used method is the 't-plot method'.[73] Information on mesoporosity can also be obtained from the gas adsorption isotherm in the medium and high relative pressure ranges.

Several methods were developed to describe simultaneous multilayer adsorption and capillary condensation. The most common one is the 'BJH method' [74]. The importance of the derivative plot is that the abscissa is proportional to the free energy of adsorption. Thus, the derivative curve can be considered as a fingerprint of the adsorption energy distribution of the gas probe. Such a curve can be further analysed on a quantitative basis using the 'derivative isotherm summation' (DIS) method.[75] When nitrogen is used, specific interactions can take place between the probe molecules and the polar surface sites. As a consequence, the shape of the nitrogen derivative plots differs from that of argon, and the plots are less easy to interpret. High-energy sites, identifiable with empty ditrigonal holes, are present on basal surfaces of clay minerals, which can also be observed. Additional sites, corresponding to interaction between nitrogen and surface cations were identified in synthetic saponites[76] and probably exist in other charged minerals.

1.4 Properties of clays

1.4.1 Ion exchange

Isomorphous substitution of cations in the lattice by lower valent ions, for example, the substitution of aluminium for silicon, magnesium and/or ferrous ion for aluminium or lithium for magnesium, leaves a residual negative charge in the lattice that is balanced by other cations[77]. These loosely bound ions can be readily replaced by other cations when brought into contact with these ions in aqueous medium.

1.4.2 Swelling

Many clay minerals absorb water between their layers, which move apart and the clay swells. For efficient swelling, the energy released by cations and/or layer preservation must be sufficient to overcome the attractive forces between the adjacent layers. In 1:1 (OT) clay minerals, water forms strong hydrogen bonds with hydroxyl groups on hydrophilic octahedral layers, allowing swelling to occur. With 2:1 (TOT) clay minerals, the ability to swell depends on the solvation of interlayer cations and layer charge. Clays with 2:1 structures and low layer charge, (e.g. talc and pyrophyllite) have very low concentration of inter layer cations and therefore do not swell readily. Those with very high layer charge (e.g. mica), have strong electrostatic forces holding alternate anionic layers and the interlayer cations together, thus preventing swelling. Those with univalent interlayer cations swell readily and with divalent, trivalent and polyvalent cations, swelling decreases accordingly. The extent of swelling can be observed by measuring interlayer separations using powder XRD.

1.4.3 Intercalation and cation exchange

In swelling clay minerals such as smectites, the interlayer cations can undergo exchange with cations from external solutions. The concentration of external cations called CEC, is measured in milli-equivalents per 100g of dried clay. Since smectites have the highest concentration of interlayer cations, they have the highest cation exchange capacity. Structural defects at layer edges give rise to additional CEC and small amount of anion exchange capacity[78].

1.4.4 Pillared clays

Between TOT layers of smectites, the large cationic species (e.g. aluminium chlorhydrol) can be inserted by ion exchange[79,80]. Such bulky species act like pillars, propping apart the TOT layers (typically by 0.33-1.5 mm). Slit shaped pores are formed between pillars and TOT layers, which give rise to uniform two-dimensional micropore system between adjacent TOT layers. Pore entry sizes are governed by the height of the pillars and the distance between them and can be designed to suit specific application. Wide ranges of bulky cationic species have been used to prepare pillared smectites, including organic cations (e.g. quaternary ammonium cations and 1,4-diazobicyclo[2.2.2]octane, DABCO) and inorganic cations (e.g. polyoxyhydroxides of aluminium and zirconium) [81,82]. Alumina pillars derived from aluminium chlorhydrol are the most widely used. They have strong Bronsted acidity and retain a limited ability to swell. Heating at low temperature ($<110^0$C) leads to dehydration, whereas calcination at high temperature ($\sim450^0$C) leads to irreversible conversion of ACH (aluminium chlorhydrol) cations to small particles of alumina that remain between the smectite's TOT layers. Alumina pillared clays have rigid, non-swelling, interlayer micropore structures (pore volume typically $0.1cm^3$ ml^{-1}) and moderate surface areas, but considerably lower Bronsted acidity than their ACH exchanged precursors. Their salient feature, namely, the ability to retain the micro-porosity at high temperatures (unlike non-pillared precursors) render pillared smectites as attractive catalysts or supports, for gas phase reactions where the retention of surface area is important.

1.4.5 The Acidic Character of Clay

Organic reactions that take place under acid catalysis can be very efficiently carried out using clay catalysts, which may function as Bronsted or Lewis acid or both. The Lewis acidity is due to Al^{3+} and Fe^{3+} at the crystal edges, and can be further enhanced by exchange of the interlayer cations Na^{+} and Ca^{2+} by Al^{3+} ions on treating the clay with $AlCl_3$ solution. The Bronsted acid character of clays arises mainly due to the dissociation of the intercalated water molecules coordinated to cations.

$$\left[M(H_2O)_n\right]^{3+} \longleftrightarrow \left[M(H_2O)_{n-1}OH\right]^{2+} + H^{+}$$

High levels of Bronsted acidity are achieved when highly polarizing ions such as Cr^{3+} have been exchanged for Na^{+}, Ca^{2+}, etc. present in the natural clay, and the water content is low. Besides the total acidity, the surface area and the pore volume in the clay structure also add to the efficiency of the catalyst. Total acidity can be further increased by 'proton-exchange' on treating the clay with dilute acid or driving out NH_3 by heating the NH^{4+} ion treated clay. It is clear from this description that strong corrosive acid medium can be completely avoided, if clay is used as Bronsted acid instead of mineral acids to achieve the same purpose[83].

1.5 Organic reactions using clays

To get a clear idea of the reaction mechanism involved in heterogeneous clay catalysis, a five-step mechanism is proposed. (A) Diffusion of reactants from the bulk phase to the catalytic surface. (B) Reactant molecules should be adsorbed at the surface by electrostatic forces. (C) When the reactant species are adsorbed, electron transfer process occur which result in the commencement of the reaction. (D) After the products have been formed, attempts are made to desorb the product as the reverse of the adsorption. (E) Finally the products are liberated to the product bulk phase. These processes are represented as follows (Figure 12).

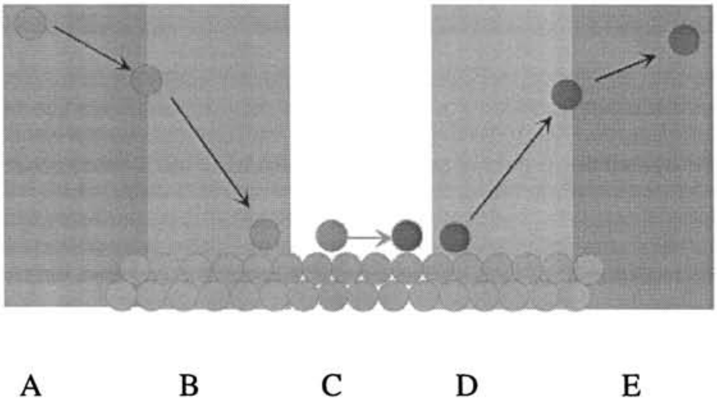


Figure 12: Schematic representation of mechanism of clay-catalyzed reaction

1.5.1 Dehydration reaction

Dehydration of alcohol is efficiently catalyzed by both Al (III) and H^+-exchanged clays. Primary alcohols give dialkyl ethers along with alkene where as secondary and tertiary alcohols give alkenes only[84] (Scheme 1). Dihydric alcohols such as ethylene glycol on dehydration yield polyethylene glycol while aromatic alcohols such as benzyl alcohol yield poly(phenylene ethylene) with aluminium exchanged montmorillonite.

$$\mathrm{RCH_2XH} \xrightarrow[\mathrm{Al(III)^+\text{-}mont}]{-\mathrm{H_2X}} \mathrm{RCH_2XCH_2R}$$

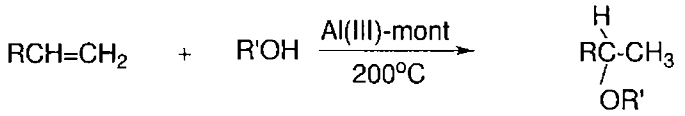
X = NH, O, S

Scheme 1: Dehydration reaction

These reactions infer the dehydrating ability of the aluminium exchanged montmorillonite clays. It should be noted that the dehydration of alcohols takes place in good yield only with primary alcohols with low or no activity for secondary and tertiary alcohols. The change could be due to the variation of stability of the carbocation intermediates such as tertiary, benzylic and allylic. It should also be noted that the synthesis of ether is a superior method compared to the conventional ether forming reactions such as Williamson's ether synthesis. On the other hand, primary amines on dehydration give dialkylamines by the loss of ammonia, and thiols yield dialkyl thioethers with the loss of hydrogen sulphide[85]. Dehydration of alcohols can also be considered to confirm the type of acidity present in the selected modified clays. Dehydration of 1-butanol through either acid or basic catalysis explains this phenomenon. A high *cis/trans* ratio is observed for the base catalyzed isomerisation and the ratio will be equal to one for an acid-catalyzed isomerisation.[86]

1.5.2 Addition reaction

Acid treated and cation exchanged montmorillonites are effective catalysts for a variety of addition reactions. The effective mechanism will be the addition of a proton or a Lewis acidic site and the subsequent rearrangement of the intermediate carbocation to generate the more stable forms that combine with the nucleophile. The products are formed by the elimination of the proton or by the Lewis acidic site.[87, 88] (Scheme 2).

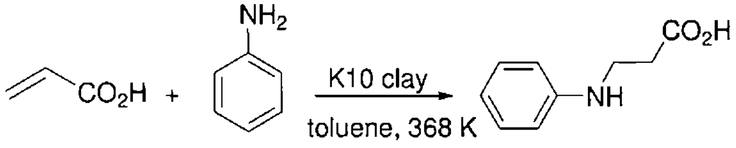


Scheme 2: Addition of alcohols to alkenes

Hydrogen sulfide and thiols add to alkenes in the presence of acid-treated and aluminium ion exchanged montmorillonites at 200°C to provide dialkyl sulfides in good yields. Likewise, ammonia can also add to ethyne over acid montmorillonite to yield both pyridine and piperidine. Esters can be prepared by the addition of carboxylic acids to alkenes in the presence of aluminium exchanged or proton exchanged montmorillonites[89].

The activity of montmorillonite clays as a catalyst for the hydroamination of α,β-ethylenic compounds with amines was tested. Aniline and substituted anilines reacted with α,β-ethylenic compounds in the presence of catalytic amount of commercially available clay to afford exclusively *anti*-Markovnikov adduct in excellent yields (Scheme 3) . Aniline reacted with ethyl acrylate to yield only *anti*-Markovnikov adduct, *N*-[2-(ethoxycarbonyl)ethyl]aniline (mono-addition product). No Markovnikov adduct (*N*-[1-

(ethoxycarbonyl)ethyl]aniline and double addition product *N,N*-bis[2-(ethoxycarbonyl)ethyl]aniline were formed under selected reaction conditions.[90] For a better exploitation of the catalytic activity in terms of increased activity and improved selectivity for the mono-addition product, the reaction parameters were optimized in terms of temperature, solvent, reactant mole ratio. Under optimized reaction conditions, montmorillonite clay K-10 showed a superior catalytic performance in the hydroamination of ethyl acrylate with aniline with a conversion of aniline to mono-addition product (almost 100% chemoselectivity) with a high rate constant 0.3414 min^{-1} compared to the reported protocols.



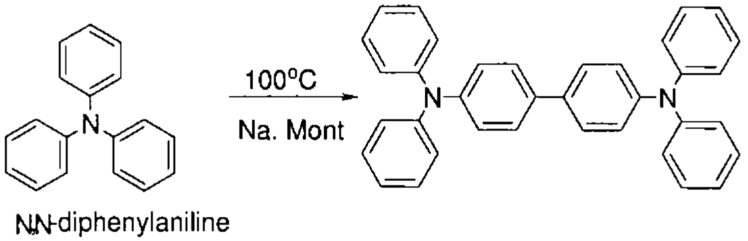
Scheme 3: Hydroamination of ethylacrylate with aniline

The dependence of conversion of aniline over different types of montmorillonite clays (K-10, K-20, K-30, Al-Pillared clay and untreated clay) has also been discussed. The activities of clay for the hydroamination of different aromatic and aliphatic amines have also been investigated. Under harsh reaction conditions (increased temperature and long reaction time) small amounts of di-addition products were observed. The kinetic data have been interpreted using the initial rate approach model[91].

Thia-Michael addition reaction is recently reported using montmorillonite clays. The reaction of aryl and aryl alkyl thiols with cyclic/acyclic α,β-unsaturated ketones/ester afforded excellent yields after 5 min to 20h. The reaction rate was found to be influenced by the (i) size of the ring in the case of cyclic enone, (ii) electronic nature of the thiol, and (iii) presence of aryl/alkyl substituent at the β position of the acyclic α,β-unsaturated ketone/nitrile. The conjugate addition of thiols took place at faster rates for five-membered and acyclic α,β-unsaturated ketones than the six-membered analogue. Aryl thiols reacted at faster rates than aryl alkyl and alkane thiols and the differential reaction rates were attributed to the relative acidic strength of the thiols. The reaction of α,β-unsaturated ketones having an aryl/alkyl group at the β-carbon took longer times and higher temperature. The difference in the reactivity between six and five membered enones and various thiols was utilized to demonstrate selective thia-Michael addition reaction during intermolecular competition studies[92]. L-proline-anchored hydrotalcite (HTLP) has good catalytic activity in the asymmetric Michael addition reaction between β-nitrostyrene and acetone. An inversion in the asymmetric induction was observed when compared to the reaction using pure L-proline catalysis. The same Michael adduct has been prepared by two methods: first, by addition of acetone to β- nitrostyrene (an enamine-type addition) and secondly, by addition of nitromethane to benzylideneacetone (an iminium-type addition). This chiral amino catalyst (HTLP) acts as a better catalyst for both enamine-type and iminium-type additions, indicating clearly that hydrotalcite is a better support for L-proline. It also acts as a cocatalyst in the title reaction. Suitable mechanisms are proposed for both enamine- and iminium-type additions[93].

1.5.3 Oligomerization reaction

Alkenes undergo ready oligomerization in the presence of acid-treated or ion-exchanged montmorillonites. The mechanism involves protonation to generate a stabilized carbocation that will react with other alkene molecules to give oligomers after deprotonation. Triphenylamine was converted into N, N, N', N' -tetraphenylbenzidine with dimerization followed by a benzidine type rearrangement[102](Scheme 4). The first reaction reported for the clay catalyzed dimerization is polymerization of styrene with the presence of acid-treated montmorillonite[94].



Scheme 4: Oligomerization of diphenylaniline

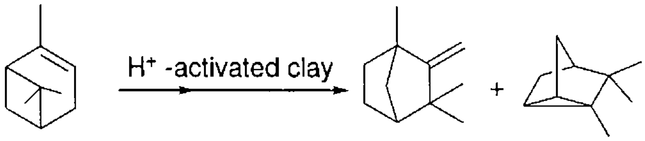
Oligomerization reaction has been very well applied in the field of biochemical synthesis, such as RNA. Adenosine-5-methylphosphate (MepA) initiates the oligomerization of the 5-phosphorimidazolide of uridine (ImpU) in the presence of montmorillonite clay. The MepA initiates 69–84% of the 5–9 charge oligomers, respectively[95]. The relative rates of the reactions were determined from an investigation of the products in competitive reactions. There is no correlation between the extent of binding to the montmorillonite and reaction rates in the formation of longer oligomers. The central role that catalysis may have had in the prebiotic formation of biopolymers is discussed.

Activated mononucleotides oligomerize in the presence of montmorillonite clay to form RNA oligomers. In the reported study, effects of salts, temperature and pH on the clay-catalyzed synthesis of RNA oligomers were investigated. This reaction is favored by relatively high concentration of salts, such as 1M NaCl[96]. It was shown that the presence of divalent cations was not required for this reaction. High concentration of NH_4^+ and HCO_3^- and 0.01M HPO_4^{2-} etc. inhibited the reaction. The yields of RNA oligomers decreased as the temperature was raised from 4° C to 50° C. The catalytic activity of a variety of minerals and three meteorites were investigated, but none of them except galena catalyzed the oligomerization. ATP was generated from ADP but it was due to the presence of HEPES buffer and not due to the minerals. Meteorites catalyzed the hydrolysis of the pyrophosphate bonds of ATP. The results suggested that oligomers of RNA could have formed in pH 7–9 solutions of alkali metal salts in the presence of montmorillonite clay.

1.5.4 Isomerization and Rearrangement reaction

In clay interlayer, framework aluminium acts as a Lewis acid, catalyzing Fries rearrangement of phenyl and naphthyl esters.[97] An increase in the size of migrating group/substrate causes an increase in the formation of 2-isomer. This reaction illustrates the catalytic efficiency of clays and also the susceptibility of the rearrangement to steric effects in the migrating group/substrate, which is more pronounced when the substrates are present in a more constrained environment of the clay interlayer.

Isomerization of α-pinene to camphene and longifolene to isolongifolene has been carried out in good yields on acid treated montmorillonite. A good number of rearrangement/isomerization reactions have been carried out using clay catalysts. Isomerization of *n*-alkanes to branched chain alkanes in clay media is one of the most important processes in petrochemical industry. Montmorillonite clay with Bronsted acidity is well suited for catalyzing such reactions, and excellent results have been achieved[98] (Scheme 5).



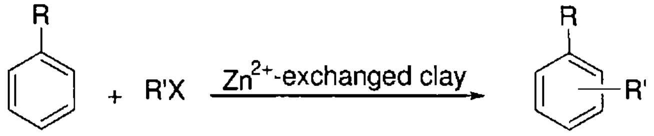
Scheme 5: isomerization of α-pinene

Acid-treated montmorillonites belonging to the K series were tested as heterogeneous catalysts for the liquid-phase acylation of 1,3-dihydroxybenzene with benzoic acid; this reaction may represent an environmentally friendly alternative to the use of benzyltrichloride as the acylating agent[99]. The extent of conversion was proportional to the Al content in the samples; the catalytic activity was associated to the Brønsted acidity generated by the interaction of water molecules in hydrated clays with Al. The removal of water from samples by preliminary thermal treatment indeed led to the decrease of the catalytic activity. The reaction mechanism was found to consist of the direct O-benzoylation with formation of resorcinol monobenzoate, while no primary formation of the product of C-benzoylation (2,4-dihydroxybenzophenone) occurred. The latter product was formed exclusively by consecutive Fries rearrangement upon the benzoate.

Liquid phase catalytic isomerisation of α-pinene with natural Indian Montmorillonite modified by sulphuric acid treatment and cation exchange was studied. More than 96% α-pinene conversion was observed for acid treated clays with camphene selectivity ranging from 39 to 49%[100]. For acid treated clays prepared by treating with low normality acid (1–4N), limonene was the main product whereas clay samples prepared with high normality (5–9N) acid, α-terpene was the main product among monocyclic terpenes. Ce^{3+}, Fe^{3+}, La^{3+}, Ag^{+}, exchanged clays showed higher than 90% conversion for α-pinene with 39–49% selectivity for camphene. However, Li^{+}, Ca^{2+}, Mg^{2+} exchanged clay showed poor conversion (4–12%) for α-pinene. Observed conversions and selectivities have been explained in terms of surface acidity, structural and textural features of the modified clays determined using X-ray diffraction and N_2 adsorption at 77 K. Correlation of α-pinene conversion with cyclohexanol dehydration showed that α-pinene conversion was a Bronsted acid catalyzed reaction.

1.5.5 Aromatic electrophilic substitution reaction

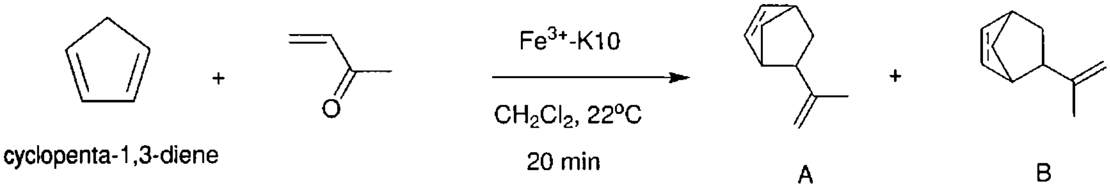
To overcome the disadvantages of the aluminium trichloride catalyst for Friedel-Crafts alkylation reaction, montmorillonite supported transition metal salts (zinc and nickel chlorides) have been used.[101, 102] (Scheme 6). Moderately activated benzenoid compounds undergo alkylation with allylic chlorides and particularly allylic alcohols over solid acid catalysts[103]. Acidic K10 clay is the optimal catalyst and allows almost exclusive attack at the terminal position of the intermediate allyl cation to yield 1-aryl-2-alkenes. Catalytic hydrogenation quantitatively yielded the corresponding 1-arylalkanes. Phenol also reacts readily but gives a significant quantity (*ca.* 12%) of 3-aryl-1-butene along with 1-aryl-2-butene. An alternative and environmentally benign pathway for selective synthesis of diindolylmethanes from indole and several aromatic aldehydes is reported.[104] The electrophilic aromatic substitution (EAS) reactions are achieved with good yield and short reaction time employing infrared irradiation as the energy source and a bentonitic clay as catalyst and reaction medium, in solvent-free reaction conditions.



Scheme 6: Substitution reaction in aromatics

1.5.6 Diels-Alder reaction

Diels–Alder reaction is a thermally allowed [4+2] cycloaddition process, it does not occur spontaneously with all dienes and dienophiles. However, the rates of slow reactions are greatly accelerated when they are carried out using clay catalysts even under very mild conditions. The endo:exo ratio can be manipulated by varying the exchanged cations, because the interlayer spacing controls the transition state geometry. The catalytic character of clays in these reactions is due to their Lewis acidity.[105] (Scheme 7)



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heme 7: Formation of [4+2] adducts

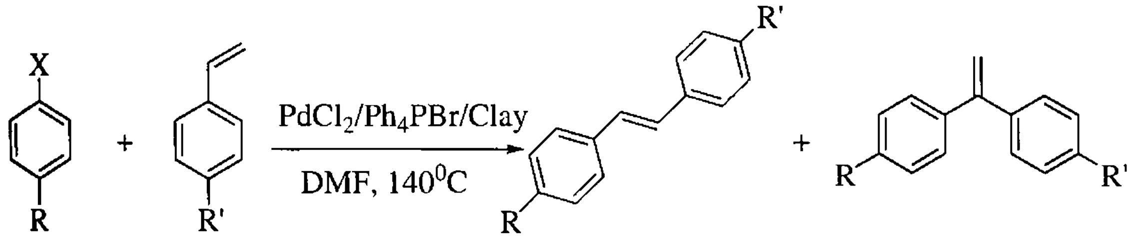
The reaction of furan with α, β-unsaturated carbonyl dienophiles catalyzed by KI0 montmorillonite in the absence of organic solvents produces the corresponding Diels-Alder adducts and, in the case of methyl vinyl ketone, Michael-type products, under much milder conditions than the conventional protocols[106]. The results are consistent with acid catalysis on the clay surface. Acrylates gave lower yields and/or decomposition products. The reaction can be extended to alkynic substrates such as DMAD to afford cycloadducts in good yields. The strategy described above meets the requirements for a "benign by design" process, and is also characterized by the technical ease of the reaction sequence, and the range of products obtainable.

Aryl amines react smoothly with cyclic enol ethers such as 3,4-dihydro-2*H*-pyran (DHP) and 2,3-dihydrofuran (DHF) on the surface of montmorillonite KSF under mild reaction conditions to afford the corresponding pyrano- and furano[3,2-*c*]-quinolines in high yields with high diastereoselectivity[107]. This reaction describes a simple and efficient method for the synthesis of tetrahydroquinoline derivatives from aryl amines and 2 equiv. of cyclic enol ethers. The notable features of this procedure are mild reaction conditions, greater selectivity, high yields of products, cleaner reaction profiles, ready availability of the reagents at low cost and enhanced rates making it a useful and attractive process for the synthesis of fused pyrano- and furano[3,2-*c*]quinolines of biological importance.

Montmorillonite K10 clay was found to catalyze the hetero-Diels–Alder reaction of 2,3-dimethyl-1,3-butadiene with o-anisaldehyde and other benzaldehyde derivatives; a transition state involving chelation of the clay's metal ions with the dienophile's heteroatoms is proposed[108]. The work reported has proved to be important in ongoing efforts to demonstrate the utility of Montmorillonite clays in organic synthesis.

1.5.7 Heck reaction

The palladium catalyzed arylation and vinylation of olefins, known as the Heck reaction, is a tolerant and versatile method for C-C bond formation. Zeolite supports including faujasite and mordenite have been functionalized with palladium via exchange with $Pd(NH_3)_4^{2+}$, or alternatively via impregnation with $Pd(OAc)_2$, $[Pd(C_3H_5)Cl]_2$, or the palladacyclic compound $Pd[P(o\text{-}C_6H_5CH_3)_2(C_6H_5CH_2)]^+$ [109] (Scheme 8). Heck reaction was also utilized for the study of activity of the catalysts since palladium is a noble metal and is costlier. The immobilization of a series of bis-carbene-pincer complexes of palladium(II) on montmorillonite K-10 affords the preparation of effective catalysts for the C–C coupling in a standard Heck reaction[110]. The supported catalysts so obtained, show catalytic activity similar to their homogeneous counterparts. The determination of Pd content on the supported catalysts by XPS and elemental analysis, before and after each catalytic reaction, shows that leaching is negligible. Once the reaction conditions were optimized, recycling the catalyst was possible at least ten times, without significant loss of activity.

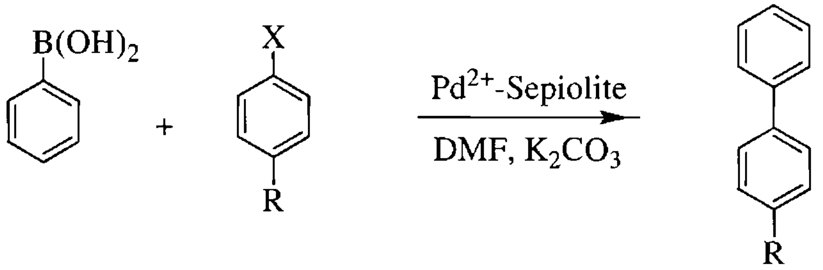


R= H, CHO; R'=H,Cl,Me,OMe; X= I, Br

Scheme 8: Heck reaction of vinylation of styrene

1.5.8 Suzuki reaction

The Suzuki reaction is the Pd-catalyzed cross coupling of arylboronic acids with aryl or alkenyl halides or triflates in the presence of a base.[111] Typical products are biaryls, which are often found as structural element in biologically active compounds (e.g., Rosoxacin, Diflunisal, the potent long-acting angiotensin II antagonist), in nucleoside analogues, in supermolecules and in liquid crystals[112] (Scheme 9).

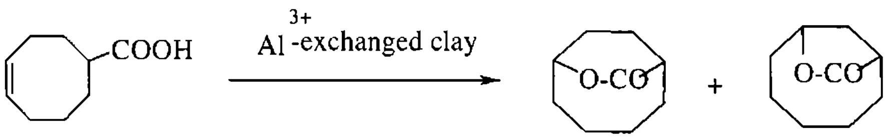


Scheme 9: Suzuki Coupling of arylboronic acid with substituted alkyl benzene

Palladium-supported sepiolite clay has effectively catalyzed the Suzuki cross-coupling reaction of phenylboronic acid with aryl halide including less reactive electron-rich aryl bromides[113]. The cross-coupling of aryl bromides with phenylboronic acid are efficiently catalyzed by Pd^{2+}-sepiolite prepared by simple ion-exchange. This novel catalyst provides clean and convenient alternative for Suzuki reaction in view of the advantages such as higher turnover number (TON) than previously reported heterogeneous Pd catalysts, simple reaction procedures and low-cost, possibility of minimizing waste and recyclization of the catalyst. $[Pd(NH_3)_4]^{2+}$-exchanged sepiolite clay (Pd–sepiolite) has been applied to the catalytic Suzuki-type carbon–carbon coupling reactions of 4-bromophenol with phenylboronic acid or sodium tetraphenylborate in water[114]. The Pd–sepiolite effectively catalyzed the reaction under mild reaction conditions (at room temperature in air). The Pd–sepiolite system exhibits higher yield than unsupported Pd(II) salts, $[Pd(NH_3)_4]Cl_2$ impregnated SiO_2 (Pd–SiO_2), and a commercially available Pd/C consisting of Pd metal particles. The structure of Pd species in the catalysts before and after the reaction was well characterized and results confirmed the formation of metal particles after the reaction by unsupported Pd(II) salt and Pd–SiO_2. The change in the structure of Pd species after the reaction was not significant; the highly dispersed Pd(II) complex, present before the reaction, was still the main Pd species together with the small Pd clusters (2–7 nm) as minor species. As a result of the high stability, Pd–sepiolite was reused without losing its activity. Significantly high turnover numbers (TON= 940,000) were also attained at reflux temperature. It is suggested that Pd metal precipitation during the reaction is inhibited by a strong electrostatic interaction of sepiolite with Pd(II) species.

1.5.9 Esterification reaction

Addition of carboxylic acid to an olefinic compound leading to an ester can be brought about in acid-activated montmorillonite clay as indicated below. The second compound is formed after isomerization of the double bond (Scheme 10). Substitution of alkyl halide by carboxylic acid has been achieved by heating the reactants in the presence of acidic clay in an autoclave. Refluxing a mixture of alcohols or phenols with carboxylic acids with clay catalysts in solvents resulted in esters[115].



Scheme 10: Esterification reaction

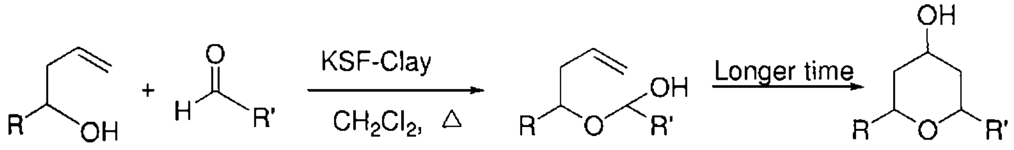
β-Keto esters have a remarkably wide range of uses that cover several industrial sectors including pharmaceuticals, agrochemicals and dyestuffs. However, while solid catalysts such as zeolites and alumina have some activity, drastic conditions or large catalyst quantities restrict the value of the methods[116]. A simple and efficient synthesis of β-keto esters using montmorillonite K-10 catalyzed condensation of ethyl diazoacetate with various aldehydes at room temperature was described. The new method would certainly seem to have more widespread use, and general environmental benefits compared to many others described in the literature.

Transesterifications are important reactions in many sectors of the chemical industry. They are traditionally carried out using soluble strong acids which need to be washed from the product mixture and are lost as waste[117]. The transesterification of β-ketoesters is especially problematic and while numerous methods have been reported, none are entirely satisfactory. Ethyl/methyl β-keto esters react with various alcohols in the presence of a catalytic amount of Envirocat EPZG or natural clay and undergo transesterification effectively. The use of a commercial clay-based catalyst was described. The new method has been widely applicable giving good product yields, but, since the catalyst can be easily separated and reused, there is no acidic waste and catalyst lifetime can be maximised. Like intra-molecular esterification, transesterification also plays an important role in the field of synthetic chemistry, leads to several useful products[118]. One such reaction is the method of lowering the viscosity of palm oil by the conversion of the palm oil into its short chain alkyl esters, which are more appropriate to be used as a diesel engine fuel. In this work, the conversion of palm oil into methyl esters was carried out by a transesterification method that used hydrochloric acid, nitric acid and sulfuric acid activated clays (e.g. refined kaolinite TK25 and Trufeed sodium bentonite) as transesterification catalysts and with palm oil and methanol in the ratio of 1:3 and 2:3 by volume and the products were analyzed by HPLC. Time and concentration of acids for the catalyst activation processes were investigated. It was found that 20 g of Trufeed Sodium Bentonite activated with 0.5 M of sulfuric acid for 4 hours and with a reaction time of 8 hours, palm oil and methanol in the ratio of 2:3 gave 94.2 % of the methyl esters. Clays activated with both hydrochloric acid and nitric acid were found to be not suitable for this purpose.

1.5.10 Reaction of alcohols with aldehydes and ketones

Addition of alcohol to carbonyl compounds occurs easily in the presence of montmorillonite clays. Homoallyl alcohols have been observed to add to aldehydes leading to hemiacetal intermediates, which further undergo intramolecular transformation to give Prins-type cyclization products[119] (Scheme 11).

A series of 2-substituted and 2, 2-disubstituted 1,3-benzodioxoles have been synthesised by the reaction of catechol and pyrogallol with corresponding aldehydes and ketones catalysed by montmorillonite KSF or K-10. The reactions are completed within 3–24 h to give satisfactory yields[120]. Ketones gave better yields than aldehydes, although highly sterically hindered ketones and diaryl ketones failed to react at all.



Scheme 11: Addition of alcohols to ketones

1.5.11 Oxidation and reduction reactions

Clayfen and claycop are K-10 clay supported iron(III) nitrate and copper(II) nitrate reagents, respectively. Both are found to be excellent oxidizing reagents for alcohols, thio-compounds and many others[121] (Scheme 12).

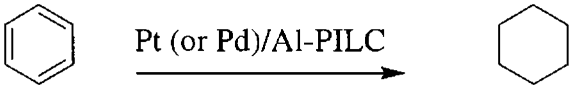
$$\text{R-SH} \xrightarrow[\text{Hexane, r.t}]{\text{Clayfen}} \text{R-S-S-R}$$

Scheme 12: Oxidation of thiol

Wet hydrogen peroxide catalytic oxidation of parachlorophenol over clay based catalysts is a well studied one. This study was utilized in the industrial effluent treatment plants. The ion-exchanged clays were the most active catalysts (100 % 4-Chlorophenol and 84 % chemical oxygen demand removal for Fe-montmorillonite) but were characterized by high leaching of iron from the structure[122]. The mixed Al-Fe oxide pillared clay displayed good catalytic activity (100 % 4-Chlorophenol and 43 % chemical oxygen demand removal) and negligible leaching (< 0.1 %) and was selected for detailed studies. Important factors affecting catalyst activity were studied, i.e. the effect of pH, temperature, catalyst concentration and the stability of the catalyst. The experimental results indicate that the use of this catalyst allows a total elimination of phenol and a significant reduction of chemical oxygen demand, without significant leaching of Fe^{3+} ions, this process being a promising advanced wastewater treatment technique for agro-food and industrial effluents.

Air oxidation of p-cresol under very mild conditions (338 K and ambient pressure) was carried out in a semi batch reactor over a solid catalyst developed by intercalating cobalt salen into the montmorillonite clay[123]. The intercalation of cobalt salen was done by a simple protocol and the characterization of the intercalated catalyst was done by XPS, FTIR and XRD techniques. A total selectivity ≥ 90 % to the oxidation products could be achieved with this solid catalyst by eliminating the undesired coupling side products in air oxidation of p-cresol under ambient pressure conditions. Effect of various process parameters on conversion and selectivity pattern were also studied and it was found that the selectivity ratio of aldehyde to alcohol could be varied by suitably changing the reaction conditions. This heterogeneous catalyst was found to give a fivefold higher turnover number than the homogeneous cobalt salen complex.

Reduction reactions are carried out by platinum or palladium exchanged aluminium-pillared clay[124] (Scheme 13).



Scheme 13: Reduction of benzene

Ruthenium-exchanged montmorillonite with different loading of ruthenium have been prepared and used for hydrogenation of benzene at 34.5 psi and 80 °C with or without the presence of thiophene. Preparation of the catalyst by ion exchange process ensures a high dispersion of metal ions into the montmorillonite matrix[125]. The catalytic reactions have been carried out in a PAAR autoclave reactor in the liquid phase. Under the experimental conditions of 500 psi (34.5 bar) hydrogen pressure and 100°C temperature, benzene was completely hydrogenated. Further modifications of the catalyst with Cu(I) and Cu(II) ions have been attempted to improve the sulfur tolerance of the catalysts. Both, impregnation of Cu(II) salt on the montmorillonite and addition of CuI to the reaction mixture significantly improved the sulfur tolerance of the Ru ion-exchanged montmorillonite, thus, providing a new approach for developing sulfur-tolerating hydrogenation catalysts.

Reduction reaction has also been applied in the field of reduction of pollution in industrial as well as transportation emissions. The selective catalytic reduction (SCR) of nitric oxide (NO) with ammonia (NH_3) over vanadia-based and pillared interlayer clay-based monolith honeycomb catalysts using a laboratory laminar-flow reactor was reported[126]. To simulate different combustion gases, a number of gas compositions (N_2, O_2 and NO) were used. A Fourier transform infrared (FTIR) spectrometer was used to determine the concentrations of the major product species (NO, NH_3, N_2O, and NO_2). The effects of various parameters including reaction temperature, oxygen concentration, NH_3-to-NO ratio, space velocity, heating area, catalyst arrangement, and vanadium coating on NO removal were investigated.

1.6 Heterogeneous Basic Catalysts

Heterogeneous basic catalysts are divided into five groups. The types with examples are mentioned here. (1) Single component metal oxide (Alkaline earth oxides, alkali metal oxides, rare earth oxides, ThO_2, ZrO_2, ZnO, TiO_2.), (2) Zeolites (Alkali ion-exchanged zeolites, alkali ion-added zeolites.), (3) Supported alkali metal ions (Alkali metal ions on alumina, alkali metal ions on silica, alkali metal ions on alkaline earth oxide, alkali metals and alkali metal hydroxides on alumina), (4) Clay minerals (Hydrotalcite, Chrysotile, Sepiolite), and (5) Non-Oxide (KF supported on alumina, lanthanide imide and nitride on zeolite).[127]

One of the reasons why the studies of heterogeneous basic catalysts are not as extensive as those of heterogeneous acidic catalysts seems to be the requirement for severe pretreatment conditions for active basic catalysts. The materials which are now known as strong basic materials used to be regarded as inert catalysts[128]. The catalysts were pretreated normally at relatively low temperatures of around 723 K. Since the surface of the catalyst was covered with carbon dioxide, water, oxygen, etc. no activity for base-catalyzed reaction was found. Generation of basic sites require high-temperature pretreatment to remove carbon dioxide, water, and, in some cases, oxygen. Basic sites are generated by either deformation of surface structure or by the leaching of the positively charged ions. (Figure 13).

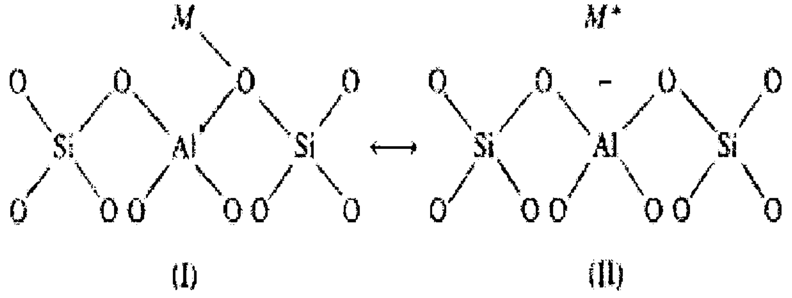
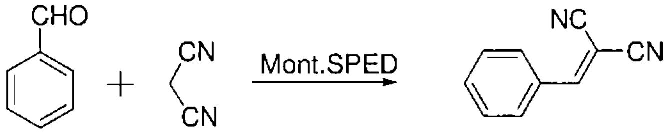


Figure 13: Schematic representation of generation of basic sites

The acidity of the clay can be greatly reduced by introducing silylpropylethylenediamine. This modification imparts very weak basic nature to the clays and is used for Knovenegal type reactions. Quaternary ammonium salts exchanged clays and clay surfactant composites are used for SN type reactions. Modified clays using 3-aminopropyl-triethoxysilane is used for the preparation of benzyl cyanides, thiocyanides and alcohols as shown below[129] (Scheme 14).



Scheme 14: Knoevenagel type reaction

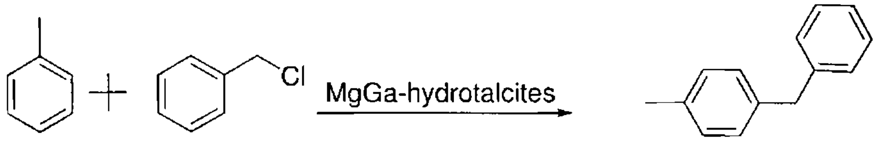
The use of 18-crown-6'doped clay as a recyclable phase transfer catalyst has provided improved yields of alkyl azides from alkyl bromides with sodium azide. The use of surfactant pillared clay materials and sonochemistry has been compared in SN type reactions. In a typical reaction alkyl bromide or α-tosyloxyketones and aqueous sodium azide in the molar ratio of 1:1.2 was refluxed with continuous stirring in the presence of organo-clay material under classical conditions or under ultrasound irradiation at very low temperature with or without organo-clay assembly[130] (Scheme 15).

$$\mathrm{RX} + \mathrm{NaN_3} \xrightarrow[\text{)))), at 0-5}^{0}\text{C, 2-6h}]{\text{W/wo surfactant pillared clay}} \mathrm{RN_3} + \mathrm{NaX}$$

X=Br, R= $C_6H_5CH_2$, 4-$NO_2C_6H_4CH_2$, 2-$MeC_6H_4CH_2$,
3-$MeC_6H_4CH_2$, 4-$MeC_6H_4CH_2$, $C_{10}H_{17}$

Scheme 15: Sonochemical SN reaction

Liquid-phase Friedel–Crafts type benzylation of aromatic compounds, using homogeneous catalysts, form the general category of Friedel–Crafts type reactions used in organic synthesis. Hydrotalcite anionic clays are known to be highly basic solids. Recently, it has been found that Ga-Mg-hydrotalcite anionic clay, after its first use in the reaction or HCl gas pretreatment, showed high activity in the benzylation of toluene and benzene, even in the presence of moisture in the reaction mixture.(Scheme 16). Fe-Mg-hydrotalcite (Mg/Fe = 3) anionic clay with or without calcination (at 200–800°C) has been used for the benzylation of toluene and other aromatic compounds by benzyl chloride[1]. Hydrotalcite before and after its calcination was characterized for surface area, crystalline phases and basicity. Both the hydrotalcite, particularly after its use in the benzylation reaction, and the catalyst derived from it by its calcination at 200–800°C show high catalytic activity for the benzylation of toluene and other aromatic compounds. The catalytically active species present in the catalyst in its most active form are the chlorides and oxides of iron on the catalyst surface.



Scheme 16: Basic clay catalyzed Friedel-Crafts alkylation

1.7 Summary

The clay minerals can catalyze a variety of organic reactions occurring on their surface and interstitial space. Synthetic organic chemists have been attracted to their tremendous potential as catalysts only recently. Modification of their properties by incorporating different metal cations, molecules or complexes, can lead to catalysts that are useful in effecting even more varieties of reactions and higher selectivity in product structure and yield. There is a theory that the molecules of life were actually developed in sedimentary clays. As the organic chemist is becoming more aware of clay's efficacy, its use in organic synthesis is bound to increase, especially because it helps in developing eco-friendly chemical processes. The dark clay has a bright future in the area of organic synthesis.

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CHAPTER II

PREPARATION AND CHARACTERIZATION OF CLAY CATALYSTS

Conspectus

This chapter describes purification, characterization and modification of clays collected from different regions in the state. Selection of the clay suitable for the present purpose was done. Using the selected clay, various types of catalysts were prepared, either by acid treatment or by intercalation of metal ions. A detailed description of the various techniques used for characterization of the prepared catalysts is presented. Some of the techniques used are Fourier Transform Infrared Spectroscopy, X-Ray Diffraction, surface area analysis, Thermogravimetry/ Differential Thermal Analysis, NH_3*-Temperature Programmed Desorption etc. The prepared catalysts were found to possess desirable properties of Lewis as well as Bronsted acidities. The results are compared with standard clays such as K10 and KSF.*

2.1 INTRODUCTION

Kaolin is a soft, white plastic clay consisting mainly of the mineral kaolinite which is a hydrated aluminum silicate $Al_2Si_2O_5(OH)_4$. Kaolin is formed when the feldspar rich rocks, like granite, are altered by weathering or hydrothermal processes. The process which converts the hard granite into the soft matrix found in kaolin pits is known as "kaolinisation". Kaolin deposits are classified as either primary or secondary. Primary kaolins result from residual weathering or hydrothermal alteration and secondary kaolins are sedimentary in origin. Kaolin is an important industrial mineral, which is used in many applications. The physical and chemical properties of kaolin has led to its extensive use as filler, extender, paper coater, ceramic raw material, pigment, and also it is an important raw material for the refractory, catalyst, cement, and fiber glass industries[1].

Some of the important physical constants of kaolin are: specific gravity, 2.60; index of refraction, 1.56; hardness (Mohs scale), 2; fusion temperature, 1850°C; dry brightness, 78-92 %, kaolins can be dispersed readily in water at 70 % solids by weight and the resultant slurry pours like fresh milk. Kaolin is hydrophilic and can be dispersed in water. Because of the nature of the chemistry of its surface, kaolin can be chemically modified so that it will become hydrophobic or organophilic, or both. Generally, an ionic or a polar non-ionic surfactant is used as the surface treating agent.

Electrophoretic studies have shown that kaolin has an overall negative charge. The exchange capacity of kaolin results from broken bonds and isomorphous substitution of aluminium for silicon in the tetrahedral sheet in the structure. The exchange sites are the locations on the surface where polar molecules can be adsorbed and oriented. The choice of surface treatment or chemical modification depends upon the polarity, structure, and composition of the organic system into which the kaolin is to be utilized and the physical and chemical properties desired in the end product[2].

2.2 Results and discussion

Seven types of clays were obtained from different sources.

Suitable clays were obtained by screening a wide variety of locally available clay materials and by finding their chemical constituents. Clays collected from different localities were purified and chemical constituents were determined. The clays which were selected for further studies are designated as follows.

Two kinds of clays obtained from M/s Golden Clay Works situated at Kizhakkambalam, around 15 Km from Aluva, Ernakulam. (These two types were renamed as G and W respectively)

One kind of clay from M/s Bharath Clay Limited situated at Vazhakkulam, around 10 Kms from Aluva, Ernakulam. (Renamed as B)

Two kinds of clays from Kerala Ceramics, Padappakkara, Kundara, Quilon District.(Assigned the names P1 and P2,) Two kinds of clays from Kerala Kaolinites, Vilichakkala, Quilon District. (Named as V1 and V2)

Their chemical composition were determined using standard methods.[3-6] The results are shown in table 1.

Table 1: Determination of chemical composition of clays

Types of clays	LOI (%wt)	SiO_2 (%wt)	Fe_2O_3 (%wt)	Al_2O_3 (%wt)	TiO_2 (%wt)	CaO (%wt)	MgO (%wt)	Alkali metals (%wt)
G	9.70	65.80	6.10	32.60	1.38	<0.01	<0.01	<0.01
W	13.55	49.87	2.58	55.50	1.24	<0.01	<0.01	<0.01
B	12.93	51.17	8.02	24.90	0.12	<0.01	<0.01	<0.01
P1	11.78	56.30	2.58	30.80	0.13	0.23	0.90	0.15
P2	10.06	55.20	2.37	24.10	0.07	0.27	0.10	0.13
V1	10.42	58.30	0.92	25.60	0.01	0.18	0.08	0.12
V2	10.80	54.40	1.42	25.90	0.07	0.16	0.09	0.11

2.2.1 Selection of suitable clays

Since the first three types of clays are tailor-made for the application industry, there might have occurred some kind of chemical treatment such as bleaching or sewing which may or may not have affected the mineral content of the clays. Moreover, the crystalline structure could have altered thereby losing their catalytic activity. This was evidenced by their XRD patterns, and not assisting any reactions when checked for catalytic activity. These clays were found to be unsuitable for the present purpose, and they were rejected. The remaining four samples were taken directly from mining points, and they were considered for the studies. Out of the four types of clays, the one which contained comparatively higher amounts of cations such as iron have been selected for the catalytic study. The sample from Kerala Ceramics of Padappakkara, Kundara (P1) has comparatively higher cation composition and was selected suitable for further studies.

The selected clay was subjected to further purification by suspending the clay in water, decanting of the sedimented particles, and filtered through a Whatmann No.1 filter paper. The dried samples were incinerated to 450°C to remove any organic matter. The purified clay was taken as the raw clay and was subjected to acid treatment and metal impregnation. Four acid activated catalysts using different acid concentrations of two acid types (HCl and H_2SO_4 of 2M and 5M respectively) have been prepared. One type each of 10% $CuSO_4$ and 10% $FeCl_3$ impregnated catalysts were also prepared. The characterization studies were conducted for the catalysts prepared and the results are compared. The prepared catalysts were classified as follows in table 2.

Table 2: Representation of catalysts on the basis of type of modification

Sl. No	Type of the catalyst	Assigned label
1	Raw clay	A
2	2M HCl activated clay	B
3	5M HCl activated clay	C
4	2M H_2SO_4 activated clay	D
5	5M H_2SO_4 activated clay	E
6	10% $CuSO_4$ treated clay	F
7	10% $FeCl_3$ treated clay	G

2.2.2 Characterization of prepared catalysts

Physicochemical characterization techniques are relevant in catalysis. A detailed characterization of the prepared catalysts was done using various spectroscopic and quantitative methods. A short description of the methods used for characterization is given here.

2.2.3 Chemical characterization

The chemical characterization of the modified clays was done according to standard procedures.[1,2] SiO_2 content was determined gravimetrically; Fe_2O_3 and TiO_2 by spectrophotometry. Al_2O_3, content was found out using titrimetry. CaO and MgO were done by atomic absorption spectroscopy methods. Na_2O and K_2O were determined by flame photometery.[6] The results are shown in table 3.

Table 3: Chemical characterization of prepared catalysts

CAT	LOI (%wt)	SiO_2 (%wt)	Al_2O_3 (%wt)	Fe_2O_3 (%wt)	TiO_2 (%wt)	CaO (%wt)	MgO (%wt)	Alkali metals (%wt)
A	13.27	47.70	33.20	2.55	0.04	0.05	0.07	0.06
B	16.90	49.70	32.20	1.14	0.02	0.06	0.06	0.04
C	13.10	51.70	26.00	1.12	0.02	0.05	0.05	0.03
D	13.50	58.10	19.90	0.90	0.01	0.05	0.05	0.03
E	13.10	69.10	13.80	0.66	0.01	0.04	0.04	0.04
F	12.80	43.30	30.20	2.31 (Cu=9.1%)	0.03	0.04	0.06	0.05
G	13.00	43.50	30.20	11.32	0.03	0.04	0.06	0.05
K10	8.60	75.70	9.36	4.80	0.03	0.26	1.00	0.04
KSF	18.40	58.40	11.69	3.25	0.02	2.25	2.15	0.03

The selected sample of clay (P1) contains mainly Al^{3+} with some Fe^{2+}/ Fe^{3+} and Mg^{2+} as octahedral cations and Na^+, K^+ and Ca^{2+} as exchangeable interlayer cations[7]. Based on these values the following assumptions are made. Silica which is in the frame work of the clay matrix is least affected by the acid treatment. All the remaining cations are prone to acid leaching. Percentage variation of cations after acid treatment is calculated and is given in table 4.

Table 4: Percentage ion variation due to acid treatment

CAT	Si (%wt)	Al (%wt)	Fe (%wt)	Ti (%wt)	Ca (%wt)	Mg (%wt)	Alkali metals (%wt)
B	(+)2.72	(-)3.01	(-)55.29	(-)47.36	-	(-)15.71	(-)27.11
C	(+)8.38	(-)3.34	(-)56.07	(-)31.57	-	(-)28.57	(-)40.67
D	(+)21.8	(-)40.06	(-)64.70	(-)92.10	(-)4.0	(-)24.28	(-)42.37
E	(+)44.86	(-)58.40	(-)74.11	(-)94.73	(-)18.0	(-)38.57	(-)27.11

The chemical analysis data have shown that there is 44.86% total increase in SiO_2 on 5M H_2SO_4 treatment, but only 2.7% increase occurs with the treatment of 2M HCl solution. Dissolution of tetrahedral silica from the clay structure has not occurred with lower acid concentration (2M HCl) as tetrahedral layer is relatively stable. Tetrahedral layer silica is affected at higher acid concentration. On the other hand, octahedral layer is affected at lower acid concentration. The observed increase in percentage silica at lower concentration of acid treatment is due to the leaching of octahedral and exchangeable cations. Leaching of cations resulted in the increase in the percentage of silica in total percentage of all minerals.

2.2.4 Si/Al molar ratio

Silica /Alumina ratio of the prepared catalysts is calculated as [8],

$$\text{Si/Al ratio} = \frac{\%\text{ of } SiO_2 \text{ x Mol.wt of } Al_2O_3}{\%\text{ of } Al_2O_3 \text{ x Mol.wt. of } SiO_2}$$

The results are presented in Table. 5

Table 5: Si/Al molar ratio of the prepared catalysts and standard clay catalysts

Sl.No	Catalysts	Si/Al molar ratio
1	A	2.44
2	B	2.61
3	C	3.37
4	D	4.96
5	E	8.51
6	F	2.43
7	G	2.44
8	K10	13.74
9	KSF	8.49

During acid activation, the silica value is found to be increased with the concentration of acid is increased. Under low acid concentration, the increase is nominal (in the case of 2M HCl (B) it is only 2.6% and in the case of 5M HCl (C) it is only 3.4%). But under high acid concentration such as 2M H_2SO_4 and 5M H_2SO_4 the increase in the silica content is substantial (around 21% and 42% respectively). This feature is attributed to the fact that silica in the clay tetrahedral network is least affected during acid treatment. The leaching of cations in the clay network may also contribute to the increase in the silica values. In the case of aluminium content, which is present in the octahedral network, is the highly leached one. This has resulted in the reduction of aluminium content in the prepared catalysts.

The silica/alumina ratio is higher in standard clays such as K10 and KSF. Silica/ alumina ratio contributes to the catalytic activity of the clay catalysts. Higher the ratio, lower will be the aluminium content. Presence of the aluminium ions lowers the activity of catalysts. Thus higher the ratio more will be the catalytic action and vice versa.

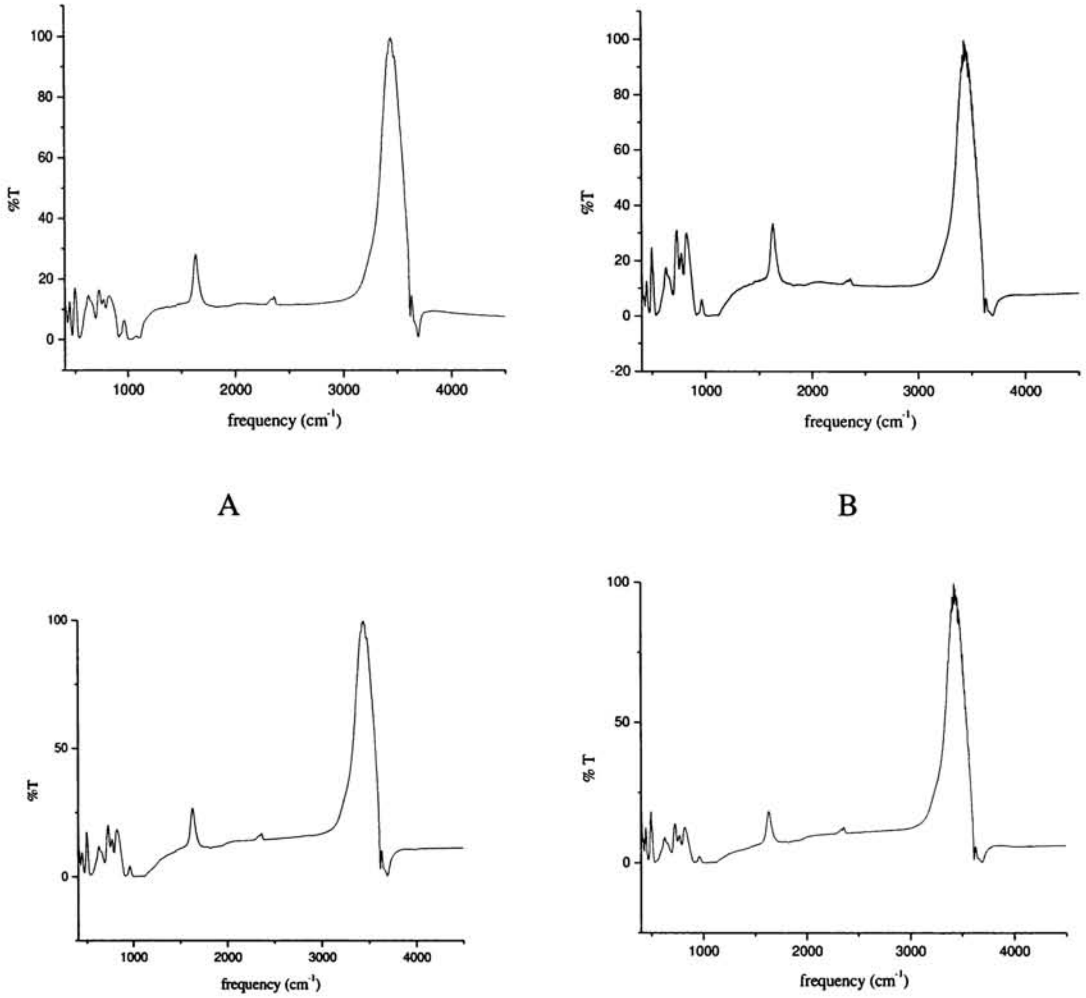
2.2.5 Infrared spectroscopy studies

The characteristic vibration frequencies of the catalysts are shown in the table 6 [9].

Table 6: FT-IR band assignments for various groups in the clay matrix

Frequency (cm^{-1})	Assignments
3697	OH stretching
3623	OH stretching
3440	OH stretching, hydration
1639	OH bending, hydration
1113	Si-O stretching, out-of-plane
1035	Si-O stretching, in-plane
1020	inplane Si-O-Si stretching, doublet for out of plane also at 1100
920	OH with Al
915	Al-Al-OH bending
875	Al-Fe-OH bending
836	Al-Mg-OH bending
820	OH with Fe
798	Amorphous silica
793	Platy form of tridymite
692	Quartz
529	Si-O bending
513	Al-O
469	Mg-O
441	Si-O-Si

Kaolinite with Al mostly in the octahedral positions has four absorption bands in the OH stretching region. Inner hydroxyl groups, lying between the tetrahedral and octahedral sheets, give the absorption near 3620 cm^{-1} [10]. The other three OH groups reside at the octahedral surface of the layers and form weak hydrogen bonds with the oxygens of the Si–O–Si bonds on the lower surface of the next layer. A strong band near 3695 cm^{-1} is related to the in-phase symmetric stretching vibration. The vibrations of two surface hydroxyls, forming stronger hydrogen bonds with the adjacent layers, are coupled and give a strong band at 3623 cm^{-1} [11]. The third layer-surface hydroxyls form weak hydrogen bonds and absorb at 3703 cm^{-1}. The representative IR Spectra of the prepared catalysts are shown in figure.1 A-G.

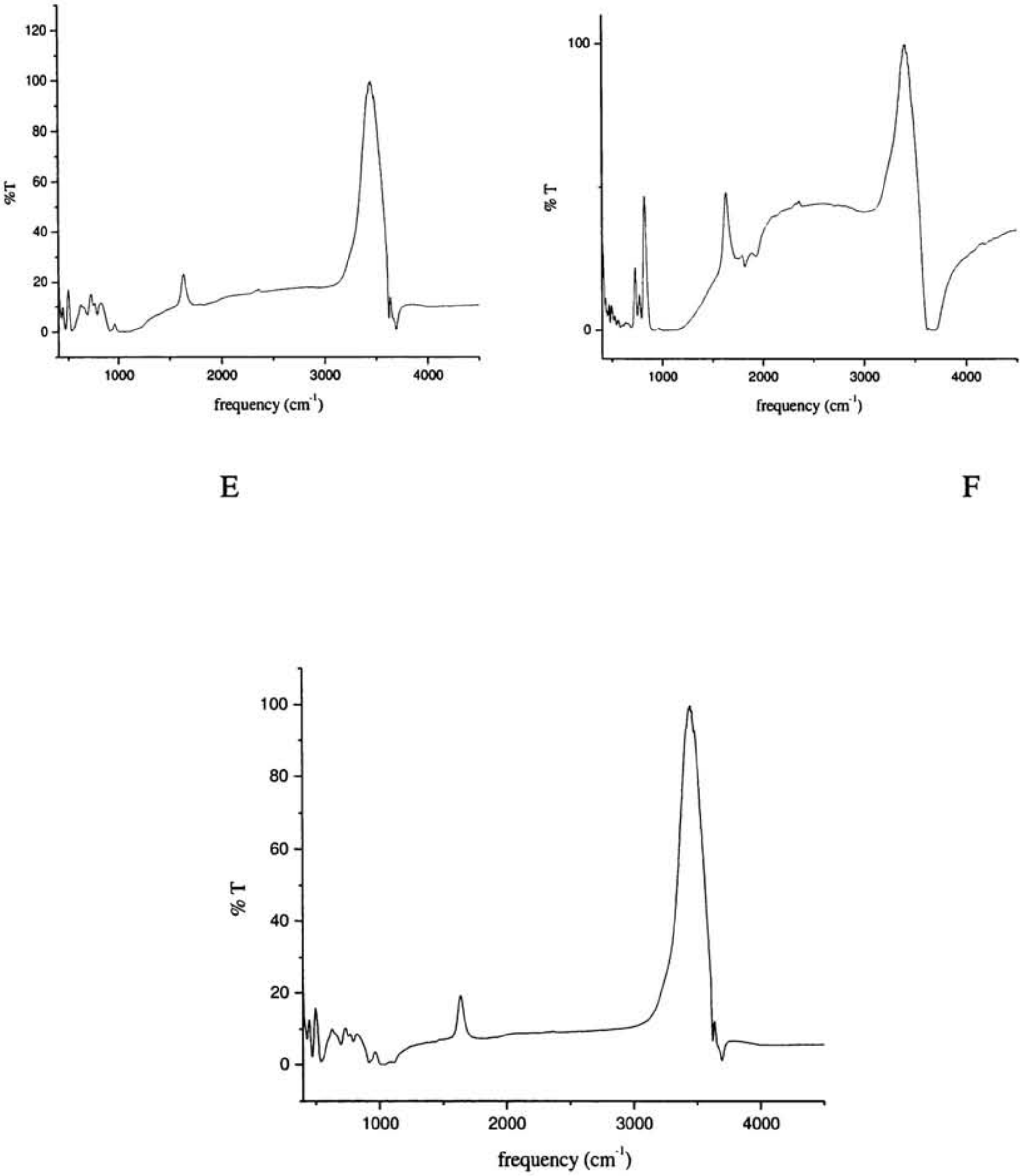


A

B

C

D



E

F

G

Figure 1 A-G: IR spectral traces for the catalysts A-G

The band at 1035 cm^{-1} is attributed to Si- O in-plane stretching and 529 cm^{-1} is due to Si-O bending vibrations[12]. The partial substitution of Al^{3+} in octahedral layer by Mg^{2+} and Fe^{2+} can be observed by FT-IR spectra as the vibrations of the protons, of OH groups are directly affected by the nearest cationic environment and provide information about the nature and content of the cations[13]. FT-IR spectrum of untreated clay shows the bands at 3693 and 3620 cm^{-1} in OH stretching region, which are assigned to hydroxyl groups coordinated to octahedral cations among which 3620 cm^{-1} is due to hydroxyl group bonded with Al^{3+} cations. The broadness of 3620 cm^{-1} band shows the substitution of octahedral Al^{3+} by Fe^{2+} or Mg^{2+} cations[14]. Three bending vibrations of hydroxyl groups associated with these cations, i.e., 915 cm^{-1} (Al-Al-OH), 875 cm^{-1} (Al-Fe-OH) and 836 cm^{-1} (Al-Mg-OH) confirm the substitution in octahedral layer. The well resolved, sharp and intense band at 3697 cm^{-1} in OH stretching region along with the band at 914 cm^{-1} in OH bending region indicates the presence of crystalline kaolinite in the sample[15]. Thus the band at 915 cm^{-1} is associated not only with Al-Al-OH vibration of kaolinite but also with the vibrations of montmorillonite. Furthermore, bands at 793 and 692 cm^{-1} show the presence of quartz admixtures present in the sample; the strong band at 793 $cm^{-1}$is assigned to the platy form of disordered tridymite and 696 cm^{-1} for quartz content[16].

FT-IR spectra of untreated and treated clay samples show the effect of acid concentration on overall clay structure. The decrease in the intensities of the bands indicates more decrease for Mg^{2+} than Fe^{3+} cations[17]. The chemical analysis data also show higher leaching of MgO than Fe_2O_3 after treatment with the acids. It clearly shows that Mg^{2+} ions are more prone to acid attack. The shape of Si-O stretching band at 1033 cm^{-1} shows the changes in Si environment after acid treatment[18]. The Si-O bending vibration at 529 cm^{-1} is shifted towards higher frequency at 539 cm^{-1} and its intensity increases with increasing acid concentration. It shows the effect on tetrahedral sheet at higher acid concentration.

The band at 793 cm^{-1} (tridymite) shifts to 798 cm^{-1} and the intensity of the band significantly increases even after acid treatment which further increases with increasing intensity of acid treatment. The band at 696 cm^{-1} (quartz) also shows the increase in intensity after acid treatment. The chemical analysis data also show total increase of SiO_2, of which, substantial increase occurs after the treatment with higher acid concentration[19]. The intensity of hydroxyl stretching bands at 3697 and 3620 cm^{-1} also reduces with increasing acid concentration. It is due to the removal of octahedral cations causing the loss of water and hydroxyl groups coordinated to them. Thus the treatment of clay used with varied concentration of acid resulted into catalytic active clay having Bronsted acid sites[20].

When interpreting the IR spectra, intensity of bands plays an important factor in which each group imparts its own characterization. In quantitative experiments, this intensity calculation occurs as an important tool to ascertain the presence and strength of the specified group. In this section, attempts have been made to calculate the intensity to determine the strength and weakness of the concerned bonding vibrations. The comparison of intensities at various frequencies of the prepared catalysts are shown in the table 7.

Table 7: Comparison of intensities at different frequencies

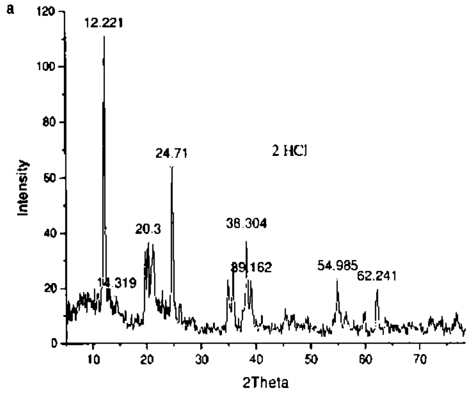
Sl.No	Catalysts	Intensity at various frequencies (cm^{-1})					
		At 440 Si-O-Si	At 469 Mg-O	At 692 Quartz	At 798 Amorphous silica	At 920 Al-Al-OH	At 1035 Si-O stretching in plane
1	A	3.20	0.86	6.23	10.76	0.87	0.02
2	B	1.27	0.33	1.42	2.81	0.06	0.01
3	C	7.21	2.52	11.13	21.49	0.56	0.01
4	D	14.29	5.56	64.64	19.40	3.48	0.19
5	E	10.09	1.94	16.52	19.40	1.09	0.06
6	F	4.12	1.59	20.22	53.00	0.93	0.01
7	G	4.60	1.41	10.33	27.70	0.35	0.02

FT-IR spectroscopy is very sensitive to modification of the clay mineral structure upon acid treatment[22]. During the acid attack, protons penetrate into the clay mineral layers and attack the structural OH groups. The resulting dehydroxylation is connected with successive release of the central atoms from the octahedra as well as with removal of Al from the tetrahedral sheets. At the same time, a gradual transformation of the layered tetrahedral sheet to a three-dimensional framework proceeds. The final reaction product is an amorphous partly protonated silica phase.

In the case of IR spectra, there is a marked change in the intensities of the absorption spectrum. The quartz structure at 692 cm^{-1}, the intensity of the said wavelength is decreased with the 2M HCl treatment, but steadily increases until the 2M H_2SO_4, afterwards there is decrease in the intensity showing that the structure is collapsing at the higher acid concentration. The leaching of the aluminium content is evident on observing the intensity at 920 cm^{-1}, which is the characteristic of Al-Al-O vibration. Here also the higher acid concentration plays the significant role in the leaching of aluminium concentration. The overall structure of silica network can be inferred with the absorption of 1035cm^{-1}, which is the Si-O in plane vibration. In the spectrum, the intensity is increased with the increasing the acid concentration but decreases at the 5M H_2SO_4 concentration showing that the silica plane is destabilized with the increased leaching of other cations. The band at 798 cm^{-1} is the characteristic absorption of amorphous silica. The increasing content of amorphous silica is attributed to the increasing intensity of the band at 798 cm^{-1}. Increase in the intensity of the amorphous silica is characterized with reduction in crystalline structure of catalysts. The reduction in the Alumina network is characterized with decreased intensity of the band at 920 cm^{-1} (attributed to the Al-OH absorption). The high energy absorption of the Si-O-Si, at 440 cm^{-1} signifies increasing silica network. Treatment of acid with higher concentration, decreases the intensity of silica due to the tetrahedral destabilization.

2.2.6 X-Ray diffraction studies

Powder X-ray diffraction patterns were recorded with a Rigaku D-max C X-ray diffractometer using Cu Kα radiation, recording from 2μ = 3–608, with a step angle of 0.028. The X-ray diffraction patterns for the samples A-G are given in figure 2 A-G.


a
12.221
24.71
2 HCl
20.3
38.304
14.319
39.162
54.985
62.241
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2Theta
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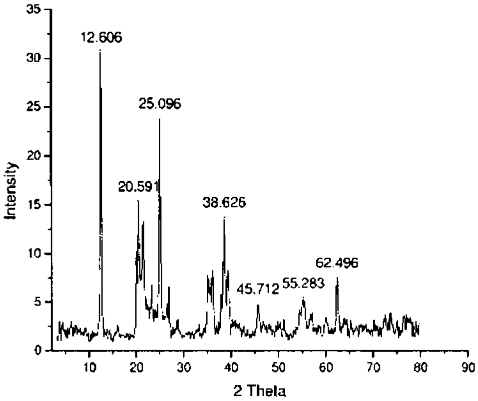
20
40
60
80
100
120
10
20
30
40
50
60
70

A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45.712
55.283
Intensity
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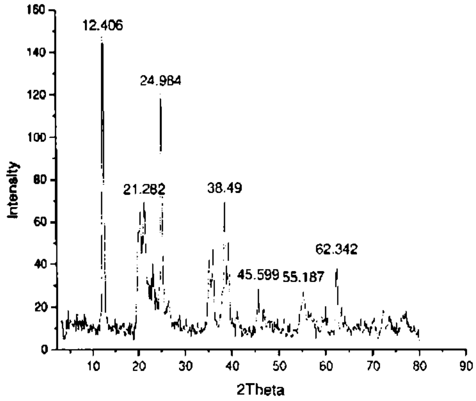
B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21.282
38.49
62.342
45.599
55.187
Intensity
2Theta
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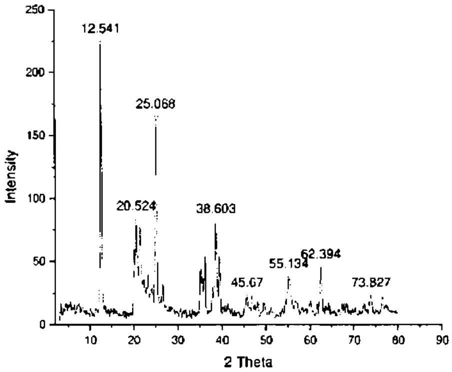
50
60
70
80
90

C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38.603
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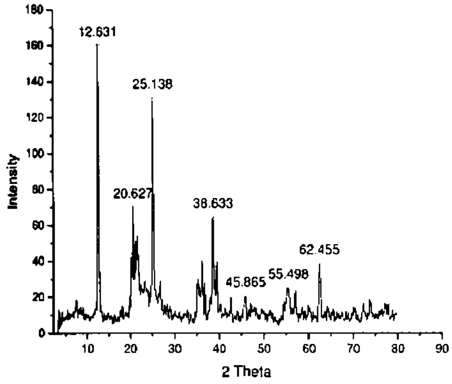
D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62.455
45.865
55.498
Intensity
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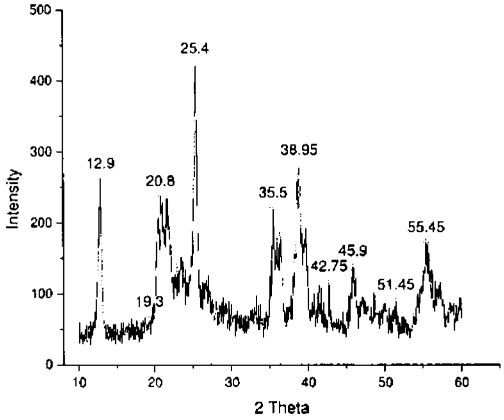
90

E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12.9
20.8
38.95
35.5
55.45
45.9
42.75
51.45
19.3
Intensity
2 Theta
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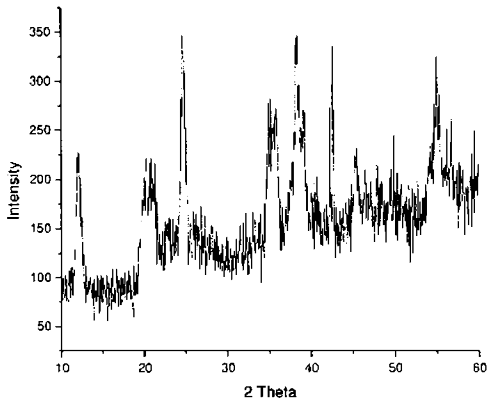
F



G

Figure 2: A-G. X-Ray Diffraction Patterns for catalysts A-G

The interpretation of the XRD patterns of the bulk samples, and of fine clay fraction led to the identification of the mineral phases,[23] kaolinite (at 2θ value of 11-12, 24-26). The data are given in table 8.

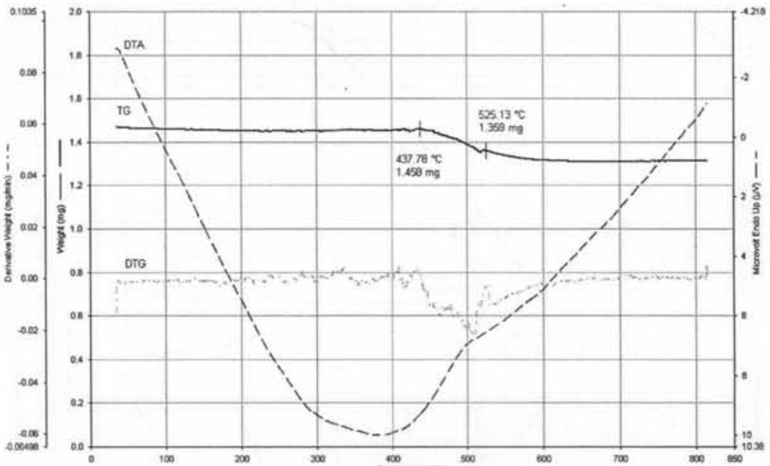
Table 8: Comparison of intensities (in arbitrary units) of two main refractions of the catalysts

Sl.No	catalysts	At 2θ≈12 of kaolinite	At 2θ≈24 of kaolinite
1	A	31	25
2	B	110	65
3	C	140	120
4	D	210	160
5	E	160	130
6	F	210	430
7	G	210	350

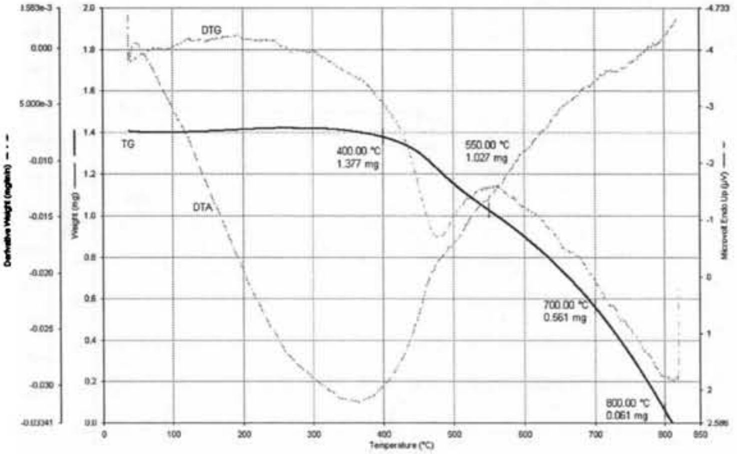
The intensities of the peaks 2θ at 12° and 24° increase with increasing the acid concentration. This phenomenon was prevailed up to the acid concentration of 2M H_2SO_4, and decreases at 5M H_2SO_4 treatment. This is due to the effect of excess aluminium leaching and the destabilization of crystalline structure. In the case of metal impregnated clays the replacement of alumina is carried out with incoming metal ions. So the intensities have increased when compared to the acid treated catalysts. The deformed nature of iron impregnated catalyst suggests that there is excess substitution of iron atoms and hence there is significant reduction of interstitial volume.

2.2.7 Thermogravimetry

Shimadzu TGA-50 instrument was used for carrying out thermogravimetric studies. About 2mg of the sample was used at a heating rate of 10°C per minute in the temperatire range of 50-800°C. The TG/DTG/DTA curves for the samples A-G are given in figure 3 A-G.



A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TG
DTA
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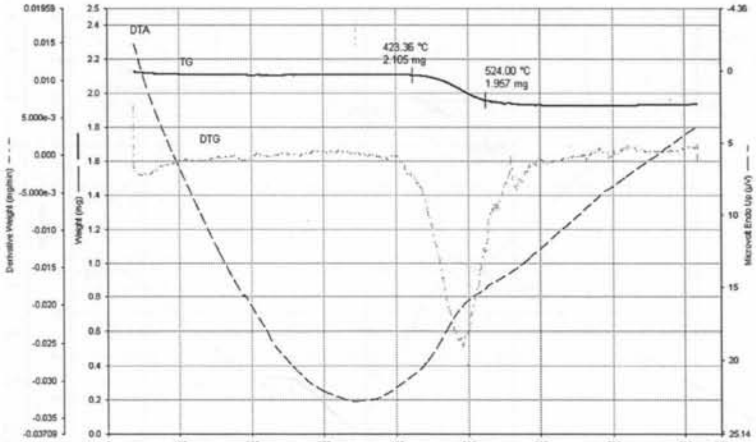
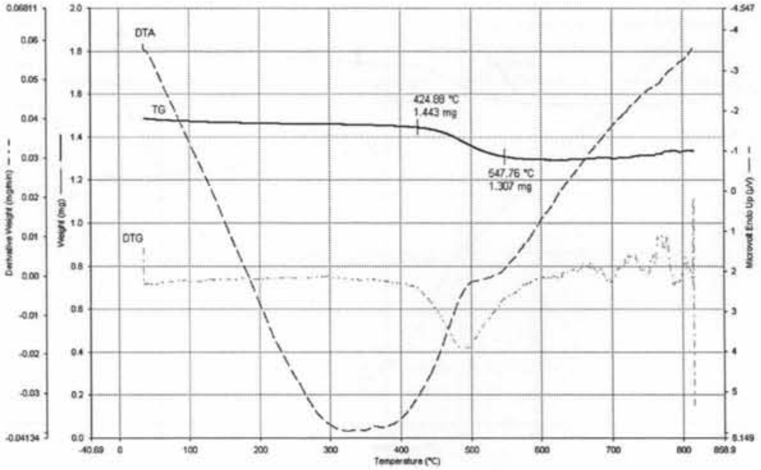
1.377 mg
550.00 °C
1.027 mg
700.00 °C
0.561 mg
800.00 °C
0.061 mg
Derivative Weight (mg/min)
Weight (mg)
Microvolt Endo Up (µV)
Temperature (°C)
1.583e-3
0.000
5.000e-3
-0.010
-0.015
-0.020
-0.025
-0.030
-0.03341
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-4.733
-4
-3
-2
-1
0
1
2
2.586
0
100
200
300
400
500
600
700
800
850

B


DTA
TG
DTG
423.36 °C
2.105 mg
524.00 °C
1.957 mg
Derivative Weight (mg/min)
Weight (mg)
Microvolt Endo Up (µV)
Temperature (°C)
0.01959
0.015
0.010
5.000e-3
0.000
-5.000e-3
-0.010
-0.015
-0.020
-0.025
-0.030
-0.035
-0.03709
2.5
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-4.36
0
5
10
15
20
25.14
0
100
200
300
400
500
600
700
800
850

C


DTA
TG
DTG
424.88 °C
1.443 mg
547.76 °C
1.307 mg
Derivative Weight (mg/min)
Weight (mg)
Microvolt Endo Up (µV)
Temperature (°C)
0.06811
0.06
0.05
0.04
0.03
0.02
0.01
0.00
-0.01
-0.02
-0.03
-0.04134
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-4.547
-4
-3
-2
-1
0
1
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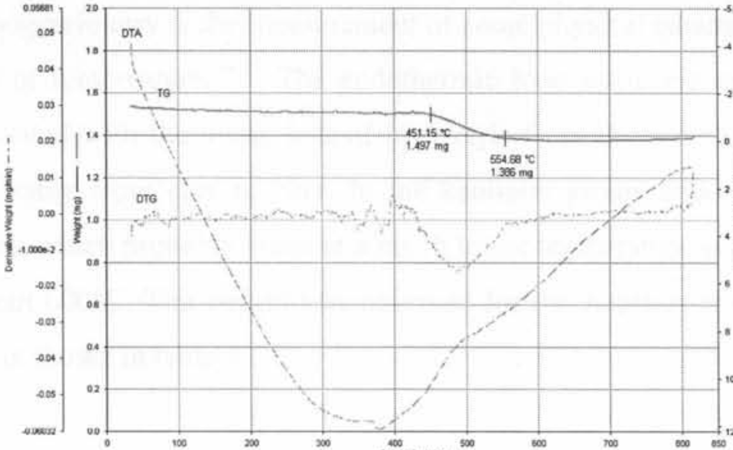
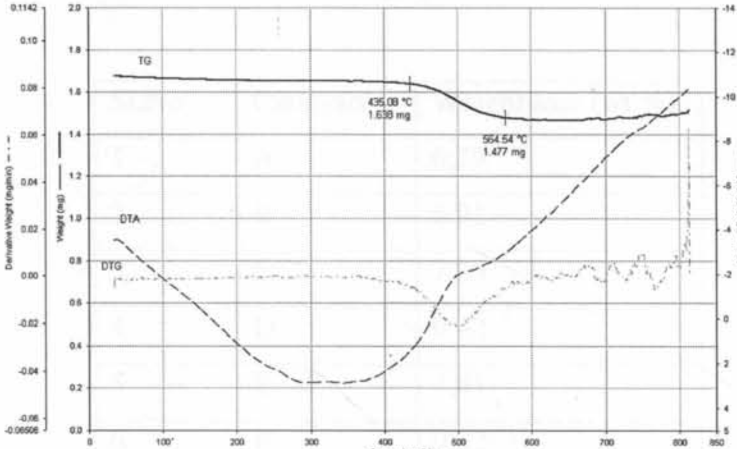
0
100
200
300
400
500
600
700
800
858.9

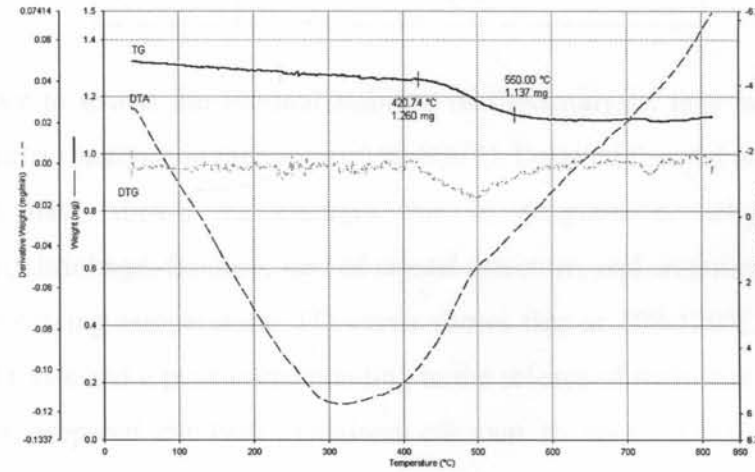
D



E



F



G

Figure 3: A-G. TG/DTG/DTA curves of catalysts

Thermogravimetry is the measurement of some physical parameter of a system as a function of temperature.[24-27] The endothermic loop occurring at mid temperature range is associated with the major loss of hydroxyls from the octahedral layer and this varies considerably from clay to clay. In the kaolinite group, endothermic loop is an intense reaction which probably starts at a much lower temperature at about 450°C[28] and to peak at about 600°C. The weight loss observed for the catalysts at the temperature of 430 to 530°C is shown in table 9.

Table 9: Weight loss observed for the catalysts during the temperature range 430-530°C

Sl.No	Catalysts	Weight loss (wt %)
1	A	6.79
2	B	6.91
3	C	7.03
4	D	9.42
5	E	7.41
6	F	9.82
7	G	9.76

In order to assess the thermal stability of the catalysts, they were subjected to thermogravimetric analysis in the range of 50-800°C. Detailed thermal analysis data of all clay samples have shown the changes due to dehydration, dehydroxylation, re-crystallization, shrinkage, fracture, loss of crystal structure, and sintering, which occur as a result of increasing temperature. TG curve shows that at 100-120°C, a characteristic gradual weight loss and a peak corresponding to the release of water has taken place. The weight of the prepared catalysts remained constant to about 430°C after this small variation.

The weight loss at 450°C can be attributed to the dehydroxylation of cations there by destabilizing the structure of the clay. Thermogravimetric graph show endothermic loop that occurred at around 500°C. This endothermic loop have intensity low for raw clay, and was gradually increased up to 5M HCl acid treatment. The intensity of the loop decreased towards the 5M H_2SO_4 acid treatment. The two metal impregnated catalysts showed characteristic endothermic loop similar to raw catalyst. The weight loss at the specified temperature (430-530°C) showed that the stability of the catalysts is constant up to the temperature of 430°C. Calcination done at 450°C during the purification of catalysts, contribute the stable nature of prepared catalysts.

2.2.8 Surface Area Measurement

The most convenient approach for textural characterization of clays is to obtain the adsorption isotherm at a temperature lower than or equal to critical adsorbate temperature. N_2 (at 77.2 K) is traditionally used as adsorbate. As gas pressure increases, adsorption proceeds by pore filling, starting from smaller pores. The potential energy fields from neighboring surfaces overlap and the total interaction energy with adsorbate molecules become substantially enhanced giving rise to high gas volume adsorption at very low relative pressures. The surface area of the catalysts was obtained by applying BET equation. The range of validity of BET equation for these materials is usually between $P/P_o = 0.01$ and 0.1. However, for microporous solids like clays where the interlamellar distance is of the order of a few molecular diameters, monolayer formation on silicate layers occurs.

The adsorbing properties of clay minerals, and in particular smectites, can be improved either by intercalation of organic, inorganic, or organometallic molecules in the interlamellar space, or by heat or acid treatments. Acid activation of smectites has been extensively studied as it strongly affects clay layers, and modified materials can be used in various applications, e.g., for environmental protection and in the paper, chemical, and food industries. In the last case, one of the main uses is linked to the discoloration and stabilization of vegetable oils. Discoloration efficiency depends, however, on the rate of acid activation, as it was established that beyond certain activation rate a reduction in the bleaching properties of clays was observed [29].

The first step of acid activation is the exchange of interlayer cations with H^+ to form H-kaolinites. However, H-kaolinites are generally unstable, as auto transformations occur upon aging due to the exchange of surface and interlayer protons with tetrahedral and octahedral Al^{3+}, Fe^{2+}, and Mg^{2+} ions. In a second step, acid activation results in the dissolution of clay layers and the formation of amorphous materials. Decomposition of kaolinites is realized through the dissolution of octahedral and tetrahedral cations. The extent and kinetics of the decomposition depend on many factors such as clay type, time, temperature, and nature and concentration of acid.

The value of surface area of the catalysts so obtained is presented in table 10.

Table 10: BET Surface area of the catalysts

Sl.No	Catalysts	Surface area (m^2/g)
1	A	13.96
2	B	21.10
3	C	30.60
4	D	29.91
5	E	52.65
6	F	14.83
7	G	20.41

The surface area has been found to increase upon an increase in the concentration of acid treatment. Lower the acid concentration, lower the surface area and vice versa. The lower surface area values during low concentration of acid treatment were attributed to the removal of the exchanging ions, such as excess or edge aluminium removal. The higher surface area values during higher concentration of acid treatments were attributed to the leaching of the cations in the skeletal structure such as excess removal of aluminium ions both in the tetrahedral and octahedral network. It can also be mentioned that higher acid concentration may attribute to the deformation of the crystal structure. This phenomenon led to the formation of amorphous nature in the catalysts which results in the increase surface area. The impregnation of metal ions fill the void volume as well as interlamellar regions thereby reducing the surface area values in metal impregnated catalysts.

2.2.9 Acidity measurement

Acidity of the modified clays came from two sources: the original clay, and the modification due to acid treatment and the metal impregnation. The generally accepted view of acidity of the catalysts is that Lewis sites are mainly resident on metal oxides and whereas, Bronsted acid sites are associated with structural hydroxyl groups present on the layers of the host clay. The number of Bronsted acid sites decreases with increase in temperature and these sites are practically lost at temperatures above 500°C. Protons from different sources may not be at the origin of acidity of prepared catalysts.[30]

Ammonia is an excellent probe molecule for testing acidic properties of solid acid catalysts as its strong basicity and small molecular size allow detection of acidic sites located at very narrow pores also. Usually IR spectroscopy, differential scanning calorimetry and temperature programmed desorption techniques are employed to achieve information on the interaction of ammonia with solid acids. Although, there is widespread use of TPD in the studies of surface acidity, NH_3-TPD spectra are often poorly resolved. However, the procedure is a standardization method since ammonia allows the determination of both protonic and cationic acidities by titrating acid strengths of any strength.

Ammonia adsorption on the catalysts can be physical (ΔH = 13 Kcal mol^{-1}) or chemical (ΔH = 33 Kcal mol^{-1}) type. Acid site distribution profile shows the presence of weak (ammonia desorbed between 35-200°C), medium (201-400°C) and strong (400-600 °C) acid sites. Ammonia-TPD method lacks in discriminating the type of acid sites

(Bronsted and Lewis sites). However it is generally accepted that evacuation of ammonia adsorbed at 400°C removes most of the Bronsted acid-sites. Coordinatively bound ammonia on strong Lewis site can be desorbed only at high temperatures and hence acidity in strong region can be correlated to the amount of Lewis sites.[31]

Many techniques have been developed for the characterization of surface acidity, most involve either some form of titration with a base under aqueous, non-aqueous or gas phase conditions, or measurements based upon activity and selectivity toward some particular catalytic reaction. No single technique can yield both a quantitative and qualitative determination of the surface acidity and a number of methods are normally used. TPD measurements were carried out from 373 to 1073 K. Purified and acidified clays were preheated at 573 K for 2h and then allowed to return to room temperature, the clay (100 mg, 80–100 mesh) was cleaned by TPD in ultra-high vacuum system. Temperature Programmed Desorption values obtained are given in table 11.

Table 11: Ammonia TPD values for the catalysts

Catalysts	Ammonia desorbed (mmol/g)			
	Weak acidic sites	Medium acidic sites	Strong acidic sites	Total acid amount
A	0.27	0.37	0.23	0.87
B	0.30	0.44	0.31	1.05
C	0.49	0.35	0.34	1.18
D	0.43	0.44	0.43	1.30
E	0.46	0.29	0.67	1.42
F	0.23	0.29	0.25	0.77
G	0.11	0.13	0.14	0.38

As in the case of the surface area values, the acidity values also increase with the increasing concentration of acids. The weak acidic sites are attributed to the Bronsted acidity and the strong acidic sites are attributed to Lewis acidity. The liberation of the cations at higher acid concentration contributes to the higher Lewis acid sites. The TPD values of the prepared catalysts showed that a steady increase was found when treated with higher concentration of acids. A trend was observed by a decrease in the acidity values for the copper and iron treated catalysts. This has led to the inference that aluminium content was so much decreased in the case of the samples treated with higher concentration of acids. When treated with the metal ion solution, the vacancies of the edges were filled with heavy ions thereby decreasing the surface acidity.

2.3 Experimental methods

2.3.1 Method of purification and acid activation

The raw clay was subjected to coning and quartering to obtain a sample which was representative of the bulk. This was subjected to slacking to remove soluble impurities and was then sieved. The fine grained clay particles obtained were dried and powdered. The clay was calcined at 450°C for 1h. The sample was activated with 2M HCl, 5M HCl, 2M H_2SO_4, 5M H_2SO_4 in the solid to liquid ratio 1:10 (200mL solution for 20g clay) for a period of 1h and filtered. The samples were washed thoroughly with distilled water for removing chloride and sulphate ions and dried in an air oven at 250°C for 2 h.

2.3.2 Preparation of the metal impregnated catalysts

The sample was refluxed with 10% $CuSO_4$ and 10% $FeCl_3$ solution in the solid to liquid ratio 1:10 (200mL solution for 20g clay) for a period of 1h and filtered. The samples were washed thoroughly with distilled water for removing chloride and sulphate ions and dried in an air oven at 250°C for 2h.

2.3.3 Characterization studies

2.3.3.1 IR spectral studies

The KBr pressed disc technique (0.2 to 0.6 mg of sample and 200 mg of KBr) was used to record the IR spectrum. FTIR spectra were obtained on a JASCO 4100 FTIR spectrometer. FT-IR spectra were recorded, in the range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} with KBr pellets technique. To make more vivid spectrum in the finger-print region(400-1200cm^{-1}), a separate spectrum was taken for each sample.

2.3.3.2 Surface Area Analysis

The BET surface area of the catalysts was obtained from nitrogen adsorption data at 77 K. Clays were activated for 24h at 250^0 C under vacuum prior to adsorption. The surface area of samples was characterized by the BET method, performing adsorption of nitrogen at 77K with the Surface Area Analyser Quantachrome Autosorb-1. This instrument operates by measuring the quantity of nitrogen adsorbed onto the solid surface at some equilibrium vapour pressure by the static volumetric method. The data are obtained by admitting a known quantity of adsorbate gas, which is nitrogen, into the sample cell containing the solid adsorbent maintained at a constant temperature below the critical temperature of the adsorbate. An adsorption occurs, the pressure on the sample cell changes until equilibrium is established. The quantity of gas adsorbed at the equilibrium pressure is the difference between the amount of gas admitted and the amount required to fill the surface of the adsorbent. The software performed data acquisition, reduction, and calculation.

2.4 Conclusion

Seven types of clays from different sources were obtained. They were purified, and their chemical composition was determined. Based on their chemical composition, their X-ray diffraction data and the activity towards catalytic action, a particular type of clay was selected. The selected clay was subjected to modification by acid treatment and metal ion incorporation. The modified clays were purified, calcined and were characterized by techniques such as elemental analysis, Infrared spectroscopy, X-Ray Diffraction, Surface area, Thermogravimetry/ Differential Thermal analysis, and acidity measurement using Temperature Programmed Desorption using Ammonia were done. Based on the preparation method, classification of the catalysts was done. Using these different catalysts, organic reactions were carried out to check the relative activity of these catalysts.

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CHAPTER III

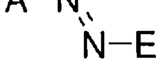
CLAY MEDIATED DIAZOTISATION AND COUPLING

Conspectus

Seven catalysts were prepared by using acid activation and metal impregnation techniques. All of them were used in the model diazotization reaction. Their yields were compared with standard clays such as K10 and KSF. High yielding catalyst was used for five different combinations of reactants. The products have been thoroughly characterized. Recycling study of high yielding catalyst was conducted.

3.1 Introduction

Azo dyes are by far the most important class, accounting for over 50% of all commercial dyes, and having been studied more than any other class. Azo dyes contain at least one azo group but can contain two (disazo), three (trisazo), or, more rarely, four (tetrakisazo) or more (polyazo) azo groups. The azo group is attached to two groups, of which at least one, but more usually both, are aromatic. They exist in the *trans* form in which the bond angle is 120°, the nitrogen atoms are sp^2 hybridized, and the designation of A and E groups is consistent with Cahn and Ingold usage.[1]



In monoazo dyes, the most important type, the A group often contains electron-accepting substituents, and the E group contains electron-donating substituents, particularly hydroxyl and amino groups. If the dyes contain only aromatic groups, such as benzene and naphthalene, they are known as carbocyclic azo dyes[2]. If they contain one or more heterocyclic groups, the dyes are known as heterocyclic azo dyes. These illustrate the enormous structural variety possible in azo dyes, particularly with polyazo dyes[3]. Azo dyes are made by diazotization of a primary aromatic amine followed by coupling of the resultant diazonium salt with an electron rich coupling agent. The diazotization reaction is carried out by treating the primary aromatic amine with nitrous acid, normally generated in situ with hydrochloric acid and sodium nitrite[4]. The nitrous acid nitrosates the amine to generate the *N*-nitroso compound, which tautomerises to the diazo hydroxide. A diazonium salt is a weak electrophile and hence reacts only with highly electron rich species such as amino and hydroxy compounds. Even hydroxy compounds must be ionized for reaction to occur[5]. Consequently, hydroxy compounds such as phenols and naphthols are coupled in an alkaline medium (pH, p*Ka* of phenol or naphthol; typically pH 7-11), whereas aromatic amines such as *N*,*N*-dialkylamines are coupled in a slightly acid medium, typically pH 1.5. This provides optimum stability for the diazonium salt (stable in acid) without deactivating the nucleophile.[6]

Depending on the basicity and solubility of the amines being diazotized, the following diazotization methods find industrial use:

a) Direct Diazotization: The primary aromatic amine is dissolved or suspended in aqueous hydrochloric or sulfuric acid, and a concentrated aqueous sodium nitrite solution is added. An excess of 2.5 - 3 equivalents of acid per equivalent of amine is used. A temperature of 5 °C is maintained by adding ice.[7]

b) Indirect Diazotization: Amines with sulfonic or carboxylic acid groups are often difficult to dissolve in dilute acid. Therefore, the amine is dissolved in water or a weak alkali, and the calculated amount of sodium nitrite solution is added to this amine solution which is stirred into the ice-cooled acid solution already in the vessel. The acid can also be added to the amine nitrite mixture already at hand[8].

c) Diazotization of Weakly Basic Amines: Weakly basic amines are dissolved in concentrated sulfuric acid and diazotized with nitrosylsulfuric acid, which is easily prepared from solid sodium nitrite and concentrated sulfuric acid[9].

d) Diazotization in Organic Solvents: The water-insoluble or sparingly soluble amine is dissolved in glacial acetic acid or other organic solvents and, where necessary, diluted with water. After the addition of acid, it is diazotized in the usual manner with sodium nitrite solution. Nitrosylsulfuric acid, nitrosyl chloride, alkyl nitrites, or nitrous gases can also be used instead of sodium nitrite.[10] Temperature, pH, and the concentration of the diazotizing solution often have a considerable effect on the progress of diazotization. Physical properties (distribution, particle size) and the addition of emulsifiers and dispersing agents influence the diazotization of slightly soluble amines. Certain aromatic amines require special diazotizing processes.[11]

1-Aminonaphthols, such as 1-amino-2-naphthol and several 1-aminonaphthol sulfonic acids, such as 1-amino-2-naphthol-4-sulfonic acid, are oxidized to the respective quinone by nitrous acid[12]. Diazotization can, however, take place under normal conditions in the presence of catalytic quantities of metal salts, such as copper or zinc salts.

Aryl diazonium ions ($Ar\text{-}N{\equiv}N^+$) are weak electrophiles and give strongly colored azo compounds (Ar-N=N-Ar') by electrophilic substitution, but only on aromatic rings which are strongly activated by hydroxy or amino groups[13]. This is called azo coupling and is the key step in the synthesis of azo dyes, the most commonly employed of all dyestuffs. Most dyeing operations utilize hot aqueous solutions of the dyes, many of which bear sulfonic acid groups to improve their water solubility[14, 15].

Azo dyes are compounds that contain azo groups linked to methine or aromatic sp^2-hybridized C-atoms. The formation of diazotizing reagent starts with protonation of nitrous acid under strongly acidic conditions, and azo coupling carried out at low temperature in the presence of nucleophilic coupling components, the reactivity of a nucleophilic substrate increases with increasing basicity of phenolates and amines.[16] These conventional acid base catalyzed processes are effective for the near quantitative formation of the desired products. But the main limitation of such synthetic processes is their environmental incompatibility. The acidic and basic effluents from the laboratory and industry produce permanent damage to the environment and disturb the ecological balance[17-20].

3.2 Diazotization using solid acid catalysts

Kaolins are smectite group of clays comprising of both Lewis and Bronsted group of acid sites[21]. The Bronsted type acidity is further enhanced by replacing metal ions from the kaolin surfaces by treatment with mineral acids. Preparation of various catalysts was effected by the reaction of locally available raw kaolin with different types of mineral acids. These catalysts are employed to conduct diazotization of aromatic amines. In conventional route, to prepare diazonium salts, mineral acids to the tune of twice the mole of substrate are necessary. This causes severe environmental hazards. By using acid activated kaolin, we can avoid the mineral acid altogether and diazotize the amines. The diazonium salts thus obtained can be coupled with suitable coupling agent, such as amines or phenols to make azo dyes. A number of dyes such as methyl orange, Orange II etc have been prepared. The products obtained were in good yield and were characterized by spectroscopic techniques. Possibility of recycling of the catalyst was ascertained.

3.3 Results and discussion

3.3.1 Preparation of methyl orange using modified clays

To check the activity of the prepared catalysts, preparation of methyl orange was taken as the reference reaction. The general scheme of the reaction is outlined here (Scheme 1).

$$\mathrm{RNH_2} + \mathrm{NaNO_2} \xrightarrow[<5^{\circ}\mathrm{C}]{\text{modified kaolin 0.5g}} \mathrm{RN_2\text{-}Clay} \xrightarrow{\mathrm{R'X}} \mathrm{R{-}N{=}N{-}R'X}$$

Scheme 1: Preparation of azo-dyes

The yield of the methyl orange obtained with modified clays is shown in table 1. The yield of methyl orange obtained using standard clay is also given in the table for comparison.

Table 1: Comparison of yield of methyl orange with prepared catalysts and standard clays

Sl.No	Catalysts	Yield (%)*
1	A	24
2	B	48
3	C	69
4	D	68
5	E	39
6	F	70
7	G	77
8	K10	72
9	KSF	49

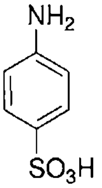
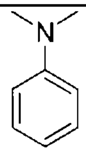
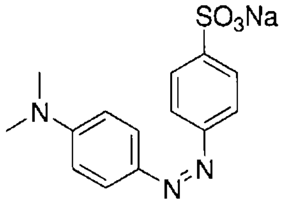
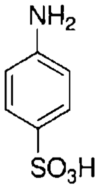
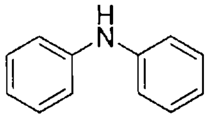
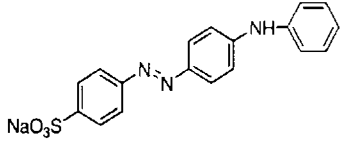
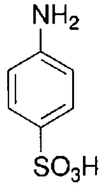
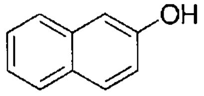
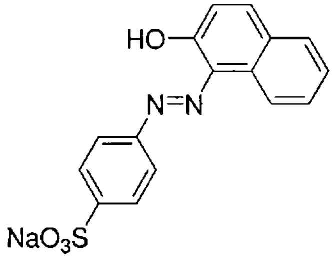
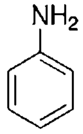
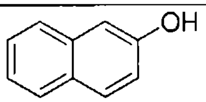
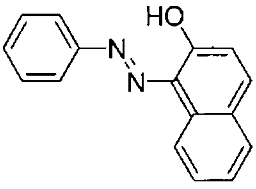
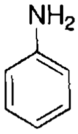
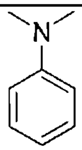
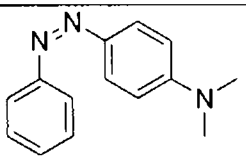
* Reaction conditions: amine: 12.5mmol, Sodium nitrite: 12.5mmol, amount of catalyst: 0.5g, coupling agent: 12.5mmol, temperature: 0-5°C, isolated yield,

The raw clay was also found to be catalytically active due to its inherent catalytic acid sites, but the yield was quite low. The yield of the product was gradually increased while increasing the concentration of the acid. On using the 5M H_2SO_4 (E) activated clay, the yield was decreased from 68 to 38%, showing that this catalyst lost its catalytic activity either by deformation of the crystalline structure or by leaching of the cations. The metal impregnated catalysts showed significant activity, the iron impregnated catalyst has shown more.

3.3.2 Preparation of azo dyes using iron impregnated catalyst

The high yielding, iron impregnated catalyst (G) was used for the preparation of five different azo dyes. They are Methyl orange, Orange IV, Orange II, Sudan I, and Butter yellow. The yield of azo-dyes prepared with iron impregnated catalyst is shown in table 2. The azo dyes were characterized by determining the physical constants and by spectral methods.

Table 2: Yield of azo-dyes prepared with iron impregnated catalyst

Sl.No	Amine	Coupling agent	Product	Yield (%)*
1			 (Methyl Orange)	77
2			 (Orange IV)	74
3			 (Orange II)	76
4			 (Sudan I)	76
5			 (Butter Yellow)	71

* Reaction conditions: amine: 12.5mmol, Sodium nitrite: 12.5mmol, amount of catalyst: 0.5g, coupling agent: 12.5mmol, temperature: 0-5°C, isolated yield,

3. 4 Recycling of the catalysts

For this purpose, the catalysts after the removal of the azo dyes were washed several times with acetone and dried at 110°C in an air oven for overnight. This oven dried catalyst was calcined at 250°C for 1h and used for performing the reaction. This process was repeated for two times and no considerable reduction in the yield was observed. The yield obtained during recycling study of the catalyst is shown in the table3.

Table 3: Recycling study of the catalyst

Catalyst	Product	Yield (%)*		
		Fresh	First cycle	Second cycle
Iron impregnated clay	Methyl Orange	77	76	75

* Reaction conditions: amine: 12.5mmol, Sodium nitrite: 12.5mmol, amount of catalyst: 0.5g coupling agent: 12.5mmol, temperature: 0-5°C, isolated yield,

Conventionally, azo dyes are prepared using mineral acid to the tune of thrice the amount of reactants. From these studies it is concluded that the mineral acid component can be eliminated from the reaction medium and the alkali needed to neutralize the excess acids also can be reduced. This makes the reaction a green one and making the azo-dyes procedure a simple one. The products were characterized using physical constants and spectral data. Iron impregnated catalyst was further studied for the reusability. The results are shown in the table 4. There is no significant reduction in the activity even though the catalyst was used for the third cycle. This renders the catalyst more reusable.

3. 5 Mechanism of the clay catalyzed type

Mechanism of the diazotization can be represented as follows in figure 1.

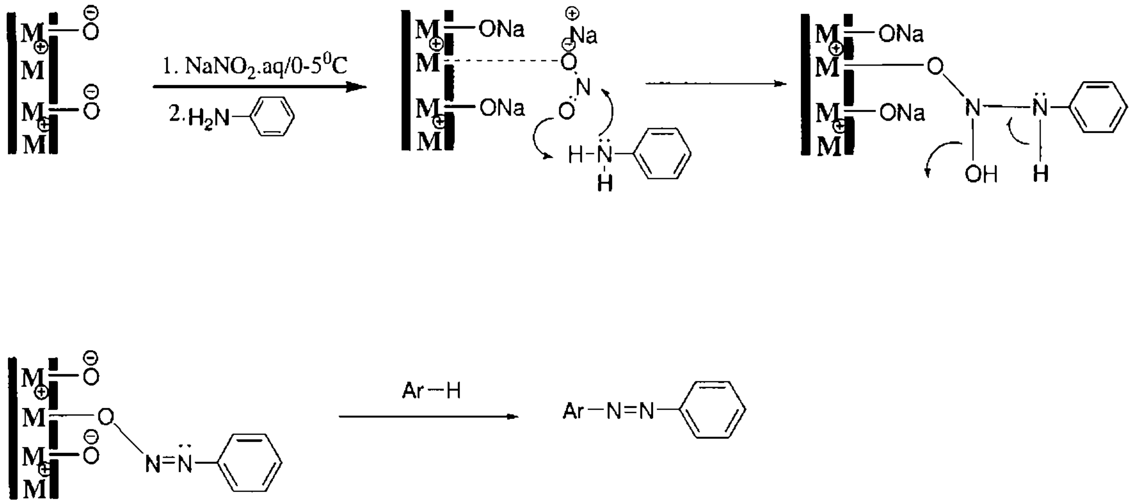


Figure 1: Mechanism of diazotization reaction with clay catalyst

After the formation of the diazonium-clay complex, the edge hydroxyls of the clay platelets are believed to get converted into –ONa species by consuming the Na^+ ions from $NaNO_2$ solution used for diazotization. This –ONa species helps to maintain the pH of the medium neutral or slightly alkaline for a quantitative coupling of the diazonium ion with the coupling agent.

3.6 Conclusion

The aim of the work was to study the diazotization reaction using the prepared catalysts. That was achieved with great success by metal impregnated and acid activated catalysts. The yield was comparable with available standard catalysts. The products were characterized using standard spectral methods. Recyclability of the catalyst render its use as a green alternative.

3.7 Experimental section

3.7.1 Methods and materials

The amines were purchased from M/s Qualigens and M/s Merck company and are used as such. Melting points reported were determined by open capillary method. Azo dyes formed were systematically characterized by CHN analysis, ^{1}H NMR and IR spectral analysis.

3.7.2 Preparation of Methyl orange

Sulphanilic acid (2.62g, 12.5mmol) and sodium carbonate (1.32g, 12.5mmol) were dissolved in 25mL of water and warmed. The solution was cooled, to below 5°C. This cooled solution was slowly added to the beaker containing sodium nitrite (0.925g, 12.5mmol) and 0.5g of catalyst in 5mL of water. After stirring for 15 minutes, N,N-Dimethyl aniline (1.57mL, 12.5mmol) dissolved in glacial acetic acid (0.75mL) was added into the reaction mixture. After 10 minutes, sodium hydroxide (1g, 25 mmol) was added with stirring, and heated to boil. The solution was decanted to remove the clay. Sodium chloride (2g) was added to salt out the methyl orange precipitate. The crude product was filtered and dried. The crude product was recrystallised using hot alcohol.

3.7.3 Preparation of Orange IV

Sulphanilic acid (2.62g, 12.5mmol) and sodium carbonate (1.32g, 12.5mmol) were dissolved in 25mL of water and warmed. The solution was cooled, to below 5°C. This cooled solution was slowly added to the beaker containing sodium nitrite (0.925g, 12.5mmol) and 0.5g of catalyst in 5mL of water. After stirring for 15 minutes, Diphenylamine (4.6g 12.5mmol) in 10mL of ethyl alcohol was added to the diazotizing mixture. The solution was filtered to remove the catalyst. Water was removed by evaporation. The crude product was recrystallised using alcohol.

3.7.4 Preparation of Orange II

Sulphanilic acid (2.62g, 12.5mmol) and sodium carbonate (1.32g, 12.5mmol) were dissolved in 25mL of water and warmed. The solution was cooled, to below 5°C. This cooled solution was slowly added to the beaker containing sodium nitrite (0.925g, 12.5mmol) and 0.5g of catalyst in 5mL of water. After stirring for 15 minutes, β-Naphthol (3.6g, 12.5mmol) in 10mL of ethyl alcohol was added to the diazotizing mixture. The mixture was suspended in water (50mL) and filtered to remove the catalyst. Water was removed by evaporation. The crude product was recrystallised using alcohol.

3.7.5 Preparation of SudanI

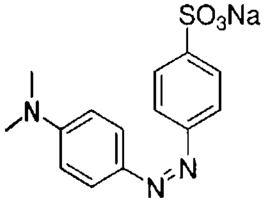
Aniline (2.34g, 12.5 mmol) of was adsorbed on 0.5g of clay catalyst and cooled to 0°C. Sodium nitrite (0.925g, 12.5mmol) crystals were added slowly. After stirring for 15 minutes, β-Naphthol (3.6g, 12.5mmol) in 10mL of ethyl alcohol was added to the diazotizing mixture. The mixture was suspended in water (50mL) and filtered to remove the catalyst. Water was removed by evaporation. The crude product was recrystallised using alcohol.

3.7.6 Preparation of Butter Yellow

Aniline (2.34g, 12.5 mmol) of was adsorbed on 0.5g of clay catalyst and cooled to 0°C. Sodium nitrite (0.925g, 12.5mmol) crystals were added slowly. After stirring for 15 minutes, N,N-Dimethyl aniline (1.57mL, 12.5mmol) dissolved in glacial acetic acid (0.75mL) was added into the reaction mixture and stirred for 10 minutes. The crude product was extracted three times with ethyl alcohol (15mL each). The solvent was evaporated under vacuum. The crude product was recrystallised from alcohol.

3.8 Characterisation of the products

a. Methyl orange



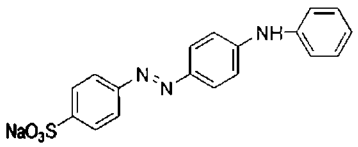
Reddish orange crystals.

Elemental analysis (%) (Calculated values for Molecular formula $C_{14}H_{14}N_3O_3S$ are in brackets): C = 51.2 (51.37), H = 4.4 (4.31), N = 12.8 (12.84), S = 10.0 (9.8), O = 14.4 (14.66).

FTIR (KBr ν_{max} (cm^{-1})): 1367 (νSO_2), 1519 (νN=N),

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.31(d, 4H), 8.5(d, 4H). 3.1(s, 6H)

b. Orange IV



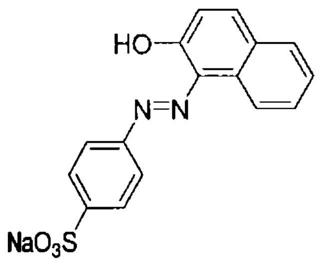
Orange solid

Elemental analysis (%) (Calculated values for Molecular formula $C_{18}H_{14}N_3O_3S$ are in brackets): C = 57.6 (57.59), H = 3.6 (3.76), N = 12.2 (11.19), O = 18.4 (18.79), S = 8.2 (8.5)

FTIR (KBr ν_{max} (cm^{-1})): 1239 (νSO_2), 1499 (νN=N),

^{1}H NMR δ ($CDCl_3$, 300 MHz): 6.6 (s, 1H), 7.6 (m, 4H), 8.1(d, 4H), 4.05(m, 1H), 7.0 (d, 2H)

c. Orange II



Orange crystals.

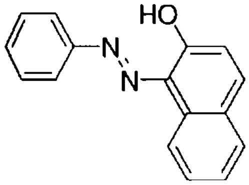
M.P(°C) (Literature value is in parenthesis): 162 (164)

Elemental analysis (%) (Calculated values for Molecular formula $C_{16}H_{11}N_2O_4S$ are in brackets) C = 55.2 (54.86), H = 2.9 (3.16), N = 7.85 (8.00), O = 18.0 (18.27), S = 9.3 (9.15);

FTIR (KBr ν_{max} (cm^{-1})): 1297 (νSO2), 1513 (νN=N), 1631, 3450(ν-OH)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.15 (m, 6H), 7.35(d, 4H), 8.14 (s, 1H),

d. Sudan I



Orange Solid.

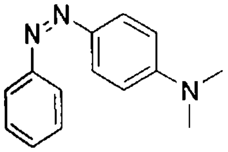
M.P (°C) (Literature value is in parenthesis): 131. (131)

Elemental analysis (%) (Calculated values for Molecular formula $C_{16}H_{12}N_2O$ are in brackets): C = 77.6 (77.40), H = 4.6 (4.87), N = 11.5 (11.28), O = 6.24 (6.44)

FTIR (KBr ν_{max} (cm^{-1})): 1631(vN=N), 3446(v-OH)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.0 (m, 1H), 7.4 (m, 6H), 8.0(m, 2H)

e. Butter yellow



M.P(°C) (Literature value is in parenthesis): 114 (116)

Elemental analysis (%) (Calculated values for Molecular formula $C_{15}H_{15}N_3$ are in brackets): C = 74.8 (74.64) H = 6.43 (6.71) N = 18.3 (18.65)

FTIR (KBr, ν_{max} (cm^{-1})): 1400 (vN=N)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.8(s, 6H), 7.19(m, 9H)

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CHAPTER IV

SYNTHESIS OF DIAMINODIPHENYLMETHANES USING MODIFIED CLAYS

Conspectus

Protonated formaldehyde reacts with aromatic amines to give 4,4'-diaminodiphenylmethanes. Protonation of formaldehyde can be done with acid activated and transition metal impregnated clays. This chapter deals with the condensation of aniline with formaldehyde using acid treated as well as metal impregnated catalysts. The yields are compared with the standard clays such as KSF and K10. The products were characterized with physical constants and spectral methods. The recyclability of the prepared catalysts were checked.

4.1 Introduction

The synthesis of fine chemicals and pharmaceuticals has traditionally been achieved via homogeneous catalytic methods. Heterogeneous catalysis is an attractive alternative to these processes because of its inherent waste minimization and the potential to consolidate steps in a process. Some examples are worth to mention in this context. The synthesis of flavanones (i.e., condensation of 2′-hydroxyacetophenone and benzaldehydes to form a 2′-hydroxychalcone followed by an isomerization leading to the corresponding flavanone) represents an example of an important, homogeneously-catalyzed reaction that can be successfully heterogenized over solid catalysts[1-4].

Substitution effects have been observed for both the homogeneously and heterogeneously base-catalyzed Claisen-Schmidt condensation of ketones and aldehydes with functional groups substituted in the para-position. A clean method for the rapid and solventless synthesis of herbicides based on 2, 4-dichlorophenoxyacetic acid (2, 4-D esters) has been described in which clays act as catalysts. This reaction is strongly accelerated when subjected to microwave irradiation, a popular technique for clay-catalyzed reactions. These esters are extensively used around the globe as effective hormonal herbicides with high selectivity in applications to crops including cereals, grazing land and sugar cane plantations[5-7].

Large amounts of clay minerals are used as pesticide carriers. The 2, 4-D(2, 4-dichlorophenoxyacetic acid) prepared on clay could be applied as is, *i.e.* on the mineral used to catalyze its formation[8]. This idea could be applicable to other agrochemical products amenable to clean synthesis methods based on clay minerals. Two important processes for the construction of molecules, conjugate addition and alkoxyalkylation, can be carried out using commercially available and reusable clays. The products of such reactions are industrially important. For example, alkoxyalkylation leads to intermediates in the production of quinolines, which have value as bioactive compounds. Addition reactions have widespread applications in commercial processes[9]. They are likely to be increasingly favoured over alternatives as they can be 100% atom efficient. The reaction conditions using clay catalysts required are mild, and relatively benign hydrocarbon solvents are employed. The use of clays in Michael reactions may be considered as examples of reactions employing the dual catalytic nature of the materials.

Clays have multilayered structure which is characterized by the presence of Lewis acidic sites which are located mostly on the edges of the layers, capable of activating Michael reaction donors, and Bronsted acid sites which are mainly in the interlamellar region and which can activate Michael reaction acceptors (Thus ethyl and benzoyl acetate reacts readily with methyl vinyl ketone in the presence of acid-treated clays at room temperature in a solvent such as hexane). The catalyst can be used several times with little loss in activity[10,11].

The alkoxyalkylation reaction of carbonyl compounds can be considered as an orientated cross-aldol condensation between two masked carbonyl compounds, an acetal and silyl enol ether. The key step involved is the formation of an electrophilic species by reaction of the acetal with catalytic amounts of a Lewis acid and the right catalyst can lead to excellent diastereo- and enantioselectivities. Clays are satisfactory catalysts in these reactions, with the acid treated clay Kl0 performing better than the more powerfully acidic clay KSF. In reactions employing new stereogenic centres, however, a poor degree of stereoselectivity was observed. The composition of the diastereoisomeric mixtures varied considerably after the purification procedure because of the ready enolisation of the 1,3-dicarbonyl product. Triphasic systems involving clays pillared with surfactants as catalysts offer versatile routes to a range of useful benzylic compounds. By using the organoclay assemblies with sodium cyanide, thiocyanate and hydroxide, it is possible to prepare benzonitriles, benzyl thiocyanates and benzyl alcohols from the corresponding benzyl chlorides. Most of these reactions occur in yields of 80%.[12-15]

While clays are commonly associated with acid-catalyzed reactions, their environmental acceptability, good availability and ease of use makes them attractive materials for other applications. Some clay materials can be used as solid bases. These include magnesium hydrotalcites, which can be used, for example, in the synthesis of coumarins, which are important biologically active materials for which cleaner synthetic methods are required. The coumarins are synthesised *via* Knoevenagel condensation of various phenols with 2-substituted ethyl acetates in hot toluene. Product yields are generally good when using Mg-Al hydrotalcite although other solid bases including alumina and CsX-zeolite give no reaction[16-19].

The Henry reaction is an important class of C-C bond forming reaction catalysed by bases. It gives nitroalkanols, which are important intermediates for various useful compounds such as amino alcohols. Difficulties that give rise to waste include dehydration and Cannizzaro reaction of the aldehyde component. Mg-Al hydrotalcites seem to overcome these problems giving selective and clean reactions under mild conditions. The mechanism of the reaction can be assumed to involve the abstraction of a proton from the active methylene group of the nitro compound which gives a carbanion that can be stabilised by the Al sites in the lattice of the hydrotalcite. This carbanion further adds to the carbonyl compound to form an intermediate, which removes a proton from water to give the final nitro aldol product. Solid bases without Bronsted hydroxy groups such as decarbonated hydrotalcites are not active in this reaction. The Mg-Al hydrotalcite catalyst is non-toxic and can be recycled with little loss in activity[20].

The polymer industry requires large quantities of 4, 4'-diaminodiphenylmethanes. These compounds find use in various applications as polymer additives. Current synthetic methods involve the condensation of anilines with formaldehyde under acidic conditions. As is common for such reactions, a substantial amount of waste acid needs to be neutralised, generating substantial aqueous salt waste which is likely to be contaminated with residual anilines and/or formaldehyde, both compounds of considerable toxicity. While a completely green solution to this problem might involve the replacement of this chemistry with an inherently less toxic combination of reagents, the replacement of the current homogeneous catalysts with a heterogeneous catalyst might ease the problems of a waste aqueous phase. Such a catalyst switch might improve the situation by allowing the easy separation of catalyst from product, without the need for neutralisation. Thus, the aqueous waste stream can be avoided, and the catalyst can be recovered[21].

Diaminodiphenylmethanes find use in a variety of applications including curing agents and chain extenders in polymers. The conventional preparation is tedious involving specific use of mineral acids and alkalis at various stages. Polymerization is unavoidable resulting in poor selectivity. Heterogeneous catalysis on clays under solvent conditions with ultrasound irradiation and also in dry media under microwave conditions have been extensively studied compared to catalysis over clays in aqueous media. It is known that kaolinites intercalate with molecules as polar as water, formamide, *N,N*-dimethylformamide, dimethyl sulfoxide and dimethylselenoxide within their layers. Nevertheless, the catalytic activity of kaolinitic clays has been seldom exploited contrary to their smectite counterparts.

4.2 Results and Discussion

To check the activity of the prepared catalysts, preparation of diaminodiphenylmethane was taken as the reference reaction. Formaldehyde was made to react with aniline in the presence of prepared catalysts. The reaction scheme is given in the figure 1.

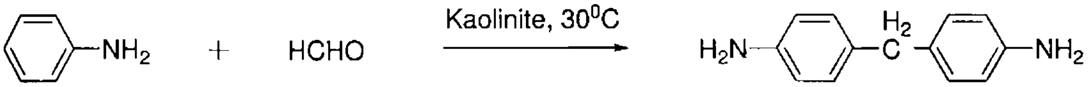


Figure. 1 Scheme of the reaction

The yield of the diaminodiphenylmethane obtained with modified clays is shown in table 1. The yield obtained using standard clay is also given in the table for comparison.

Table 1: Comparison of yield of diaminodiphenylmehane with prepared catalysts and standard clays

Sl. No	Catalysts	Yield (%)*
1	A	25
2	B	47
3	C	69
4	D	68
5	E	54
6	F	79
7	G	89
8	K10	85
9	KSF	51

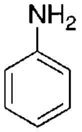
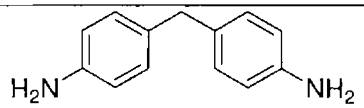
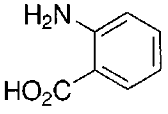
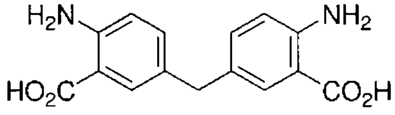
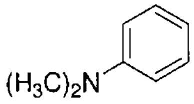
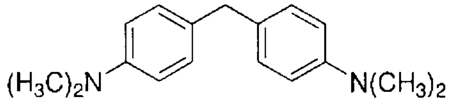
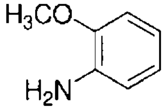
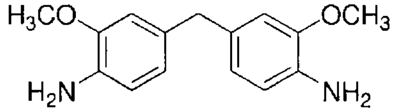
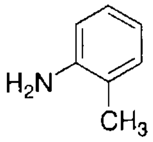
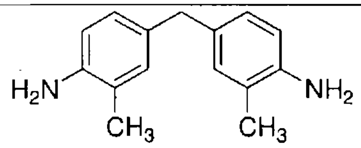
* Reaction conditions: 0.1mol aniline, 0.05 mol formaldehyde, 2g catalyst, isolated yield.

It is concluded that the catalyst type G (iron impregnated clay) has the highest yield for the reaction. To ascertain the superiority of the said catalyst it was decided to do similar reactions with other substrates.

4.2.1 Derivatives prepared using the selected (iron impregnated clay) catalysts

A series of experiments were conducted using the high yielding catalyst, and the results are shown in table 2. Five derivatives, such as 4,4'-Diaminodiphenylmethane, 4,4'diamino-3,3'-dicarboxyldiphenylmethane, 4,4'-N,N,N'N'-tetramethyldiaminodiphenylmethane, 3,3'dimethoxy-4,4'-diaminodiphenylmethane 3,3'-dimethyl-4,4'-diaminodiphenylmethane using different substrates were prepared using the iron impregnated catalyst. The products obtained are characterized using standard spectral methods.

Table 2: Yield of derivatives of diaminodiphenylmethanes with iron impregnated catalyst

Sl.No	Amine	Product	Yield (%)*
1			89
2			82
3			79
4			80
5			82

* Reaction conditions: 0.1mol aniline, 0.05 mol formaldehyde, 2g catalyst, isolated yield.

4.2.2 Recycling of the catalyst

The used catalyst was extracted several times with ether followed by water and dried at 250°C for 1h and reused. This process was repeated two more times and no considerable reduction in the yield was observed. The yield obtained during recycling study of the catalyst is shown in the table 3.

Table 3: Recycling study of the catalyst

Sl.No	Product	Yield (%)*		
		First cycle	Second cycle	Third cycle
Iron impregnated clay	4,4'Diaminodiphenylmethane	89	78	78

* Reaction conditions: 0.1mol aniline, 0.05 mol formaldehyde, 2g catalyst, isolated yield.

4.3 Conclusion

The raw clay also exhibits catalytic activity due to its inherent catalytic acid sites though the yield was quite low. The yield of the products was gradually increased while increasing the concentration of acid. On using the 5M H_2SO_4 activated clay, the yield was decreased from 68 to 54%,. This may be due to reduction in crystalline structure or by deformation. So the high yielding catalyst was chosen to further check the activity by preparing various derivatives.. The recyclability of the catalyst was also studied. The results have shown that the catalyst was stable for further studies, and with little difference in the yield of the products. The products are well characterized and the purity of the products was good.

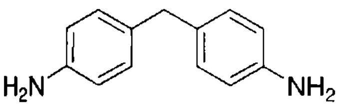
4.4 Experimental details

Formaldehyde (4.5mL, 50mmol, 37%) was stirred with catalyst (2g) in water (200mL) for 15min. Amine (100mmol) was slowly added into the stirring mixture and stirring continued for 30 minutes. The precipitated product was filtered and extracted with ether. The catalyst was removed and the solvent was dried using sodium sulphate. The solvent was evaporated to obtain the product. The crude product was recrystallised from hot ethanol. The products were characterized using spectral methods.

4.5 Characterization of the products

Characterization of the products was done by determining the physical constants and by spectral methods

a. 4,4'-Diaminodiphenylmethane

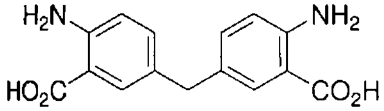


Appearance: Colorless solid

Elemental analysis (%) (Calculated for Molecular formula $C_{13}H_{14}N_2$ values are in brackets): C = 78.05 (78.75), H = 8.0(7.12), N =14.05 (14.13)

FTIR (KBr ν_{max} (cm^{-1})): 2845(>CH_2 symm. str.), 3380(Ar-NH_2)

b. 4,4'diamino-3,3'-dicarboxyldiphenylmethane

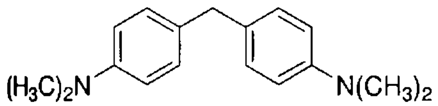


Appearance: Colorless solid

Elemental analysis (%) (Calculated for Molecular formula $C_{15}H_{14}N_2$ O_4values are in brackets): C = 62.1 (62.93), H = 5.1 (4.93), N = 9.9(9.79), O = 22.5(22.35);

FTIR (KBr ν_{max} (cm^{-1})): 1710(Ar-C=O str), 2860(>CH_2 symm. str.), 3540(Ar-NH_2).

c. 4,4'-N,N,N'N'-tetramethyldiaminodiphenylmethane

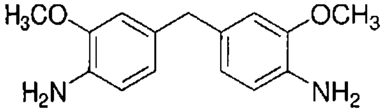


Appearance: Pale blue solid

Elemental analysis (%) (Calculated for Molecular formula $C_{17}H_{22}N_2$ values are in brackets): C = 80.05(80.27), H = 8.9(8.72), N = 11.0(11.01)

FTIR (KBr ν_{max} (cm^{-1})): 1320(3°C-N str), 2843(>CH_2 symm. str.),

d. 3,3’dimethoxy-4,4’-diaminodiphenylmethane

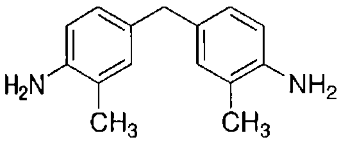


Appearance; Pale yellow solid

Elemental analysis (%) (Calculated for Molecular formula $C_{15}H_{18}N_2O_2$ values are in brackets): C = 69.4(69.74), H = 7.1(7.02), N = 10.9(10.84), O = 12.5(12.39),

FTIR (KBr ν_{max} (cm^{-1})): 1445($-OCH_3$), 2855($>CH_2$ symm. str.), 3520($Ar-NH_2$)

e. 3,3’-dimethyl-4,4’-diaminodiphenylmethane



Appearance; Colorless solid

Elemental analysis (%) (Calculated for Molecular formula $C_{15}H_{18}N_2$ values are in brackets): C =79.4(79.61), H = 7.9(8.02), N =12.6 (12.38);

FTIR (KBr ν_{max} (cm^{-1})): 1460 ($-CH_3$), 2865($>CH_2$ symm. str.), 3520($Ar-NH_2$),

4.6 Reference

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CHAPTER V

CLAY CATALYSED VAPOUR PHASE REACTIONS

5.1 Vapour phase Friedel-Craft's alkylation

Conspectus

One of the important methods for introducing alkyl substituents into the aromatic systems is through Friedel-Crafts alkylation. Homogeneous Lewis acidic catalysts are used for the reaction. This introduces several problems such as tedious work up, use of corrosive chemicals, moisture sensitivity, decreasing regioselectivity and so on. To overcome the drawbacks, replacement of soluble Lewis acids is made by solid acids which facilitates improved procedures. In this chapter, Friedel-Crafts alkylation is presented using the prepared kaolin catalysts. The products are characterized and the yields are compared with standard clay catalysts. Recycling nature of the catalyst was examined.

5. 1. 1 Introduction

Friedel-Crafts alkylation is an important means of attaching alkyl chains to aromatic rings and hence is a key reaction in organic chemistry. Traditionally, homogeneous Lewis acid catalysts like $AlCl_3$, BF_3, and $SnCl_4$ are used for Friedel-Crafts alkylation. However use of Lewis acid catalysts is encountered with several problems like difficulty in separation and recovery of products, deactivation of spent catalyst, corrosion, high toxicity etc. These Lewis acids also catalyze other undesirable reactions like alkyl isomerizations and trans alkylation reactions. In order to reduce isomerization and disproportionation in aromatic alkylation catalyzed by $AlCl_3$, the reactions are generally carried out at low temperature and in solvents like carbon disulphide and nitromethane, which are more hazardous in nature. Moreover, these catalysts are moisture sensitive and hence demand moisture free solvent and reactants, anhydrous catalysts and dry atmosphere for their handling. Most of the catalysts have to be added in stoichiometric amounts, thereby adding to the cost of the desired product. Hence, worldwide, efforts have been made to replace the present environmentally sensitive catalysts with solid acid catalysts[1].

The alkylation reaction of phenol with *t*-butyl alcohol is of industrial relevance and also of academic interest. The product, *p*-*t*-butyl phenol (*p*-TBP) is used as a raw material for the production of a variety of resins, durable surface coatings, varnishes, wire enamels, printing inks, and so forth. Other applications of *p*-TBP include surface-active agents, rubber chemicals, antioxidants, fungicides, and petroleum additives. Although both homogeneous and heterogeneous catalysts are used in alkylation reaction systems, the trend is definitely towards solid heterogeneous catalysts, due to the inherent advantages of their higher activity, better selectivity, ease of separation from reaction products, chemical stability, reusability, environmental friendliness, and absence of corrosion problems.

Montmorillonite supported zinc and nickel chlorides are found to be highly active and selective catalysts for Friedel-Crafts alkylation. Clays are the most promising catalysts and hence much of the active research has been concentrated in this field. Benzylation of benzene was carried out in the presence of clay catalysts originating from K10 montmorillonite. It was found that iron pillared clays were the most efficient catalysts producing quantitative conversions with greatly reduced amounts of catalysts in lesser reaction times[2].

Laszlo and co-workers have reported that K10 montmorillonite ion-exchanged with various transition metal cations are efficient catalysts for Friedel-Crafts alkylation of aromatics. Alkylation was done with wide range of alkylating agents such as alcohols, alkenes and alkyl halides. Based on these findings, the catalytic activity of transition and main group metal exchanged K10 in the alkylation reaction between anisole and dienes was also determined[3]. The samples exchanged with H^+, Al^{3+}, La^{3+} and Fe^{3+} gave a large amount of monoalkylated product. But the yield decreased with time because of retro-alkylation followed by diene polymerization occurred. The use of clays which were thoroughly dehydrated at 550°C before use strongly reduced these side reactions. Calcination under these conditions eliminates most of the Bronsted acid sites which are thought to be responsible for diene polymerization and retro-alkylation.

The enhancement in catalytic activity of cations such as Zn(II) has been achieved both through ion exchange as well as deposition of Zn(II) salts onto clay surfaces.[4] This has contributed to the study of the acidity and catalytic activity of such ions when incorporated directly into the lattice sites of synthetic clay minerals. Lewis acid sites are generated on Zn^{2+}-substituted fluorohectorite. The Zn^{2+} -substituted fluorohectorite was synthesised by a sol-gel route. The sol was allowed to crystallize in a Parr autoclave at 250° C for 24 hours. The Lewis acid sites were identified as Zn^{2+} at the edges of the fluorohectorite crystallites and were active towards the Friedel-Crafts alkylation of benzene with benzyl chloride.

The heterogeneous catalysts tested produced smaller amounts of the *ortho* isomer, the pillared montmorillonite being the most selective in this respect, giving only 15% of *ortho* product. The catalyst with a lower proportion of micropores such as delaminated synthetic hectorite and K10 gave lower yields *of meta* and *para* isomers than the microporous pillared clays.[5] The explanation for this low yield is that the *ortho* isomer diffusion, being slower than that of the *meta* and *para* isomers, isomerises or undergoes a second alkylation more readily than the other isomers. With catalysts containing a large proportion of micropores, diffusion control becomes important and the yield of the *ortho* isomer depends on the surface area contained in the micropores. This was confirmed by the fact that the yield of *ortho* isomer decreased as the particle size was increased.

There are a number of commercially available acid-treated clays and although K10 (available from Fluka) has been very popular for alkylation reactions, other acid-treated clays have been found to be equally effective in certain cases.[6] For example, the acid-treated clay Engelhard F-24 was found to be a very effective catalyst for the alkylation of diphenylamine with α-methylstyrene. The dialkylated diphenylamines produced in this reaction are industrially important as antioxidants and heat stabilisers in polypropylene and polyethers. Natural clays have also been used as catalysts for Friedel-Crafts alkylation reactions.

Natural vermiculite has been used as a highly active and selective catalyst for the Friedel-Crafts alkylation reaction between benzene and 4-methylbenzyl chloride. The important feature of vermiculite for this reaction appears to be its unusually high structural iron content. Indeed, vermiculite containing a much smaller amount of iron exhibited a lower activity than H^+ montmorillonite. Results from powder X-ray diffraction measurements indicated that the interlayer spacing of vermiculite did not change during the reaction. This implies that the interlayer region is too narrow to accommodate the reactants and only Lewis acid sites on the external surfaces, probably Fe^{3+} cations, are responsible for catalyzing the reaction[7].

A natural montmorillonite was used to catalyse the intermolecular condensation of toluene in the presence of bromine to produce *ortho-* and *p*-phenyltolylmethanes. The reaction was carried out at reflux using carbon disulfide as the solvent. The first stage of the reaction is believed to be the generation of benzyl bromide[8]. A bromide ion is abstracted from benzyl bromide by a Lewis acid site on the clay surface. The resulting electrophilic benzyl cation then attacks toluene. It has been found that Al^{3+}-exchanged natural saponite prepared by cation exchange with $Al(NO_3)_3$ exhibits a high catalytic activity towards the alkylation of toluene by methanol. The Al^{3+} saponite retained a high surface area even after calcination at 400°C and this is due to its unique three-dimensional structure. Saponites tend to form the so-called 'house-of-cards' structure, due to the electrostatic interaction between negatively charged faces and positively charged edges of the clay platelets.

The X-ray diffraction pattern of saponite exhibits a relatively weak and broad (001) reflection compared with montmorillonite, indicating a lack of long-range layer ordering. This characteristic of saponite can be ascribed to the three dimensional voluminous house-of-cards structure[9]. The house-of-cards structure also contributes to the high catalytic activity in comparison to montmorillonites, which do not form the house-of-cards structure. Alkylation activity depends directly on the type of exchanged cation. The saponites exchanged with Zr, Al or Ti cations, which have large hydration energies, exhibited very high activities comparable to that of alumina-pillared montmorillonite. The use of clay-based supported catalysts in Friedel-Crafts reactions adds a new dimension to this area and has resulted in successful application on an industrial scale.

Cerium exchanged NaX zeolite was used as catalyst for cumene synthesis by the alkylation of benzene with isopropyl alcohol with good activity and selectivity. No formation of *n*-propylbenzene was observed in the reaction product. A time on stream study showed that the catalyst was quite stable at an operating temperature of 473 K. Based on the product distribution, a reaction mechanism was proposed together with a rate expression for the disappearance of isopropyl alcohol. The kinetic and the adsorption constants of the rate equation were estimated by best fit. The activation energy for the cumene synthesis reaction was determined to be 110 kJ/mol.[10]

The alkylation of phenol with *tert*-butyl alcohol was carried out in batch mode with various catalysts. The zeolite Beta catalyst was observed to be the most efficient. Complete conversion of the limiting reactant could be observed with zeolite Beta catalyst. The zeolite obtained from fly ash and Ce-modified 13X zeolite also showed better results[11]. The 13X zeolite and virgin fly ash appeared to be less active when compared on the basis of equal loading. However, the activity of Ce-exchanged 13X zeolite was found to be comparable with other catalysts. The effects of various parameters, such as temperature, reactant composition, catalyst loading, and so forth, on phenol conversion as well as product selectivity were studied. An interesting feature of this study is the use of fly ash as the catalyst for the phenol alkylation reaction. Fly ash, which is a disadvantage to thermal power plants due to environmental pollution, could be converted to harmless byproducts by suitable treatment. This will definitely open up new areas of research.

5.1.2 Results and discussion

5.1.2.1 Optimization study of Friedel-Crafts Reaction

The effect of various reaction variables on the reaction was checked using catalyst G(Iron impregnated clay).A representative study of tertiary butylation of phenol using iron impregnated catalyst (Scheme.1) is considered and taken throughout the optimization studies. The reaction variables such as catalyst amount, reactant flow-rate, ratio of the reactant, and temperature are to be optimized. Only one variable was checked while keeping the other variables constant. With these details the standard reaction condition was set.

$$\mathrm{ArH} + \mathrm{RX} \xrightarrow[\text{VPR}]{\text{modified kaolin}} \mathrm{Ar.R} + \mathrm{HX}$$

Scheme 1: General scheme of Friedel-crafts alkylation

5.1.2.1.1 Effect of catalyst amount

Amount of catalyst plays an important role in any reaction and the optimum level was to be adopted. A series of reactions using different amounts of the catalyst were conducted. The results are shown in the table 1.

Table 1: Effect of amount of catalyst with yield of *t*-butylphenol

Sl. No	Amount of catalyst (g)	Yield (%)*
1	0.5	35
2	1.0	45
3	2.0	76
4	3.0	77

Reaction conditions: flow-rate: 6-9ml/h; temperature: 250°C

On going through the values of the yield of *t*-butylphenol, it is found that on increasing the amount of catalyst the yield also increased. When considering the optimization of the catalyst amount, the 2g catalyst will be of much significance and optimal amount for the reaction.

5.1.2.1.2 Effect of flow-rate

The flow-rate of any reactant in a vapour phase reaction is an important deciding factor for the optimization of the reaction. Increase in the flow of the reactant decreases the contact time with the catalytic surface and reduction in the yield of the product. The experiments were conducted with varying flow-rate and the results obtained are shown in the table

Table 2: Variation of yield with respect to flow-rate

Sl. No	Flow- rate (ml/h)	Yield (%)*
1	1-3	83
2	3-6	79
3	6-9	76
4	9-12	65

*Reaction conditions: catalyst amount: 2g; temperature: 250°C

From these values it can be concluded that the optimum flow-rate will be 6-9 ml/h when compared with other flow-rates. This flow-rate was considered to be optimum while considering comparatively better yield with the flow of the reactant.

5.1.2.1.3 Effect of ratio of the reactants

Though the reactant ratio is a much deciding factor, one of the reactants, *t*-butylalcohol, in these reactions is of solvent in nature. So the effect of reactant ratio is insignificant in this context. The solvents were taken in much excess to avoid the reactant ratio conflict.

5.1.2.1.4 Effect of temperature

Catalytic studies were conducted using the iron impregnated catalyst under the reaction conditions of 2g catalyst and flow-rate at 6-9ml/h. The effect of variation in temperature is shown in table 3.

Table 3: Effect of temperature on the yield of the product

Sl.No	Temperature (°C)	Yield (%)*
1	200	56
2	250	76
3	300	72
4	350	66

*Reaction conditions: catalyst amount: 2g; flow-rate: 6-9ml/h

5.1.2.2 Preparation of *t*-butylphenol using different catalysts

Catalytic studies were conducted to ascertain the efficiency of the prepared catalysts. Preparation of the *p*-tertiarybutylphenol was taken as the model reaction to study the efficiency of the catalysts. The results are shown in the table. 4. Reaction conditions are optimized as Amount of catalyst: 2g; flow-rate of reactants: 6-9 mL/h; temperature: 250°C.

Table 4: Comparison of yield of *t*-butylphenol obtained for prepared catalysts

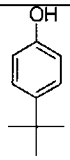
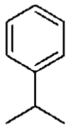
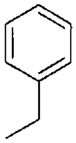
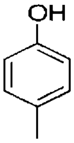
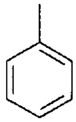
Sl. No	Catalysts	Yield (%)*
1	A	20
2	B	25
3	C	26
4	D	28
5	E	18
6	F	73
7	G	76
8	KSF	72
9	K10	20

*Reaction conditions: catalyst amount: 2g; flow-rate: 6-9ml/h; temperature: 250°C

5.1.3 Friedel Crafts alkylation using iron impregnated catalyst

From the results, iron impregnated clay, the more reactive catalyst, was adjudged to be the better one. Five derivatives, such as tertiary butylphenol, Cumene, Ethyl benzene, *p*- Cresol and Toluene were prepared using the same catalyst. The results are shown in the Table 5.

Table 5: Alkylation of aromatics catalysed by iron impregnated clay (G)

Sl.No	Reactant I	Reactant II /Solvent	Product	Yield (%)*
1	Phenol	Tertiary butanol		76
2	Benzene	Isopropyl alcohol		72
3	Benzene	C_2H_5OH		73
4	Phenol	CH_3OH		74
5	Benzene	CH_3OH		77

*Reaction conditions: catalyst amount: 2g; flow-rate: 6-9ml/h; temperature: 250°C

5.1.4 Recycling studies of the catalyst

The used catalyst was powdered well, washed with solvents such as acetone, and water. It was dried at 250°C and again pelletized. Using this catalyst the *t*-butylation of phenol was carried out. Three cycles were conducted and the results are shown in the table 7.

Table 7: Recycling studies of the selected catalyst

Sl. No	product	Yield(%)*		
		First cycle	Second cycle	Third cycle
1	t-butylphenol	98	92	89

*Reaction conditions: catalyst amount: 2g; flow-rate : 6-9ml/h; temperature: 250°C

5.1.5 Mechanism of the Friedel-Crafts alkylation

Friedel-Crafts alkylation involves the introduction of an alkyl group onto an aromatic substrate by treating the substrate with an alkylating agent such as alkyl halide, alkene, alkyne and alcohol in the presence of a Lewis acid. The mechanism of the clay catalysed Friedel-Crafts reaction is shown in the figure.1

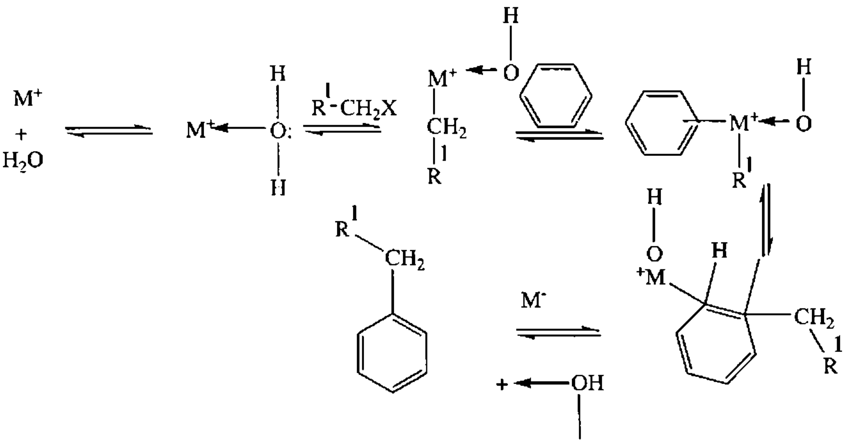


Figure 1: Mechanism of Friedel-Crafts alkylation

5.1.6 Advantages of the present approach

As per the normal procedure on Friedel-Crafts alkylation, there will be the use of aluminium trichloride, which is poisonous in nature. Moreover, handling of the moisture free condition makes the process tedious. Large amount of catalyst was needed for the reaction to take place. After the reaction, deactivation of catalyst and purification of the products were done by as much amount of chemicals. The yield of the products was comparatively low.

These draw backs were completely eliminated when vapour phase alkylation has been used as described in this chapter. The procedure has the advantage of total simplicity; the advantage of one of the reactant acts as solvent, makes the process quite simple and efficient. The yield obtained was comparable with the standard clays such as K10 and KSF. The catalyst showed appreciable stability even after prolonged reaction conditions. The reactivation can be done with much simpler procedure. The products were further characterized with GC, and standard spectral methods.

5.1.7 Conclusion

Friedel-Crafts reaction of various substrates and various catalysts were studied in detail. Raw clay exhibits least activity when compared with the highly active iron impregnated clays. The yield of the product was varied with the increasing acid concentration used for the clay activation. High activity was found for the iron impregnated clays which was comparable with the standard clays such as KSF and K10.

5.1.8 Experimental Section

5.1.8.1 Description of the vapour phase reactor

A glass column consisting of 40 cm length and 1.5 cm inner diameter has been used as the vapour-phase reactor. A furnace was constructed for inserting this glass column and to provide the required reaction temperature up to 500°C. A thermostat controlled Pneumatic instrument was used to control the temperature. The furnace was arranged in such a way that the internal temperature of the furnace would be within the limits of 5°C with the displayed temperature. Reactants which are flown from the external source are controlled manually. The reactor was filled with required catalyst and with supporting base. Supporting base consisted of silica beads of insulator quality. Since the reactor was held vertically, gravitation force was used to get the flow of the reactant and to get the product out. The product was cooled immediately on leaving the reactor by a coiled water condenser. The products were analyzed with Gas chromatography to ascertain the yield of the product. The products were further purified by physical methods such as column chromatography and characterized by spectral methods.

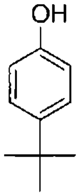
5.1.8.2 Shape of the catalyst

Since the reactions are to be done in vapour-phase, the shape of the catalyst plays an important role. Powdered catalysts render higher yield of the product, handling the powder make the process more hazardous. Moreover highly hazardous glass wool has to be employed to position the catalyst and supports in their place. Sintering of powdered catalyst was observed when reaction was in progress. So it was decided to have pellatized catalysts. More amount of catalyst means increase in the size of the pellets, and reduction in the contact area of the catalyst. The catalyst with minimum amount and maximum contact area was found to be a good alternative. With that intention a dye which could make pellets with 1cm diameter was prepared. The thickness of the pellets will be more if the amount of catalyst is more. If the amount of catalyst is less, thickness will be less and the catalyst will be more delicate and fragile in nature. So an average amount of 200mg was found to be quite sufficient for pellets of size 1cm in diameter. It was considered to be the standard size for the entire set of reactions.

5.1.8.3 Characterization studies of the products obtained

Characterization of the products so obtained is shown here. The products were characterized by spectral methods and by the physical constants.

a. *p*-tertiarybutyl phenol



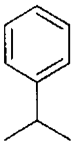
Appearance: Colorless Solid

M. P (°C) (Literature value is in parenthesis): 97 (99)

Elemental analysis (%) (Calculated for Molecular formula $C_{10}H_{14}O$, values are in brackets): C = 80.1(79.96), H = 9.2(9.39), O = 10.7(10.7)

FTIR (KBr ν_{max} (cm^{-1})): 1390($-C(CH_3)_3$), 3600(-OH)

a. Isopropylbenzene



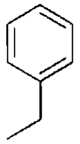
Colorless liquid

B. P.(°C) (Literature value is in parenthesis): 156 (152)

Elemental analysis (%) (Calculated for Molecular formula C_9H_{12}, values are in brackets): C = 90.2(89.96), H = 9.8(10.06)

FTIR (KBr ν_{max} (cm^{-1})): 1145(-CH(CH$_3$)$_2$), 2980(-CH$_3$)

b. Ethylbenzene



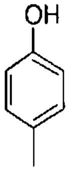
Colorless liquid

B. P. (°C) (Literature value is in parenthesis): 137 (136)

Elemental analysis (%) (Calculated for Molecular formula C_8H_{10}, values are in brackets): C = 90.3(90.51), H = 9.7(9.39)

FTIR (KBr ν_{max} (cm^{-1})): 2920 (-CH$_2$-CH$_3$)

c. *p*-Cresol



Colorless solid

M. P. (°C) (Literature value is in parenthesis): 34 (35.5)

Elemental analysis (%) (Calculated for Molecular formula C_7H_8O, values are in brackets): C = 76.5(77.75), H =8.0 (7.46), O = 15.2(15.5)

FTIR (KBr ν_{max} (cm^{-1})): 2970 (-CH$_3$), 3610(-OH)

5.1.9 Gas Chromatographic conditions for alkylation products

Column : 30% carbowax 20M

Oven : 170°C (Isothermal)

Injector : 200°C, N_2-1.05 Kg/cm^2 (15psi)

Detector : 200°C (FID)

Gas Chromatographic conditions for t-butylphenol

Gas Chromatographic separation of p-teriarybutyl phenol consists of two columns. Pre column consists of liquid phase 10% PFA, Solid support CHW, Mesh 80/100, length – 15cm, dia 0.31cm (1/8"). Actual Column consists of 10%PFAP, 2M length, and 0.31cm (1/8") dia.

Injector : 170°C

Detector : : FID 200°C

Oven temperature : 170°C

Flow : 1.92 Kg/cm^2 (27.3 psi)

5.1.10 Reference

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5.2 Vapour Phase Esterification using clay catalysts

Conspectus

Esters represent an important class of chemical compounds with applications as solvents, plasticizers, flavors and fragrances, pesticides, medicinals, surfactants, chemical intermediates, and monomers for resins. In this chapter attempts have been made to prepare esters of carboxylic acids through vapour-phase reactions. Five different esters were made and the products were characterized using physical constants, FT-IR and other spectral methods. The yields are compared with standard clays. Recyclability of the prepared catalysts has also been tested.

5.2.1 Introduction

Esters are most commonly prepared by the reaction of a carboxylic acid and an alcohol with the elimination of water. They are also prepared by the methods using acid anhydrides, acid chlorides, amides, nitriles, unsaturated hydrocarbons, ethers, aldehydes, ketones, alcohols and esters (transesterification). The choice of the proper catalyst for an esterification reaction is dependent on several factors. The most common catalyst used are strong mineral acids such as sulphuric and hydrochloric acids. Lewis acids such as boron triflouride, tin, zinc salts, aluminium halides, organo-titanates have been used. Cation-exchanged zeolites are also often employed. Catalytic esterification of alcohols and acids in the vapor phase has received attention because, the conversions obtained are generally higher than in the corresponding liquid-phase reaction[1].

5.2.2 Clay as the catalyst

Use of homogeneous acid catalysts leads to post treatment pollution problems apart from the quality-related issues. The current work is focused in an eco-friendly and benign catalytic process, employing solid acid catalysts. Smectite, atapulgite and vermiculite clay have been found to catalyse efficiently transesterifications and enamino ester formation in one-pot reaction from β-keto esters, carbohydrate derivatives and amines, in good to excellent yields without decomposition of the carbohydrate moieties[2-4]

Acidified clay is provided with more surface area and acid sites. Molecular ammonia desorption on purified clay and acidified clay occurs at temperatures 873 and 1000 K, respectively, shown for the existence of strong acid sites. The process of substitution occurs apart from octahedral aluminium which implied that acid sites are located around the octahedral aluminium, and substitution of Al^{3+} for tetrahedral Si will be favorable for the surface acidity enhancement.[4-6]

In two reactions of the tetrahydropyranylation of n-propanol and the esterification of cyclo-2-pentene with acetic acid, it is shown that the acidified clay displays better catalytic activity for the above two organic reactions. Solid acid catalysts such as dodecatungstophosphoric acid (DTP) supported on K-10 clay, ion-exchange resins, sulfated zirconia, etc. have been used for esterification of p-cresol with phenylacetic acid to p-cresylphenyl acetate. The catalyst has excellent reusability and that the reaction was 100% selective towards p-cresyl phenyl acetate.[7-12]

Esterification of succinic anhydride to di-(p-cresyl) succinate over heterogeneous acid clay catalysts was reported. Montmorillonite clay samples exchanged with different cations were prepared and catalytic activity of the resulting materials was investigated in the synthesis of di-(*p*-cresyl) succinate esters. [13] Among the exchanged clay catalysts, Al^{3+} and H^{+}-montmorillonite were found to be more active for the esterification of succinic anhydride with p-cresol. The influence of molar ratio of reactants, reaction time, and catalyst amount on the esterification reaction was investigated. The esterification was found to follow the second order kinetics and the kinetic parameters such as rate constant (k), equilibrium constant (K) and Gibbs free energy (ΔG°) for the reaction have been determined. The activity of Al^{3+}-mont clay catalyst for the esterification of succinic anhydride with phenol, *m*-cresol, *o*-cresol, *p*-nitrophenol and resorcinol has been studied. Regeneration and reusability of the clay catalyst has also been investigated.

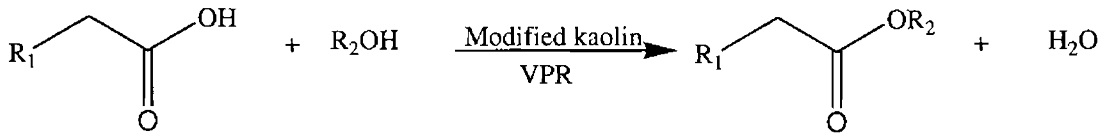
A pseudo-homogeneous kinetic model was developed from the experimental data and activation energy was found to be 14.2 Kcal/mol, which also suggested that this reaction was intrinsically kinetically controlled.[14] Fe^{3+}-montmorillonite clay catalyst was used for the first time to esterify various aliphatic, aromatic, α, β-unsaturated mono- and dicarboxylic acids and long chain fatty acids with alcohols under mild reaction conditions in good to excellent yields. The reported heterogeneous catalytic system was a potential candidate not only for laboratory practice but also for commercial application and offered an environmentally safer alternative to the existing processes.[15-17] The addition of aliphatic acids to a wide variety of alkenes to form esters was heterogeneously catalyzed by ion-exchanged sheet silicates. Cation exchange of the silicate is a prerequisite since natural montmorillonite is a poor catalyst for these reactions. Exchange with almost any multivalent ion induces some degree of catalytic activity, but Al_2O_3 and CrO_3 with H^+ ion-exchanged clays proved the most efficient catalyst in the present context. The reactions were carried out in pressure vessels, the reaction temperature range depending on the nature of the alkene employed. Esterification is in competition with alkene oligomerisation, and the synthesis of *t*-alkyl esters failed at temperatures much above room temperature due to the rapidity of the competing process[18].

Esterification of acetic acid with cyclohexene was carried out in the temperature range of 70-120°C with Amberlyst-15 (cation-exchange resin) and Filtrol-24 (acid-treated clays) as catalysts. The effect of the mole ratio of acetic acid to cyclohexene and the effect of the temperature on the selectivity of the ester (cyclohexyl acetate) were studied. The possibility of using aqueous acetic acid to produce cyclohexyl acetate and cyclohexanol simultaneously were also explored. Transesterification of cyclohexyl acetate with n-butanol was studied in the temperature range 120-160°C with the above catalysts. The transesterification reaction was accompanied by a side reaction leading to the formation of butyl cyclohexyl ether which may well be of value to the perfume industry. Optimum conditions for selectively producing cyclohexanol were delineated. It was also possible to change the operating conditions to give up to 80% butyl cyclohexyl ether[19, 20].

5.2.3 Results and Discussion

Catalytic studies were conducted to ascertain the efficiency of the prepared catalysts. Preparation of ethylbenzoate was taken as the standard reaction to study the activity.

The reaction scheme is denoted in scheme 2



Scheme 2: Esterification reaction

The yield of the products was compared with the standard catalysts such as KSF and K10. The results are shown in table 8. Reaction conditions are optimized as amount of catalyst:2g; flow-rate of reactants: 6-9 mL/h; temperature: 250°C.

Table 8: Preparation of ethyl benzoate using the catalysts

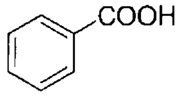
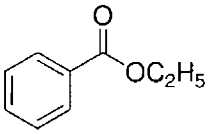
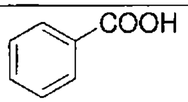
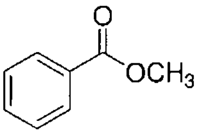
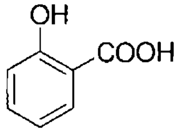
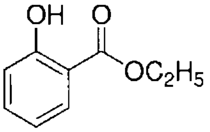
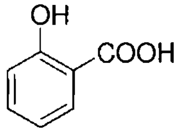
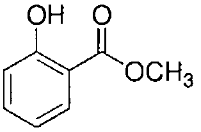
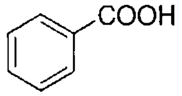
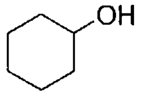
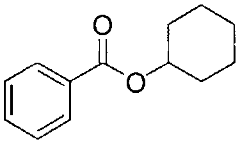
Sl.No	Catalyst	Yield obtained (%)*
1	A	43
2	B	59
3	C	72
4	D	72
5	E	62
6	F	93
7	G	96
8	KSF	90
9	K10	89

*Reaction conditions: catalyst amount: 2g; flow-rate: 6-9ml/h; temperature: 250°C

5.2.3.1 Preparation of esters catalysed by modified clays

From the above results, the highly reactive catalyst was adjudged to be the iron impregnated clay. Different esters were prepared using the selected catalyst. The prepared derivatives are ethylbenzoate, methylbenzoate, ethylsalicylate, methylsalicylate and cyclohexylbenzoate. The results are shown in the table 9.

Table 9: Preparation of esters using iron impregnated clay catalyst

Sl. No	ReactantI	ReactantII/ Solvent	Product	Yield* (%)*
1		C_2H_5OH		96
2		CH_3OH		96
3		C_2H_5OH		89
4		CH_3OH		86
5				90

*Reaction conditions: catalyst amount:2g; flow-rate: 6-9mL/h; temperature: 250°C

5.2.3.2 Recycling studies of the catalysts

The recycling study of the catalyst was conducted using the highly active iron catalyst. The used catalyst was powdered well, washed with solvents such as acetone, and water. It was dried at 250^{o}C and again pelletized. The pelletized catalyst was used for esterification reaction. Three cycles were conducted and the results are shown in table 10.

Table 10: Recycling studies of the selected catalyst

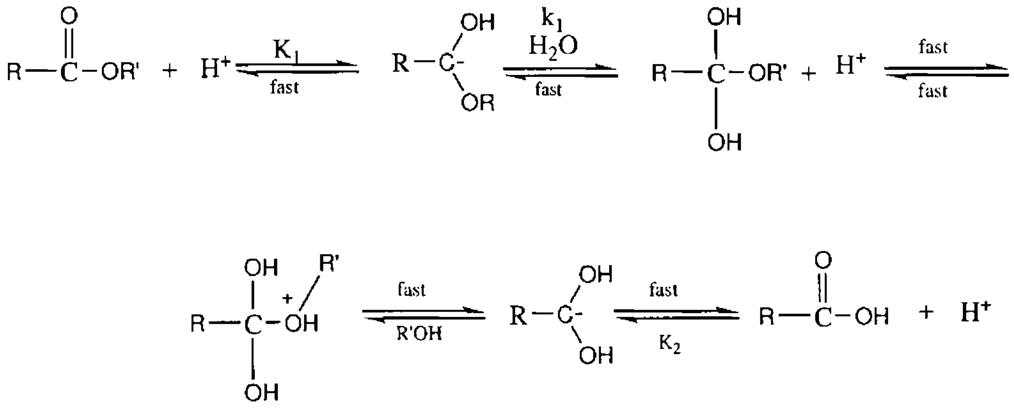
Sl. No	product	Yield(%)*		
		First cycle	Second cycle	Third cycle
1	Ethyl benzoate	96	92	89

*Reaction conditions: catalyst amount :2g; flow-rate : 6-9mL/h; temperature : 250^{o}C

5.2.3.3 Conclusion

Vapour-phase esterification reaction has also been carried out using the same methods and procedures. The esterification reaction of benzoic acid with ethyl alcohol was taken as the reference reaction and was studied for the activity of the prepared catalysts. The advantage of the vapour phase reaction is that it is conducted in a continuous flow reactor. The yields of the products can be controlled by adjusting the flow of the reactants into the reactor. Since the reaction is in vapour phase condition, monitoring the progress of the reaction is easier. Catalyst removal and thereby the regeneration of the catalysts is made easy. The simple method of conducting the esterifcation process, relatively low amount of by-products, easier method of purification, requirement of relatively low amount of supporting reagents and conditions render the reaction a green one.

5.2.3.4 Mechanism of the Esterification Reaction



5.2.4 Experimental Section

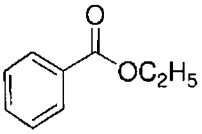
5.2.4.1 Typical experimental conditions

Vapour phase reactor and the necessary accessories were described in length in the section of Friedel-Crafts alkylation reaction. The conditions necessary for the optimization of the reaction like shape of the catalyst, variables like amount of catalyst, flow rate, reactant ratio and the temperature were adopted from the vapour phase alkylation section. The products were cooled to room temperature and the yield was calculated using Gas Chromatography methods. Excess solvents have been removed by vacuum distillation. The products were dissolved in ether and extracted with aqueous solution of sodium bicarbonate. The ether extract was washed with water to neutral and dried over anhydrous sodium sulphate. Evaporation of the solvent yielded crude esters. The products were purified by column chromatography and characterized using standard spectral methods.

5.2.4.2 Characterization studies of the products obtained

Yields were calculated using Gas-chromatographic method and products were characterized with standard spectral methods.

Ethyl benzoate



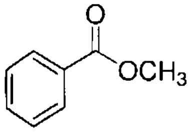
Appearance: Colorless liquid

B. P(°C) (Literature value is in parenthesis): 215 (211-213°C)

Elemental analysis (%) (Calculated for Molecular formula $C_9H_{10}O_2$): C = 72.3(71.98), H = 6.5(6.71), O = 21.7(21.31)

FTIR (KBr v_{max} (cm^{-1})): 1025 (C-O-C), 1720(C=O)

Methyl benzoate



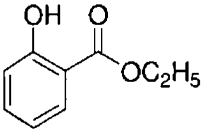
Appearance: Colorless liquid

B. P (°C) (Literature value is in parenthesis): 200 (199.6)

Elemental analysis (%) (Calculated for Molecular formula $C_8H_8O_2$): C =71.2 (70.57), H = 5.8 (5.92), O = 23.0 (23.5)

FTIR (KBr v_{max} (cm^{-1})): 1290 (C-O-C), 1710 (C=O)

Ethyl salicylate



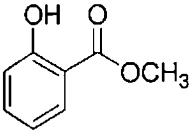
Appearance: Colorless liquid

B. P (°C) (Literature values are in parenthesis): 231 (231-234)

Elemental analysis (%) (Calculated for Molecular formula $C_9H_{10}O_3$): C = 66.0(65.05), H = 5.8(6.07), O = 29.2(28.88)

FTIR (KBr v_{max} (cm^{-1})): 1212 (C-O-C), 1725 (C=O), 3300 (-OH)

Methyl salicylate



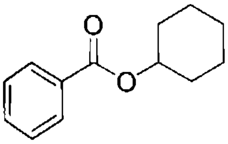
B. P (°C) (Literature values are in parenthesis): 222 (220-224)

Appearance: Colorless liquid

Elemental analysis (%) (Calculated for Molecular formula $C_8H_8O_3$): C = 62.2, (63.15), H = 5.3(5.3), O = 31.6(31.55)

FTIR (KBr v_{max} (cm^{-1})): 1709(C=O), 3225(-OH)

Cyclohexylbenzoate



Appearance: Colorless liquid

Elemental analysis (%) (Calculated for Molecular formula $C_{13}H_{16}O_2$): C = 76.0(76.44), H = 8.0(7.9), O = 15.4(15.67)

FTIR (KBr ν_{max} (cm^{-1})): 1110(aryl-C-O-C cyclic), 1290 (C-O str. cyclic), 1715(C=O)

5.2.7.3 Gas Chromatography conditions for esterification products

Column	Capillary 30M,
Oven Temperature	Initial 80°C (5 min), Rate: 5°C/min,
	Final temperature: 200°C,
Injector	180°C
Detector	FID, 200°C, H_2/Air- 1.40/15.46Kg/cm^2
(20/220 psi)	
Carrier flow (N_2)	1.21Kg/cm^2 (17.2 psi)

5.2.8 References

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CHAPTER VI

MICROWAVE ASSISTED CLAY CATALYSED REACTIONS

Conspectus

In this chapter the activity of catalysts are examined for the microwave mediated organic reactions. Clay catalysed esterification and oxidation of alcohols using chromium trioxide were carried out. Products were characterized by standard methods. Microwave oven of domestic type was employed for the purpose.

6.1 Microwave assisted organic reactions – An overview

Microwave, a nonionizing radiation incapable of breaking bonds, is a form of energy and is manifested as heat through the interaction with the medium or materials wherein it can be reflected (metals), transmitted (good insulators that will not get heated) or absorbed (decreasing the available microwave energy and rapidly heating the sample). Microwave (MW) irradiation, an unconventional energy source, has been used for a variety of applications including organic synthesis wherein chemical reactions are accelerated because of selective absorption of MW energy by polar molecules, nonpolar molecules being inert to the MW dielectric loss[1].

Dielectric loss is the amount of electromagnetic energy absorbed by molecules. Its origin is in how microwave energy is obstructed by matter (dielectric constant) and how energy is dissipated in the sample. Molecular dipoles are normally randomly orientated, but they orientate themselves according to the external electric field. For small non-associated molecules (molecular weight < few hundred, no hydrogen bonding) dielectric relaxation times are so short that they follow the external electric field of microwaves and do not heat. Small associated and large molecules (dipoles) have such long relaxation times that they do not have time to orient themselves and thus the rapidly changing electric field causes heating when dipoles hit each other when some are relaxing and some are excited again as shown in figure 1.

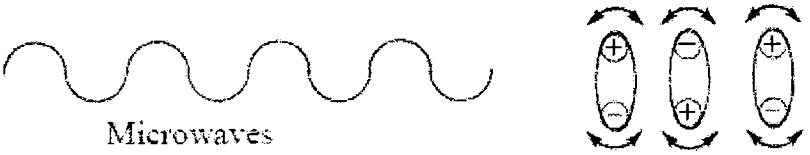


Figure 1: Microwave induced dipole rotation

The common way to explain the microwave heating effect is when a reaction is done in a polar microwave absorbing solvent. There is no microwave effect since the solvent absorbs most of the microwave energy and there is no additional energy going to the reactants. So, no matter what kind of reaction is done, no rate enhancement is detected due the microwave effect. Sometimes, however, it has been reported that rate enhancement was detected. Usually rate enhancements can be explained by the superheating of the solvent. It is possible to achieve 10-15 °C higher boiling points in polar solvents when they are heated with microwaves compared to conventional heating[2].

The first publication on the use of microwaves in assisting organic reactions is the modification of starch which came in 1974. According to most publications, the first reaction to use microwave heating have been carried out in 1986[3]. It took some time before microwave heating was widely accepted in organic synthesis, maybe due to the non-reproducible results of the domestic microwave oven. After microwave reactors were developed specially for organic chemistry (pressure, temperature and power can be precisely measured and adjusted), microwave heating has reached ever-growing popularity, especially in pharmaceutical industry. Over the last decade, microwaves have been intensively used in organic chemistry as a heating method, mainly because it is fast. There are many excellent reviews on different applications where microwaves can be used[4].

The application of microwave irradiation in conjunction with the use of catalysts or mineral-supported reagents, under solvent-free conditions, enables organic reactions to occur expeditiously at ambient pressure[5-11], thus providing unique chemical processes with special attributes such as enhanced reaction rates, higher yields, and the associated ease of manipulation. Heterogeneous reactions facilitated by supported reagents on inorganic oxide surfaces have received attention in recent years.[12] Selective and easy synthesis of acylals ($R\text{-}C(OOCR)_2$) in dry media using montmorillonite K10 clay in an Erlenmeyer flask under microwave activation in remarkably reduced reaction time was described.[13] The reaction of primary and secondary amines with epoxides in the presence of montmorillonite K10 clay, under solvent free conditions and microwave irradiation affords high yields of β-amino alcohols. Ring opening of epoxides with primary and secondary amines can be achieved within 1 minute under environmentally friendly solvent-free conditions under microwave irradiation in the presence of montmorillonite K10 clay as solid support. These organic reactions are safe and take place more rapidly and with higher yields compared to conventional heating[14].

The synthesis and characterization of aluminium-pillared rectorite was studied. The synthesis was conducted with both conventional heating and microwave irradiation. Microwave irradiation was found to enhance the intercalation and ion-exchange during synthesis, and to be able to produce the rectorite with a larger d001 and a better uniformity. The aluminium-pillared rectorite showed a high specific surface area, good thermal and hydrothermal stability, and showed promising applications as catalyst carriers and adsorbents for waste treatment. MW-expedited approach was described for the synthesis of a variety of industrially significant compounds and intermediates, namely, imines, enamines, enones, nitroalkenes, oxidized sulfur species, and heterocycles. This methodology is exemplified by a concise synthesis of flavones, tetrahydroquinolines, 2-aroylbenzofurans, and thiazole derivatives and demonstrates the exploitation of *in situ* generated reactive intermediates in one-pot synthesis of heterocyclic compounds. The adaptability of the protocols to rapid and parallel synthesis in solvent-free multicomponent reactions is demonstrated in the assembly of imidazo[1,2-

a]annulated pyridines, pyrazines, and pyrimidines (Ugi reaction) and dihydropyrimidine-2(1*H*)-ones (Biginelli reaction) [15].

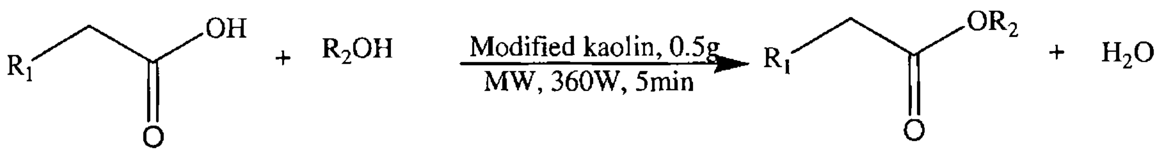
Montmorillonite KSF and K10 clays catalyzed effectively the reaction of methyl diazoacetate with various aldehydes using microwave irradiation under solvent-free conditions affording the corresponding β-keto esters in good yields and short reaction time[16]. This method is an improvement for the previous known synthetic methods and has many obvious advantages compared to them including the high efficiency, generality, high yields, operational simplicity, environmental benignity, and possibility of recycling the natural solid clays. The new method for the formation of acylals, without any solvent under microwave irradiation, offers significant improvements over the existing procedures and constitutes a useful and important addition to the present methodologies. The main advantages are mild reaction conditions, reduced reaction time, lack of side-products and excellent yields.

6.2.1 Esterification reaction under microwave irradiation

Catalytic esterification reaction by conventional methods is well known. However esterification reactions are characterized by low rate, which in turn requires large reactor size, large volume of reactants, difficulty in processing reactants and products thereby increasing manufacturing costs. Traditional esterification processes have reached their optimum performance; on the other hand due to various applications of esters the demand for the same is increasing every day. Studies on esterification using Microwave Technology can be conducted more easily, rapidly and efficiently to give esterification product with good yield and purity. Reactions which benefit more from the presence of microwaves are obviously those which have low rates under traditional conditions. Microwave irradiation is definitely a different and non-traditional, safe, inexpensive approach towards the synthesis of esters which can bring revolution in ester manufacturing industry. The effect of microwaves on chemical reactions is evaluated by comparing the time needed to obtain a given yield of the final product with respect to traditional heating. For evaluating the benefit of microwave power, the effect of above mentioned reaction parameters were also studied using same catalysts by traditional methods. It was seen that excellent results were obtained in the presence of microwave radiation. Studies were conducted using modified microwave ovens. Acid-catalyzed esterification of benzoic acid with ethanol was investigated in a continuous tubular flow reactor heated by microwaves[17]. The microwave reactor was operated at medium pressure and high temperature conditions. Esterification was catalyzed with sulfuric acid and with ion exchange resins. Kinetic parameters of esterification were determined in a stirred glass vessel using conventional heating. A mathematical model was proposed to describe temperature profiles and to predict the conversion of the reactant in the tubular flow microwave reactor. The calculated conversions of benzoic acid based on predicted temperature profiles agreed with experimental data. The operating conditions in the microwave reactor allowed to achieve high conversions at relatively low residence times.

6.2.1 Results and discussion

In this study, the prepared catalysts were used for esterification reaction. The efficiency of the catalysts in both conventional heating and microwave heating is compared. The conventional heating involved heating the reaction mixture with the refluxing vessel. The microwave heating is employed using the house hold microwave oven (LG model 192W).. The reaction is shown as scheme 1.



Scheme 1: Esterification reaction under microwave condition

Preparation of ethyl benzoate was taken as the reference reaction. The acid-catalyzed esterification of benzoic acid with ethanol using the prepared catalysts was carried out. The yields obtained from both conventional heating and under the influence of microwave are presented in table 1.

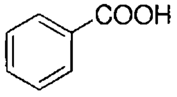
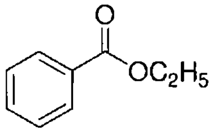
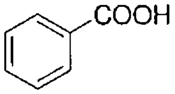
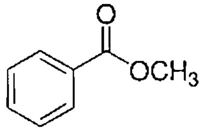
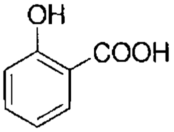
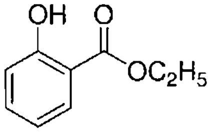
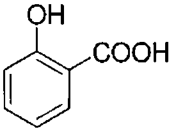
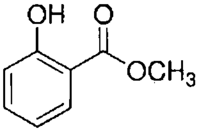
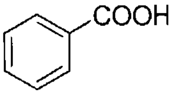
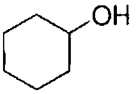
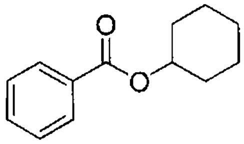
Table 1. Preparation of ethylbenzoate under conventional heating and microwave heating

Sl.No	catalysts	Conventional yield (%)	MW yield (%)*
1	A	3	40
2	B	12	67
3	C	16	76
4	D	17	79
5	E	18	82
6	F	26	91
7	G	31	95
8	KSF	27	90
9	K10	29	92

*Reaction conditions: catalyst amount-0.5g, time-5 min, 360W

The esterification of benzoic acid was carried out under reflux using magnetic stirring. This reaction was conducted for 6h which gave the best yield at 31% with iron impregnated catalyst (G). Likewise other prepared catalysts along with the standard clays gave comparatively low yield. The variation of yield obtained by other catalysts is shown in the table 1. The product obtained using iron impregnated catalyst was found to be in good yield with both in conventional heating and under the influence of microwave. Preparation of five varieties of esters such as Ethylbenzoate, Methylbenzoate, Ethylsalicylate, Methylsalicylate and Cyclohexylbenzoate were carried out using the iron impregnated catalyst under the microwave condition. The results are shown in the table 2. The products were checked for yield using Gas chromatographic methods, purified and characterized using standard methods.

Table 2: Comparison of yield of esters prepared using iron impregnated catalyst

Sl. No	ReactantI	ReactantII/ Solvent	Product	Yield (%)*
1		C_2H_5OH		95
2		CH_3OH		94
3		C_2H_5OH		88
4		CH_3OH		87
5				87

*Reaction conditions: catalyst amount-0.5g, time-5 min, 360W

The results presented in the Table 2, have shown that esterification reaction can be carried out using iron impregnated catalyst. The products obtained were in good yield.

6.2.1.1 Recycling of the catalysts

Recycling study of the iron impregnated catalyst was carried out for the ethyl benzoate preparation. The catalyst from the reaction media was purified using hot water and acetone. The catalyst was dried in an air oven and subjected to calcination at 250°C for 1h. The cycle was repeated for further studies and the results obtained are shown in table 3.

Table 3: Recycling study of selected catalyst G

Catalyst	Product	Yield obtained (%)*		
		First cycle	Second cycle	Third cycle
Iron impregnated clay (G)	Ethyl benzoate	95	93	90

*Reaction conditions: catalyst amount-0.5g, time-5 min, 360W

Even after the completion of three cycles the catalyst was found to have very good activity and is shown as a stable one.

6.2.2 Experimental

6.2.2.1Classical esterification reaction

Benzoic acid, (1.22g, 10mmol), was taken with catalyst (2.0g) and ethanol(25mL) was refluxed under anhydrous condition for 6h. The reaction temperature was maintained at the boiling point of ethanol. The reaction mixture was cooled and the yield was checked with gas chromatographic methods.

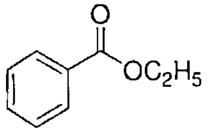
6.2.2.2 Procedure for MW assisted esterification reaction

Acid (1mmol), dry alcohol (3mL) and the catalyst (0.5g) were mixed in a glass tube with a loosely held stopper. The reaction was performed in the microwave oven at an engaged power of 360 W in an alumina bath and reaction time of 5 min. The reaction was followed by TLC (benzene: ethyl acetate 18:2) at one-minute time intervals. The alcohol was removed using a vacuum evaporator. The product obtained was dissolved in ether (10 ml) and extracted with aqueous solution of sodium bicarbonate. The ether extract was washed with water and dried over anhydrous Na_2SO_4. Evaporation of ether gave crude ester of benzoic acid[18].

6.2.2.3 Characterization studies of the products obtained

Yield was calculated using Gas-chromatographic method and the characterization was done using physical constants CHN analysis and IR spectral values.

Ethyl benzoate



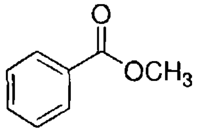
Appearance: Colorless liquid

B.P (°C) (Literature value is in parenthesis): 215 (211-213)

Elemental analysis (%) (Calculated for Molecular formula $C_9H_{10}O_2$): C = 72.3(71.98), H = 6.5(6.71), O = 21.7(21.31)

FTIR (KBr ν_{max} (cm^{-1})): 1025 (C-O-C), 1720(C=O)

Methyl benzoate



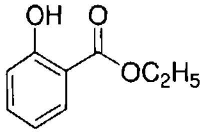
Appearance: Colorless liquid

B.P (^{o}C) (Literature value is in parenthesis): 200 (199.6)

Elemental analysis (%) (Calculated for Molecular formula $C_8H_8O_2$): C =71.2 (70.57), H = 5.8(5.92), O = 23.0(23.5)

FTIR (KBr v_{max} (cm^{-1})): 1290 (C-O-C), 1710 (C=O)

Ethyl salicylate



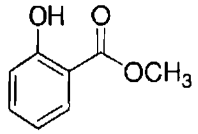
Appearance: Colorless liquid

B.P (^{o}C) (Literature value is in parenthesis): 231 (231-234)

Elemental analysis (%) (Calculated for Molecular formula $C_9H_{10}O_3$): C = 66.0(65.05), H = 5.8(6.07), O = 29.2(28.88)

FTIR (KBr v_{max} (cm^{-1})): 1212 (C-O-C), 1725 (C=O), 3300 (-OH)

Methyl salicylate



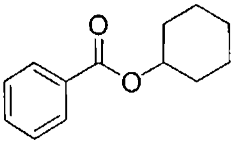
B.P (^{o}C) (Literature value is in parenthesis): 222 (220-224)

Appearance: Colorless liquid

Elemental analysis (%) (Calculated for Molecular formula $C_8H_8O_3$): C = 62.2, (63.15), H = 5.3(5.3), O = 31.6(31.55)

FTIR (KBr v_{max} (cm^{-1})): 1709(C=O), 3225(-OH)

Cyclohexylbenzoate



Appearance: Colorless liquid

Elemental analysis (%) (Calculated for Molecular formula $C_{13}H_{16}O_2$): C = 76.0(76.44), H = 8.0(7.9), O = 15.4(15.67)

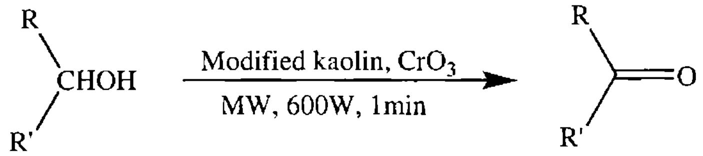
FTIR (KBr ν_{max} (cm^{-1})): 1110(aryl-C-O-C cyclic), 1290 (C-O str. cyclic), 1715(C=O)

6.3 Microwave assisted clay catalysed oxidation of alcohols

Reactions under dry conditions were originally developed in the late 1980s.[19] Synthesis without solvents under microwave irradiation offers several advantages.[20] The absence of solvent reduces the risk of hazardous explosion when the reaction takes place in a closed vessel in an oven. Moreover, aprotic dipolar solvents with high boiling points are expensive and are difficult to remove from reaction mixtures. During microwave induction of reactions under dry conditions, the reactants adsorbed on the surface of alumina, silica gel, clay, zeolites or similar material absorb the microwaves whereas the support does not, nor does it restrict their transmission. Consequently, such supported reagents efficiently induce reactions under safe and simple conditions with domestic microwave ovens instead of specialized commercial microwave systems that require sealed Teflon bombs can be used. The oxidation of alcohols to carbonyl compounds is an important transformation in organic chemistry which is attracting much current interest.[21] Although a large number of reagents are known in the literature for such a transformation, there still appears a need either to improve the existing oxidation methods or to introduce newer reagents to permit better selectivity under mild conditions and with easy work up procedures

6.3.1 Results and discussion

Oxidation of benzaldehyde was taken as the reference reaction to study the oxidation of alcohols. Two equivalents of Chromium trioxide and a weight equivalent of prepared catalyst per mol of benzyl alcohol were used and subjected to microwave irradiation for 1min. The catalysts were tested for the catalytic activity of the alcohol oxidation reaction and the results obtained are shown in table 4. The scheme of the reaction is shown in scheme 2.



Scheme 2: Oxidation of alcohol under microwave conditions

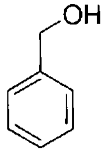
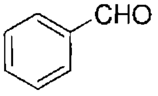
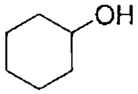
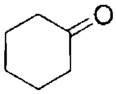
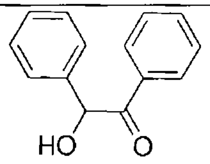
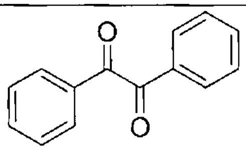
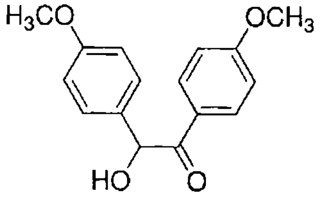
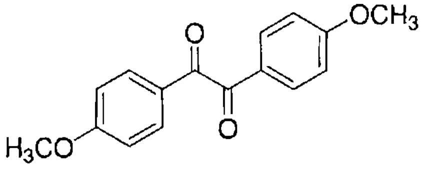
Table 4: Comparison of activity of the catalysts for the oxidation of benzyl alcohol

Sl. No	Catalyst	Yield (%)*
1	A	39
2	B	65
3	C	78
4	D	80
5	E	85
6	F	93
7	G	96
8	KSF	92
9	K10	94

*Reaction conditions: catalyst amount-1.0g, time-5 min, 600W

It can be inferred that the iron impregnated catalyst shows good yield when compared with other prepared and standard catalysts. To ascertain the superior nature of the catalyst, other carbonyl compounds such as Benzaldehyde, Cyclohexanone, Benzil and 4,4'-dimethoxy benzil were prepared using different alcohols. The reactants used and the products obtained along with yield are shown in table 5.

Table 5: Oxidation of alcohols using iron impregnated catalyst (G)

Sl.No	Reagent	Product	Yield (%)*
1			96
2			93
3			94
4			92

*Reaction conditions: catalyst amount-1.0g, time-5 min, 600W

6.3.1.2 Recycling of the catalyst

Since the activity of the iron impregnated catalyst is higher when compared with other catalysts, it was decided to do recyclability studies with this catalyst. The used catalyst was washed with water and acetone and dried. The catalyst was calcined at 250°C for 1h. This reactivated catalyst was used for the recyclability studies. The results are shown in table 6. Oxidation of benzyl alcohol was taken as the reference reaction.

Table 6: Recycling of the catalysts (G)

Catalyst	product	Yield (%)*		
		First cycle	Second cycle	Third cycle
Iron impregnated catalysts (G)	Benzaldehyde	96	93	91

*Reaction conditions: catalyst amount-1.0g, time-5 min, 600W

The activity of the catalyst was not significantly lost in the recycling steps.

6.3.2 Conclusion

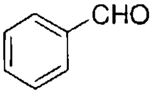
The modified clay catalysts were subjected to esterification and oxidation reactions. The efficiency of the catalysts in both conventional heating and microwave heating was compared in the esterification reaction. The conventional heating involved heating the reaction mixture with the refluxing vessel. The microwave heating was employed using the house hold microwave oven. The microwave enhanced reactions are characterized with low time and higher yield. Monitoring and control of the reaction are found to be advantageous. The product separation is much easier than conventional reactions. The products obtained are found to be of comparatively high purity. Works of this kind may be much easier if little modificationis done in the microwave oven setup. The time factor and the better procedure make the microwave reactions a green one.

6.3.4 General Experimental Procedure

Chromium trioxide(6mmol) and an equivalent of the catalyst was crushed together in a mortar so as to form an intimate mixture. Alcohol(10mmol) was added to this intimate mixture. The mixing of reactants continued thoroughly. The reactant along with the catalyst was placed in a microwave oven in an alumina bath and irradiated (600W) for one minute. The product was extracted into ether and filtered. The crude product so obtained was subjected to column chromatography using Hexane:Ethyl acetate (8:2) as eluent to get the corresponding carbonyl compound.[22]

6. 3.5 Characterization studies of the products

Benzaldehyde



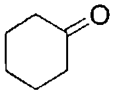
B.P (°C) (Literature value is in parenthesis): 182 (180-183)

Appearance: Colorless liquid

Elemental analysis (%) (Calculated for Molecular formula C_7H_6O): C = 79.3(79.33), H = 5.5(5.7), O = 15.2(15.08)

FTIR (KBr ν_{max} (cm^{-1})): 1700(aryl CHO), 1575 (ar C=C)

Cyclohexanone



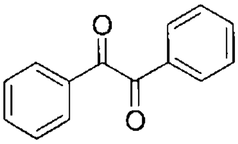
B.P (°C) (Literature value is in parenthesis): 157 (154-156)

Appearance: Colorless liquid

Elemental analysis (%) (Calculated for Molecular formula $C_6H_{10}O$): C = 76.3(76.44), H = 8.1(7.90), O = 15.6(15.67)

FTIR (KBr ν_{max} (cm^{-1})):960 (C-H bending out of plane) 1719(C=O, six membered ring cyclic)

Benzil



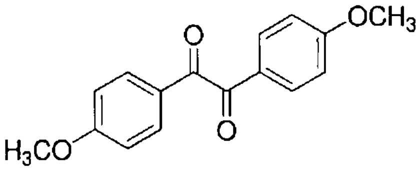
M. P (°C) (Literature value is in parenthesis): 94 (94-96)

Appearance: pale blue solid

Elemental analysis (%) (Calculated for Molecular formula$C_{14}H_{10}O_2$): C = 80.1(79.98), H = 4.7(4.79), O =15.32 (15.22)

FTIR (KBr ν_{max} (cm^{-1})): 1690(α-diketones), 1580(ar C=C)

4,4' dimethoxy benzil



Appearance: green solid

M. P (°C) (Literature value is in parenthesis): 133 (132-134)

Elemental analysis (%) (Calculated for Molecular formula $C_{16}H_{14}O_4$): C = 70.8(71.1), H = 5.3(5.22), O =23.9 (23.68)

FTIR (KBr ν_{max} (cm^{-1})): 1608(ar C=C), 1725(α-diketones), 1041 (C-O-C str)

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CHAPTER VII

TEMPLATE MEDIATED POLYMERIZATION REACTION USING MODIFIED CLAYS

Conspectus

Polyaniline (PANI) is one of the most important conducting polymers. It is commonly prepared by the oxidation of aniline with ammonium peroxodisulfate in an acidic medium. Polyaniline and polyaniline derivatives can be synthesized both chemically and electrochemically by using suitable protonation media. This chapter describes the preparation of polyaniline by template assisted polymerization using clays. Four types of polyaniline derivatives were prepared using the acid activated clay catalyst. The prepared polyaniline derivatives are Polyaniline/kaolin, Poly (o-Toluidine)/kaolin, Poly (o-Methoxyaniline)/kaolin, Poly (m-Chloroaniline)/kaolin which are characterized using IR Spectroscopy, UV Spectroscopy, SEM, Conductivity measurement and XRD techniques.

7.1 Introduction

Conducting polymeric materials containing conjugated π-bonds have attracted much interest in scientific and technological areas in recent years. Conducting polymers such as polypyrrole, polythiophene, poly(*p*-phenylene), and polyaniline have commonly been used, in scientific and industrial studies, as rechargeable batteries,[1,2] sensors,[3] and diodes, and in transistor and microelectronic devices,[4] and as modified electrodes.[5] Among the whole conducting polymers, polyaniline has a specific importance owing to its simple synthesis, good environmental stability, and ability to dope with protonic acids.[6–8] Therefore, attempts were made to overcome the unsolved problems such as solubility in common organic solvents, processibility at high temperature, and poor mechanical properties.[9–11]

Polyaniline and polyaniline derivatives can be synthesized both chemically and electrochemically by using suitable protonation media.[12–15] Works done using X-ray photoelectron spectroscopy on polyaniline and polyaniline derivatives by the protonation media were reported.[16,17] Moreover, it is demonstrated that the protonation level in e^-

acceptor groups is lower with respect to aniline and alkylanilines. Poly(*o*-toluidine) (POT) and poly(2-chloroaniline) (P2ClAn) have been synthesized using HCl, H_2SO_4, and $HClO_4$ as protonation media,[18–23] the correlation between properties of these polymers with pKa values of protonation media have been investigated. The synthesis of POT and P2ClAn using selected acids such as acetic, propionic, and boric as protonation media and the investigation of the effect of these acids on their properties have been reported.

Conducting microtubules of Polyaniline (PANI) were synthesized for the first time by the "*in situ* doping polymerization" method in the presence of β-naphthalenesulfonic acid (NSA) as dopant. Different doping methods, such as "immerse doping" and "grind doping," and different synthetic conditions, such as molar ratio of aniline (An) to NSA (An/NSA), concentration of NSA in the polymerization media, reaction temperature, and time were investigated to understand the formation of microtubules.[24] It was found that the PANI–NSA microtubules can be formed only by the "*in situ* doping polymerization" method, and the above synthetic conditions strongly affect the formation of the PANI–NSA microtubules, especially the molar ratio of An to NSA. An optimal condition was found under which tubules with 1–3 mm in diameter and 10–50 mm in length were obtained. The morphology of PANI–NSA tubules was proved by SEM and TEM, and their backbone structure was characterized by FTIR, UV-VIS, XPS, and X-ray diffraction. Results of these measurements showed that the molecular structures of the resultant PANI–NSA microtubules were identical to that of PANI–HCl synthesized by conventional method.

For the first time, it was demonstrated that the nanocomposite prepared by the aniline polymerization in montmorillonite according to the in situ polymerization was a polymer with tail-to-tail (benzidine) and head-to-tail (*p*-diaminobenzene) segments. The proposed polymeric structure was clearly contrasting with previous results using other spectroscopic techniques, showing that the Raman Resonance technique was a very powerful tool to study complex systems formed by conducting polymers and inorganic hosts[25].

Polyaniline/montmorillonite (MMT) nanocomposites containing different PANI content were prepared by the intercalation of aniline monomer into pristine MMT followed by the subsequent oxidative polymerization of the aniline in the interlayer spacings. The polyaniline/MMT nanocomposite structure intercalated with polyaniline (PANI) was examined by X-ray diffraction (XRD) and transmission electron microscopy (TEM). From the full-width at half-maximum (FWHM) of the (001) reflection peaks in the XRD patterns, the PANI/ MMT nanocomposite containing 12.3 wt% PANI (PMN12) was found to be in the most disordered state. The physical interaction between the intercalated PANI and the basal surfaces of MMT was monitored by FT-IR. The room-temperature conductivity (σRT) varied from 9.1×10^{-9} to 1.5×10^{0} S cm^{-1} depending on the PANI content in the nanocomposites. The FT-IR, σdc(T) and σRT results for the nanocomposites with varying content of PANI are consistently related to the structure of the PANI/MMT nanocomposites as revealed by the XRD patterns.[26] The structural argument was further supported by scanning electron microscopy (SEM) of all the samples. Thermogravimetric analysis (TGA) showed improved thermal stability for the intercalated nanocomposites in comparison with the pure PANI and a simple PANI/MMT mixture.

The preparation of composites in which polyaniline was deposited onto perlite particles by oxidative polymerization was reported.[27] Electrically conductive latex was prepared by homogeneously mixing submicron conductive composites with poly(vinylacetate-*co*-butylacrylate-*co*-butylversitate) resin in a desirable ratio. The conductivity of composites and latex was measured by a standard four-point probe. Morphology of composites was studied by scanning electron microscopy. Adhesion and electroactivity of the latex were also investigated.[28] Nanocomposites consisting of conducting polyaniline and clay minerals were successfully synthesized from mechanochemically intercalated anilinium fluoride; the nanocomposites prepared by the mechanochemical intercalation method contained much more polyaniline in the clay layers than those prepared by a conventional solution method. Consequently, the mechanochemical intercalation method provides a new and effective method for the preparation of PANI–clay nanocomposites.

A series of polyaniline-Fuller's Earth (PANI-FE) nanocomposites were prepared by the successive intercalation of anilinium ions followed by polymerisation within the interlayer spaces of Fuller's Earth (a type of calcium montmorillonite). The first member in the series was prepared by exchanging the calcium ions in Fuller's Earth for ammonium ions and subsequently for anilinium ions and polymerising the latter using an externally introduced oxidant. The emeraldine salt form of polyaniline formed was neutralised with ammonium hydroxide and more anilinium ions were exchanged for ammonium ions and polymerised to get the second member. In this manner, by making use of the unique chemistry of clay and polyaniline, four members of PANI/FE were prepared. In the last member, the negative layer charges of Fuller's Earth was completely neutralised by the positive charges of the polymer. The extent of polymer loading in each stage, the effect polymer has on the host structure and the electronic and ionic components of the conductivities of the new PANI/FE nanocomposites were investigated. The Fe(III) sites in FE are capable of spontaneously polymerising aniline within its inter galleries. The extent of spontaneous polymerisation was limited by the amount of Fe(III) present in the FE. The deliberate polymerisation of remaining anilinium ions by externally introduced oxidant resulted in highly conductive emeraldine salt-FE (EMS/FE) nanocomposites. The FE host accommodates higher amount of emeraldine salt and the repetitive insertions of the polymer could be done four times for complete layer charge neutralisation whereas with Bentonite, the layer charge saturation takes place with three successive insertions. The new EMS-FE nanocomposites exhibit more than order of magnitude and greater tuneable ionic and electronic conductivities compared to those of the same polymer incorporated in Bentonite.[29]

The spectroscopic characterization of polyaniline-montmorillonite clay (PANI/MMT) composites prepared by polymerization of aniline in aqueous suspensions of montmorillonite clay and camphorsulfonic acid containing persulfate ions as oxidizing agent was performed. The electrical conductivity values of composites increased from 10^{-4} to 10^{-1} S/cm^{-1} when PANI/MMT ratio was increased, and percolation threshold was observed when polymer/clay mass ratio was changed. Characterization data confirmed that PANI had emeraldine salt form for all PANI/MMT materials prepared.[30]

Recently, nanocomposites of conducting polymers of polyaniline (PANI), poly(ethoxyaniline) (PEOA) and polypyrrole (PPy) with clay prepared via either in-situ emulsion polymerization or solvent intercalation were investigated especially for electrorheological fluid (ER) application. The intercalated nanostructures analyzed via WAXD and TEM were correlated with the electrical property change originated from the nanoscale interaction between clay and conducting polymer. Moreover, their ER behavior was measured via rotational rheometer with external electric field controller[31].

The preparation, characterization and electrical conductive properties of intercalated polyaniline/Na-montmorillonite nanocomposites have been reported. These materials consisting of polyaniline and Na-montmorillonite were prepared by oxidative polymerization with benzoyl peroxide as oxidizing agent. The synthesized nanocomposites were investigated by a series of characterization techniques; including Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, and thermal analysis. X-ray diffraction and scanning electron microscopy images showed that the polyaniline was inserted into the clay layers. The modest increase in layer spacing was as much as 0.53 nm. The thermogravimetric analysis and differential thermal analysis demonstrated the improved thermal stability of the intercalated nanocomposites relative to the pure polyaniline due to the incorporated Na-montmorillonite. The room temperature electrical conductivity of nanocomposites varied from 1.0×10^{-7} to 5.8×10^{-5} Scm^{-1}.[32]

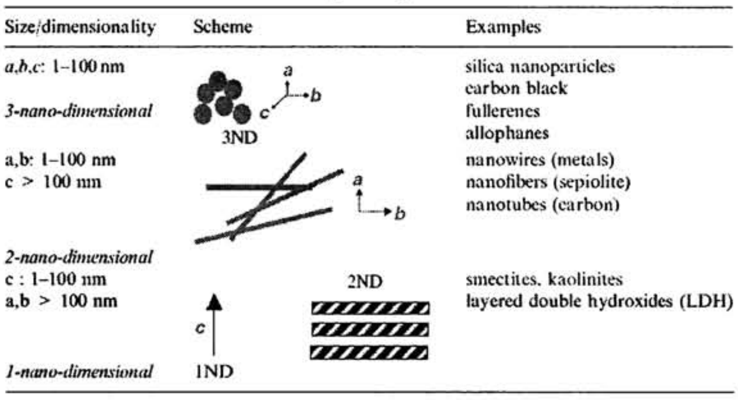
Different properties of polymer clay nanocomposite coatings consisting of different polymers were also reported.[33] These coatings may consist of conductive and nonconductive polymers. Some novel properties can be observed from the interaction of two dissimilar chemical components at the molecular level that possess enhancements in corrosion inhibition on metallic substrates.

Nanocomposites of polyaniline (PANI) with organophilic montmorillonite (O-MMT) and hydrophilic montmorillonite (Na-MMT) were prepared. It was found that PANI/Na-MMT nanocomposite had lower (5.8%) and PANI/O-MMT nanocomposite had higher (29.4%) conductivity compared to pure polyaniline. Cyclic voltammetry experiments showed that both nanocomposites were electroactive. The anticorrosive properties of a 100μm thickness coating of nanocomposites on iron coupons were evaluated and compared with pure polyaniline coating. The results showed that

PANI/MMT nanocomposites had enhanced corrosion protection effect in comparison to pure polyaniline coating. The PANI/Na-MMT and PANI/O-MMT nanocomposites have considerably different corrosion protection efficiencies in various corrosive environments.[34]

The development of inorganic-organic hybrid materials was especially trendy in the last decade. This is attested by the ever growing number of symposia, books, and specialised journals that are devoted to this subject. They parallel the intensive research activity in complex systems at the atomic/molecular scale (nanometer scale) of organic species of diverse functionality with inorganic entities, generally based on silica or silicates.

A well-accepted definition of nanocomposites is that the dispersed particles have at least one dimension in the nanometer range (nanofillers). Nanocomposites are usually classified according to the number of the nanodimensions of the filler. Thus, in the case of phyllosilicates like smectites integrated into nanocomposites, the clay–polymer nanocomposite could be considered as ''one-nano-dimensional'' (1ND) because the clay filler has one dimension at the nanometer scale, although the clay filler is two dimensional (2D) in the microscopic sense shown in figure 1.



Size/dimensionality	Scheme	Examples
a,b,c: 1–100 nm *3-nano-dimensional*	3ND	silica nanoparticles carbon black fullerenes allophanes
a,b: 1–100 nm c > 100 nm *2-nano-dimensional*		nanowires (metals) nanofibers (sepiolite) nanotubes (carbon)
c : 1–100 nm a,b > 100 nm *1-nano-dimensional*	2ND 1ND	smectites, kaolinites layered double hydroxides (LDH)

Figure 1: Dimensions of nano materials

Smectites could form nanocomposites using three preparation methods (i) direct incorporation of the polymers; (ii) in situ polymerisation of the monomers; and (iii) template synthesis of clay minerals. The clay mineral selected to prepare nanocomposites can occur in different forms such as powder, films, colloidal dispersion in water or in other polar liquids shown in figure 2. Depending on the polymer or monomer to be intercalated, the clay mineral can be used in the raw (untreated) state, or after specific modification.

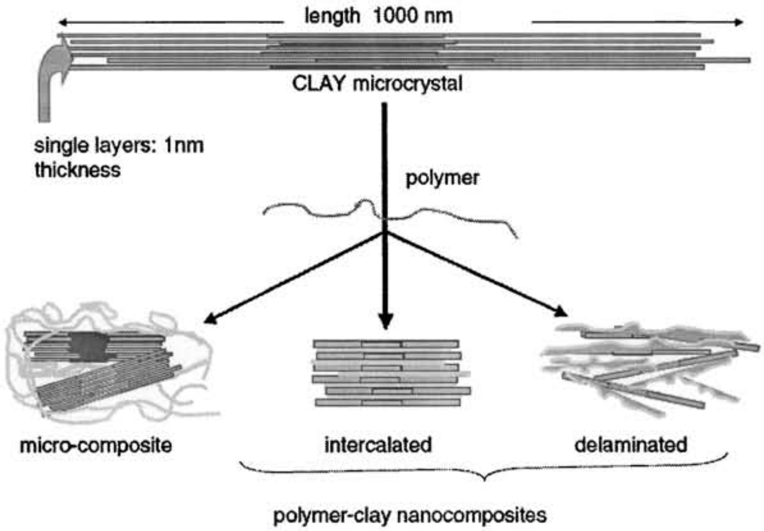


Figure 2: Types of clay nanocomposites

The possibility of achieving the homopolymerisation of unsaturated monomers, such as acrylonitrile and methyl methacrylate, previously intercalated in smectites was reported.[35] Numerous nanocomposite materials were prepared by the so-called ‘in situ intercalative polymerization’. For instance, the polymerisation of pyrrole and aniline in the interlayer space of a clay mineral was reported. In this process, interlayer exchangeable Cu^{2+} cations in smectites promote the formation of the aniline radical (by oxidation), inducing its polymerization into polyaniline (PANI). The interaction of pyrrole with iron-rich smectites, containing structural Fe(III), exchangeable Fe^{3+} species or associated oxyhydroxide of iron species, spontaneously gives clay mineral–PPy nanocomposites.

Polymers like PANI, PAN and PVP give hybrid materials with a controllable silicate/polymer ratio. This value determines both the structural arrangement and properties such as the electrical conductivity. The clay mineral–PANI nanocomposites prepared following this procedure are semi-delaminated, showing clay/polymer ratios smaller than those of their counterparts prepared by in situ polymerisation. One interesting characteristic of these nanocomposites prepared by this method is their ability to form well-dispersed systems in an aqueous medium without any loss of the polymer back into the solution.

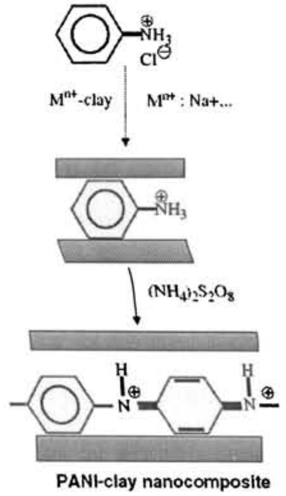


Figure 3: Schematic representation polyaniline intercalation

Polymer intercalation nanocomposites prepared using layered materials have received considerable attention because they are expected to lead to a high degree of polymer ordering and exhibit thermal stability and enhanced mechanical properties as represented in figure 3. The encapsulated conducting polymers in the interlayer spaces of organic layered materials may provide different characteristics and unique structure, which cannot be attained with a pristine conducting polymer. Therefore, nanocomposites consisting of conducting polyaniline (PANI) with various layered materials, such as MoO_3, V_2O_5 and clay minerals have been extensively studied. Among these nanocomposites, PANI–clay nanocomposites have been specially studied because clay minerals have attractive advantages such as large surface area and ion exchange properties. PANI–clay nanocomposites are usually prepared from mixtures of aniline and clays in an aqueous solution. However, it was observed that, using a mechanochemical reaction was an effective method for the preparation of PANI–clay nanocomposite. A mechanochemical reaction has obvious advantages such as being an environmentally benign process not using any solvents as well as a simple process. The control and enhancement of poly(aniline) (PANI) bulk properties is one of the greatest challenges in conducting polymer area. Synthesis of micro and nanostructured PANI can improve its electrical, thermal and mechanical stabilities. There are many routes for preparing these materials; through micellar media, interfacial, template-guided or aniline polymerization in the presence of inorganic or organic matrices resulting in PANI composites.

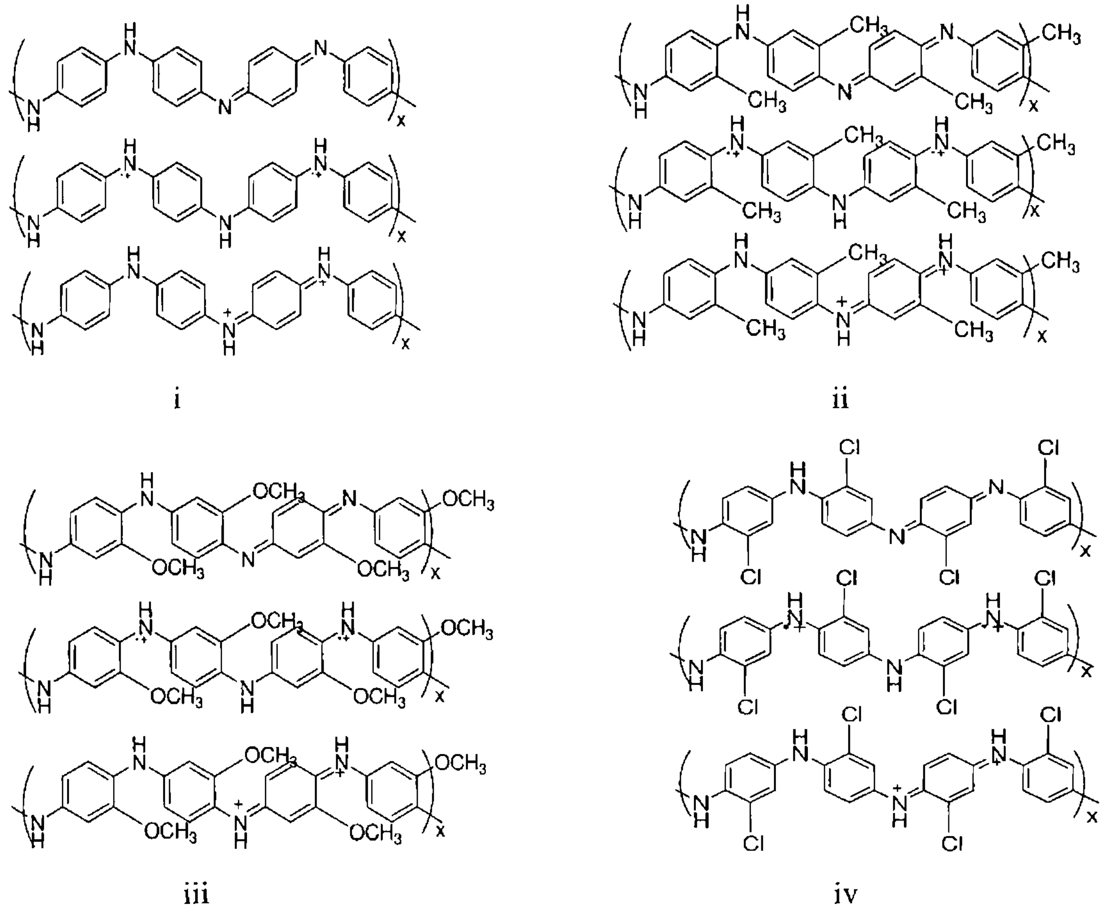
7.2 Results and Discussion

Four types of polyaniline derivatives were prepared using 5M HCl acid activated clay catalyst. The polyaniline derivatives were prepared by the reaction of corresponding aniline with potassiumperoxodisulphate in the presence of the acid activated catalyst. The prepared polyaniline derivatives are Polyaniline /kaolin, Poly (*o*-Toluidine)/kaolin, Poly (*o*-Methoxyaniline)/kaolin, Poly (*m*-Chloroaniline)/kaolin which are characterized using IR Spectroscopy, UV Spectroscopy, SEM, XRD techniques.

7.2.1 IR characterization

Schematic representation of the repeat units of the four polyaniline derivatives followed by assignments of characteristic IR bands of emeraldine salt form of polyaniline are shown in figure 4.

Frequency (cm^{-1})	Assignment
1582	ν(N Q N)
1501	ν(N B N)
1375	ν(C N) at different chemical environments
1306	
1240	
1143	B NH^+ Q
1043	δ(C H) in plane
827	δ(C H) out of plane



i ii iii iv

Figure4: Schematic illustration of polymer repeat units for (i) PANI (ii) Poly(o-toluidine), (iii) Poly(o-anisidine) and (iv) Poly(m-chloroaniline)

From FTIR bands, it was found that polymerization occurred with head-to-tail coupling. Characteristic bands corresponding to kaolin clay are shown at 1035 (v(Si–O)) and 915 (δ(Al–OH)); 990 and 450 cm^{-1} are for the Si–O–Si stretching in the infrared spectrum of acid activated clay. The FT-IR spectrum of pure PANI shows four major vibration bands at 1112 (para-substituted aromatic δ(C–H) in plane), 1296 (v(C–N)), 1487 (benzenoid ring v(C=C)) and 1562 cm^{-1} (quinoid ring v(C=C)).These bands are in good agreement with the observed frequencies of the prepared polyanilines with minor variations. It is well known that in systems intercalated with PANI, strong guest–host interactions, such as hydrogen bonding, occur in the form of NH...O, the $C_{aromatic}$ –N stretching with a 20cm^{-1} shift to 1303 cm^{-1} which is due to the hydrogen bonding.

Consequently, the frequency shift of ν(C–N) observed in the nanocomposite system is also caused by the physical interaction between PANI and the basal surface of kaolin clay (i.e.,NH...O hydrogen bonding).

The 1160–1200 cm^{-1} bands belong to the —NA-Q-AN or B—NH—B (where B denotes benzenoid and Q denotes quinoid ring) vibration bands of Poly(o-toluidine). The observed bands at 1260–1300 and 1000–1050 cm^{-1} belong to C—N stretching vibrations and C—H vibration bands, respectively. At 800–810 cm^{-1}, the peak corresponds to C—H bending vibration of *p*-phenyl rings and the peak at 850–900 cm^{-1} appears to be due to the methyl group attached to the phenyl ring. Twin bands centered around 2920 and 2850 cm^{-1} can be assigned to the aliphatic C-H stretching of the toluidine segment. Contrary to PANI, a new band appeared at 1119 cm^{-1} in the poly(*o*-toluidine) spectrum. This band is attributed to the C-C vibration in the methyl-group substituted semiquinoid (SQ) and quinoid (Q) rings.

The characteristic vibration bands of Poly(*o*-methoxyaniline)are located at 1461 and 1580 cm^{-1}, a medium-intensity peak at 1300–1325 cm^{-1} is due to the C-N stretching vibration in alternate units of quinoid–benzenoid–quinoid rings, whereas the band at 1375–1381 cm^{-1} corresponds to the C-N^+ stretching vibration. A band near 1107 cm^{-1} is assigned to C-H in-plane bending. The IR spectrum shows characteristic band at 1480 cm^{-1} for poly(*m*-chloroaniline) as its quinoid and benzenoid forms. The IR spectra of the prepared poly(*m*-chloroaniline) has characteristic band at 758 cm^{-1} attributed to the functional group of *m*-chloroaniline.

7.2.2 Conductivity measurement

Conductivity of pressed pellet of polyaniline product was measured by four probe *d. c.* technique. The van der Pauw equation (eqn (1)) below) was used to calculate the conductivity:

$$\sigma = 2 \ln 2 / (R_1+R_2) \pi d f$$

where: σ =conductivity (Scm^{-1}), R_1 and R_2=resistances of the sample in two adjacent contact configurations, d = thickness of the sample (cm), f = geometric correction factor, approximately 1.00 for symmetrical contacts. Surface conductance was found to be insignificant (i.e. the values measured were true bulk conductivities). The conductivity of the pressed pellets of polyaniline derivatives was found to be in the order of 6 x 10^{-8} S cm^{-1}, which was close to that of traditional undoped polyaniline.

7.2.3 UV-Visible spectroscopy

UV-Visible spectra were recorded using Shimadzu UVPC-3101 scanning spectrophotometer in transmission mode. The conjugated polymers are often highly colored because their π–π* energy gap falls within the visible region. Those wavelengths, which are not absorbed, are transmitted, resulting in the observed color. The UV-Visible spectrum of the polyaniline consists of four bands at 311, 443, 608, and 790 nm. The first one at 298–322 nm is assigned to the π–π* transition of the benzenoid rings. It is related to the extent of conjugation between the phenyl rings along the polymer chain. The third absorption band at 588–620 nm is assigned to the quinoid ring transition (charge transfer from the highest occupied molecular orbital of the benzenoid ring to the lowest unoccupied molecular orbital of the quinoid ring). The remaining two bands at 410–450 and 790–880 nm are due to the polaronic transitions.

7.2.4 SEM characterization

The surface morphological microstructure of the polyaniline derivatives can be examined by scanning electron microscopy. Kaolin in raw form shows primary particles in the micrometer range that consist of face-to-face stacking crystallites (tactoids). The SEM photographs of PANI/kaolin nanocomposite are presented in figure 5. While the PANI particle showed aggregation of round shaped small particles, the Kaolin image displayed sheet like plates. Thereby, the PANI/kaolin nanocomposite possesses two characteristic morphologies of round-shape of the particles and plate-like kaolin. The dissolved PANI could combine with surface of kaolin and intercalate into kaolin anticipating the nanoscopic intercalation of PANI chain with kaolin interlayers.

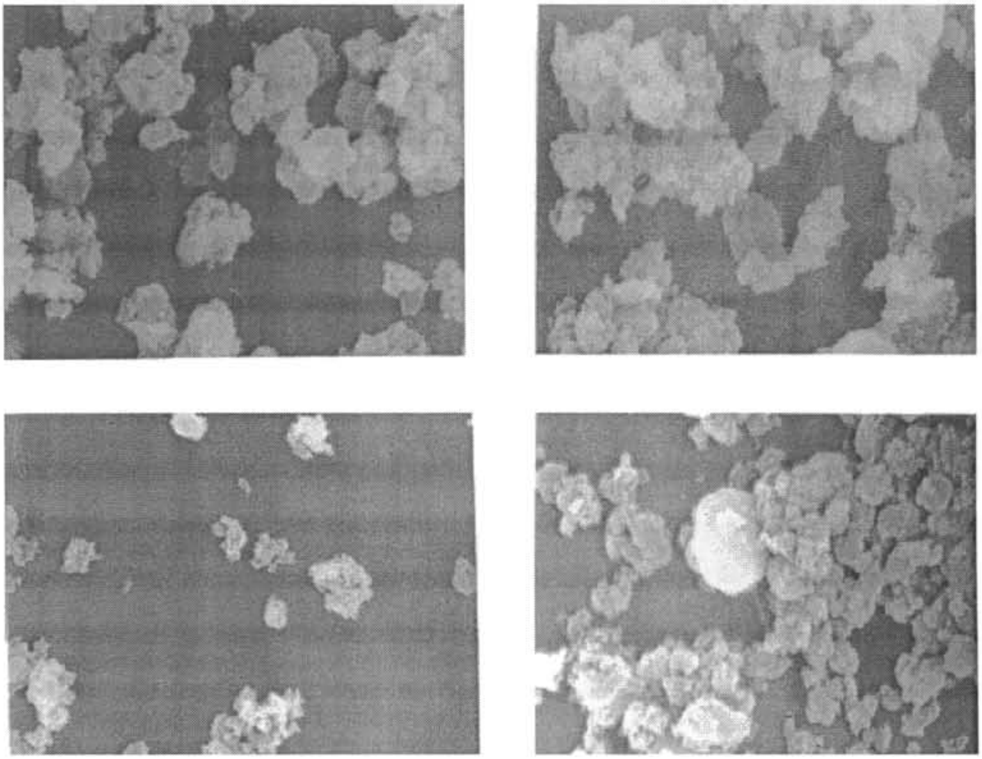


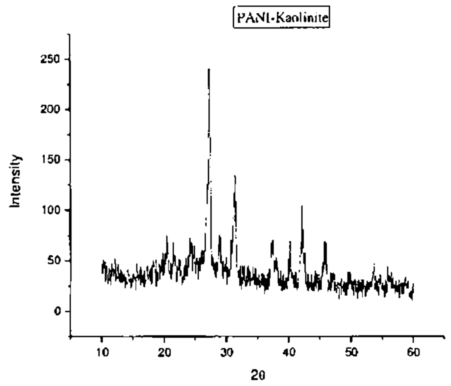
Figure 5: SEM images of PANI/Kaolin

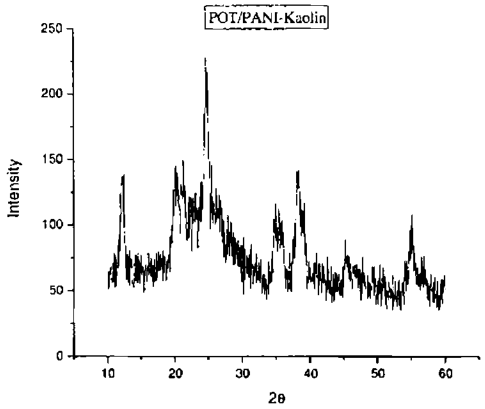
7.2.5 XRD characterisation studies of intercalated PANI/kaolin composites

The polyaniline/kaolin composites such as polyaniline, poly(*o*-toluidine), ploy(*o*-methoxyaniline) and poly(*m*-chloroaniline) were subjected to X-Ray diffraction studies and the results are shown in figure 6. For the sake of comparison the XRD pattern of the raw clay is also given. The variation of the intensity of main peaks can very well be established. The enhancement of the intensity is due to the intercalation of the polymeric material. The X-ray diffraction pattern of the product formed by polymerization did not show distinct peaks, suggesting that the clay layers were chaotically dispersed in the polymeric structure.

The d-spacings of the composites were estimated from the angular positions 2θ of the observed (001) reflection peaks based on the Bragg formula $\lambda = 2d\sin\theta$, where λ is the wavelength of the X-ray beam and θ is the scattering angle. The (001) reflection peak of the kaolin at around 2θ = 12° is shifted towards lower angles for all the composites. The average d-spacing of the composites was found to be 1.43 nm with slight variation. Upon the intercalation of PANI, the interlayer spacing is expanded from 0.97 to 1.43 nm. In the case of the PANI/kaolin composites, the interlayer expansion generally varies in the range of 0.3 to 0.6 nm. Thus, the 0.46 nm expansion in the interlayer spacing observed indicates the insertion of PANI chains between silicate layers.

Analysis of the data shows that the crystalline part of poly(*o*-toluidine) adopts increased zig-zag angle of the polymer chain and larger interchain spacing. The increased disorder in the stacking of polymer chains is caused by the bulky methyl groups. The XRD patterns for PMOA/kaolin composite is also shown in the figure. The peak at 2θ = 4.8° (*d*-spacing: 1.84 nm) corresponds to crystallographic planes of the kaolin clay layer, (001) basal spacing reflection. The *d*-spacing expansion was identified from the shift of the diffraction peak to lower angles of 2θ = 4.18° (*d*-spacing: 2.11 nm) of PMOA/kaolin.





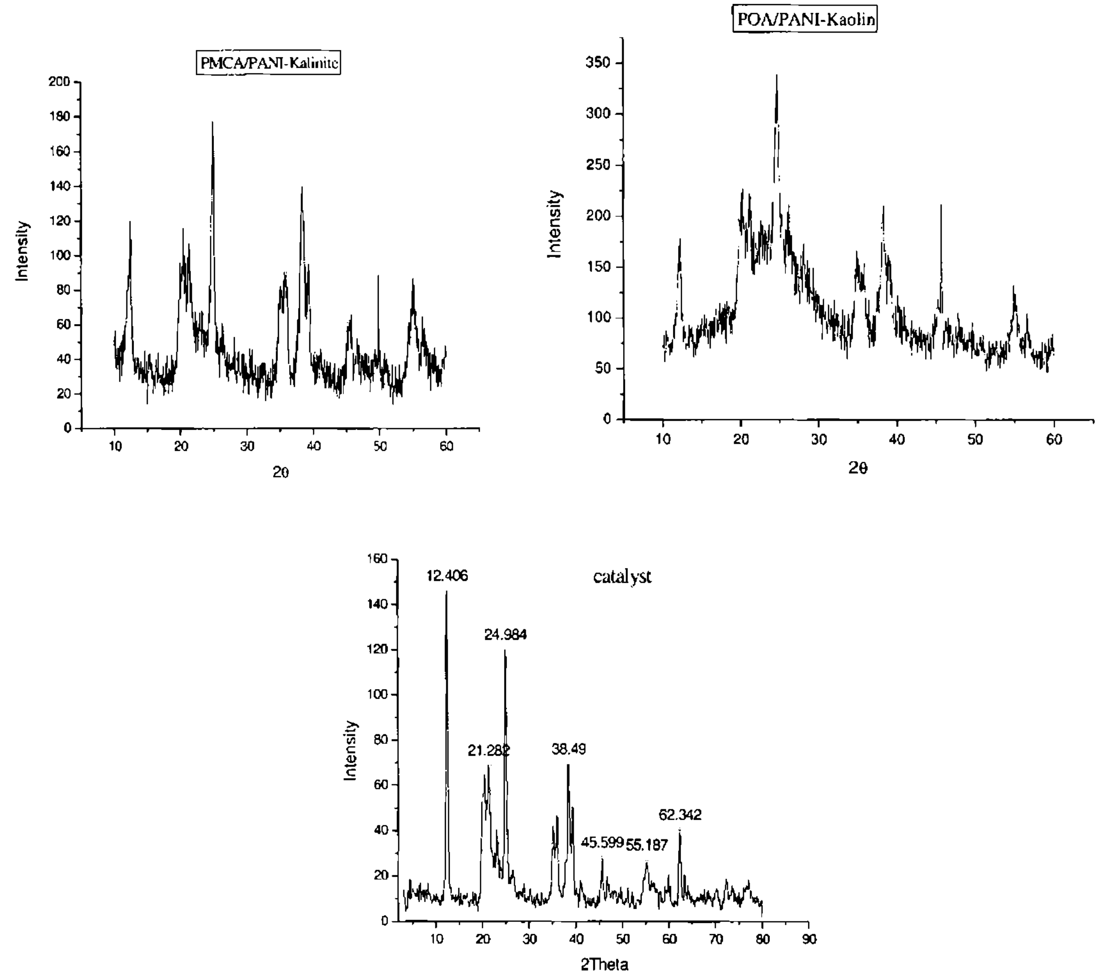


Figure 6: X-Ray Diffraction patterns of four polyaniline/kaoline derivatives with that of catalyst for comparison

7.3 Conclusion

Four types of pani-kaolin composites have been prepared and are characterized. Their structure on intercalation was compared with the XRD patterns. SEM data show that morphology of PANI-kaolin composites changes according to reactants. Surface conductance was found to be insignificant (i.e. the values measured were true bulk conductivities). The conductivity of the pressed pellets of polyaniline derivatives was found to be in the order of 6 x 10^{-8} Scm^{-1}, which was close to that of traditional undoped polyaniline.

7.4 Experimental

0.1mol of amine and 1.0g of catalyst were taken in 100 mL beaker and kept in freezing mixture for about 10 min. Equimolar quantity of potassiumperoxodisulphate was added slowly with vigorous shaking. The addition was continued to about 30min. The reaction mixture was stirred for about 3h keeping the reactants in freezing mixture. After 3h, the temperature of the mixture was gradually raised to 30°C. The mixture was filtered to free the sulphate ions and was dried. The precipitate was washed twice with Tetrahedrofuran (THF) to free the monomers. The compounds are characterized using XRD, SEM, UV-Vis DRS, Conductivity measurements and IR spectroscopy.

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CHAPTER VIII

SUMMARY AND CONCLUSIONS

The scientific knowledge of clay mineral properties progressed greatly during the last century. Many people continue to use clays without knowing the cause of the clay mineral's usefulness. For instance, some cheap clay incubators are still used to protect premature babies from the cold. In many parts of the world drinking water is cooled by evaporative processes in porous clay pots or jugs. Properties of clay minerals lend themselves well to serving as dispensers of chemicals in the pharmaceutical, crop fertilization, and insecticide industries as well as for animal waste and industrial waste adsorption. Wines, vegetable oil, and crankcase oil are all subject to clarification and purification by filtering them through beds of clay minerals. The ceramics and nanocomposite industries are also sub-sets of the field of clay science. Each of these different sub-sets requires unique education and training schedule for development of practitioners who are capable of contributing to their particular fields. Some of the sub-sets of clay science require use of equipment about which researchers in other sub-sets have no expertise.

Until the 1920s, crude oils were refined by distillation. Catalytic conversion, using acid-activated bentonite ('Houdry process') was introduced in 1937. A few years later this catalyst was replaced by acid-activated kaolinite, and in the 1950s by 'base-activated kaolinite' (i.e., zeolites A and/or X). The advent of synthetic zeolites spelt the demise of clays for petroleum refining. The complex nature of clay (different species, different properties, and different modifications of natural clays) as well as the innumerable uses and applications of clays demand that clay scientists from different universities and countries establish educational subjects and techniques. This interest in clay science is extended to undeveloped countries because naturally occurring cheap clay materials may be found in all countries and are used in many parts of our daily life. Renewed interest in clay catalysis emerged in the 1970s due to the development of pillared clays.

Catalysis is an important field in both academic and industrial research because it leads to more efficient reactions in terms of energy consumption and waste production. The common feature of these processes is a catalytically active species which forms reactive intermediates by coordination of an organic ligand and thus decreases the activation energy. Formation of the product should occur with regeneration of the catalytically active species.

Clays (raw, activated, and pillared) are being used as heterogeneous catalysts in many organic reactions. An entirely new field has grown (and continues to grow) out of clay mineralogy; the modification of clay minerals or outright synthesis of clay mineral-like substances called pillared clays, micro-composites, and ceramics.

Our aim of the study is to utilize locally available raw materials such as clay to value added products such as catalysts for the organic reactions. In this attempt modification of clays using acid activation and metal impregnation techniques are employed. The highlights of this study are explained as follows.

First chapter deals with the salient features of clay minerals, their types and classification. The structure and characterization techniques such as chemical composition, FT-IR, XRD, surface area analysis, acidity measurements etc., are explained. Their properties including ion exchange, swelling, acidic nature is mentioned. A discussion on reactions catalyzed by clay materials in the preparation of fine chemicals is presented.

Second chapter describes purification, characterization and modification of clays collected from different regions in the state. Seven types of clays from different sources were obtained. They were purified, and their chemical composition was determined. Based on their chemical composition, their X-ray diffraction data and the activity towards catalytic action, a particular type of clay was selected. Using the selected clay, various types of catalysts were prepared, either by acid treatment or by intercalation of metal ions. A detailed description of the various techniques used for characterization of the prepared catalysts is carried out. Some of the techniques used are Fourier Transform

Infra-Red Spectroscopy, X-Ray Diffraction, surface area analysis, Thermogravimetry/ Differential Thermal Analysis, NH_3-Temperature Programmed Desorption etc. The prepared catalysts were found to possess desirable properties of Lewis as well as Bronsted acidities. The results are compared with standard clays such as K10 and KSF. Based on the preparation method, classification of the catalysts was done. Using these different catalysts, organic reactions were carried out to check the relative activity of these catalysts.

Third chapter deals with the utilization of the modified catalysts into the model diazotization reaction. Their yields were compared with standard clays such as K10 and KSF. High yielding catalyst was used for five different combinations of reactants. Recycling study of high yielding catalyst was conducted. The activity of the metal impregnated and acid activated catalysts was achieved with great success. The yield was comparable with available standard catalysts. The products were characterized. Recyclability of the catalyst render it a useful one.

Protonated formaldehyde reacts with aromatic amines to give 4,4-diaminodiphenylmethanes. Fourth chapter attempts to synthesise 4,4'-diaminodiphenylmethanes by the condensation of aniline with formaldehyde using acid treated as well as metal impregnated catalysts. Seven catalysts are used with five types of amines and reacted with formaldehyde. The yields are compared with the standard clays such as KSF and K10. The products were fully characterized. The recyclability of the prepared catalysts were checked.

One of the important methods for introducing alkyl substituents into the aromatic systems is through Friedel-Crafts alkylation. Homogeneous Lewis acidic catalysts are used for the reaction. This introduces several problems such as tedious work up, use of corrosive chemicals, moisture sensitivity, decreasing regioselectivity and so on. To overcome the drawbacks, replacement of soluble Lewis acids is made by solid acids which facilitate improved procedures. In the fifth chapter, Friedel-Crafts alkylation in vapour phase is presented using the prepared kaolin catalysts. The products are characterized and the yields are compared with standard clay catalysts. Recycling nature of the catalyst was examined.

Esters represent an important class of chemical compounds with applications as solvents, plasticizers, flavors and fragrances, pesticides, medicinals, surfactants, chemical intermediates, and monomers for resins. In this chapter attempts have been made to prepare esters of carboxylic acids through vapour-phase reactions. Five different esters were made and the products were characterized using physical constants, FT-IR and other spectral methods. The yields are compared with standard clays. Recyclability of the prepared catalysts has also been tested.

Vapour-phase esterification reaction has also been carried out using the same methods and procedures. The esterification reaction of benzoic acid with ethyl alcohol was taken as the reference reaction and was studied for the activity of the prepared catalysts. The advantage of the vapour phase reaction is that it is conducted in a continuous flow reactor. The yields of the products can be controlled by adjusting the flow of the reactants into the reactor. Since the reaction is in vapour phase condition, monitoring the progress of the reaction is easier. Catalyst removal and thereby the regeneration of the catalysts is made easy. The simple method of conducting the esterifcation process, relatively low amount of by-products, easier method of purification, requirement of relatively low amount of supporting reagents and conditions render the reaction a green one.

In the sixth chapter, the activity of catalysts are examined for the microwave mediated organic reactions. Clay catalysed esterification and oxidations of alcohols using chromium trioxide were carried out. Products were characterized by standard methods. Microwave oven of domestic type was employed for the purpose. The modified clay catalysts were subjected to esterification and oxidation reactions. The efficiency of the catalysts in both conventional heating and microwave heating was compared in the esterification reaction. The conventional heating involved heating the reaction mixture with the refluxing vessel. The microwave enhanced reactions are characterized with low time and higher yield. Monitoring and control of the reaction are found to be advantageous. The product separation is much easier than conventional reactions. The products obtained are found to be of comparatively high purity. The time factor and the better procedure make the microwave reactions a green one.

Polyaniline (PANI) is one of the most important conducting polymers. It is commonly prepared by the oxidation of aniline with ammonium peroxodisulfate in an acidic medium. Polyaniline and polyaniline derivatives can be synthesized both chemically and electrochemically by using suitable protonation media. The seventh chapter describes the preparation of polyaniline by template assisted polymerization using clays. Four types of polyaniline derivatives were prepared using the acid activated clay catalyst. The prepared polyaniline derivatives are Polyaniline/kaolin, Poly (o-Toluidine)/kaolin, Poly (o-Methoxyaniline)/kaolin, Poly (m-Chloroaniline)/kaolin which are characterized using IR Spectroscopy, UV Spectroscopy, SEM, Conductivity measurement and XRD techniques. The conductivity of the pressed pellets of polyaniline derivatives was found to be in the order of 6×10^{-8} Scm^{-1}, which was close to that of traditional undoped polyaniline.

The diverse catalytic activity of clay minerals is derived mainly from four main sources, Brønsted acidity, Lewis acidity, presence of redox active species and introduction of catalytically active (mainly) transition metals or cations. Such activity can be either a natural property of the clay or can be introduced by cation exchange, acid activation or deposition of the co-catalyst onto the clay surface. The expandable layers of clay minerals provide useful two-dimensional hosts, which facilitate introduction of catalytically active metal species by cation exchange. Intercalation of metal species into the interlayer space of clay minerals is an excellent method for homogeneous catalyst heterogenisation. Metal complex catalysts intercalated into clay minerals exhibit sufficiently high activity and selectivity to make them competitive to the homogeneous catalysts.

The clay minerals can catalyze a variety of organic reactions occurring on their surface and interstitial space. Synthetic organic chemists have been attracted to their tremendous potential as catalysts only recently. Modification of their properties by incorporating different metal cations, molecules or complexes, can lead to catalysts that are useful in effecting even more varieties of reactions and higher selectivity in product structure and yield. There is a theory that the molecules of life were actually developed in sedimentary clays. As the organic chemist is becoming more aware of clay's efficacy, its use in organic synthesis is bound to increase, especially because it helps in developing eco-friendly chemical processes.