

ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
CIRCULATION

ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

**INVESTIGATION OF THE CATALYTIC NATURE OF
Fe³⁺- EXCHANGED CLAYS ON
CYCLOHEXANOL AND CYCLOHEXENE**

BY

BELINA TERFASA

JUNE, 1995

INVESTIGATION OF THE CATALYTIC NATURE OF Fe^{3+} - EXCHANGED CLAYS
ON CYCLOHEXANOL AND CYCLOHEXENE

A Thesis presented to
the School of Graduate Studies
Addis Ababa University

In partial fulfilment of
the Requirements for the
Master of science in Chemistry

by

Belina Terfasa

June, 1995

ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES

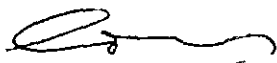
INVESTIGATION OF THE CATALYTIC NATURE OF Fe³⁺ - EXCHANGED
CLAYS ON CYCLOHEXANOL AND CYCLOHEXENE

By

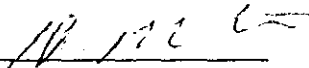
Belina Terfassa
Department of Chemistry
Faculty of Science

Approved by the Examining Board

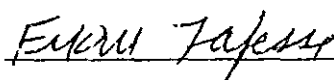
Prof. N.J. Coville, Ext. Examiner



Dr. Negussie Retta, Advisor



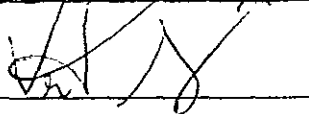
Dr. Fikru Tafesse, Examiner



Dr. Tetemke Mehari, Examiner



Dr. V. Marx, Examiner



CONTENTS

I. Dedication.....	i
II. Acknowledgements.....	ii
III. List of tables.....	iii
IV. List of figures.....	iv
V. Abbreviations.....	v
VI. Abstract.....	vi
CHAPTER 1. Introduction.....	1
CHAPTER 2. Literature survey.....	10
2.1. Composition and basic structures of clay minerals.....	10
2.2. Ion-exchange phenomena in sheet silicates.....	12
2.2.1. Smectite group clay minerals.....	15
2.2.2. Factors affecting cation exchange capacity	17
2.3. Cation-exchanged clay support catalysis	18
2.3.1. Conversion of alkenes to ethers by cation exchanged clay catalysts.....	19
2.3.2. Esterification of alkenes by cation exchanged clay catalysts.....	21
2.3.3. Dehydration of alcohols by cation exchanged clay catalysts.....	22
2.3.4. Elimination of hydrogen sulphide thiols by cation exchanged clay catalysts.....	24
2.3.5. Elimination of ammonia from amines by cation exchanged clays.....	25
2.3.6. Decomposition of esters by cation exchanged clay catalysts.....	26
CHAPTER 3. Experimental.....	28
3.1. Study of the unfractionated clays	28
3.1.1. Sieving.....	28
3.1.2. The free swell test of the clay samples.....	28.
3.1.3. Elemental analysis of the clays.....	29
3.1.4. Determination of cation exchange capacities.....	29
3.1.5. Determination of the exchangeable bases.....	31

3.1.6. Determination of exchangeable hydrogen ions.....	32
3.1.7. IR spectra of the clay samples.....	32
3.2. Fractionation of the clay samples.....	32
3.3. Preparation of Fe ³⁺ -exchanged clays.....	33
3.4. Study of the catalytic activities of Fe ³⁺ -exchanged clay samples.....	34
3.4.1. Refluxing cyclohexanol with Fe ³⁺ -exchanged clays.....	34
3.4.2. Refluxing cyclohexene with Fe ³⁺ -exchanged clays.....	35
CHAPTER 4. Results and discussion.....	36
4.1. Unfractionated clays.....	36
4.1.1. Free swell test.....	36
4.1.2. Elemental analysis.....	37
4.1.3. Cation exchange capacities of clays.....	38
4.1.4. Exchangeable bases.....	39
4.1.5. Exchangeable hydrogen ions.....	40
4.1.6. Interpretation of the IR spectra of clay samples.....	41
4.2. Study of the fraction of clays considered.....	43
4.2.1. Cation exchange capacity.....	43
4.2.2. Exchangeable hydrogen ions.....	44
4.2.3. Interpretation of the IR spectra of fractionated clays.....	45
4.3. Study of Fe ³⁺ -exchanged clay.....	45
4.3.1. Cation exchange capacities.....	45
4.3.2. Exchangeable hydrogen ions.....	46
4.4. Gas chromatographic studies of the catalytic reaction products.....	47
4.4.1. Cyclohexanol refluxed with Fe ³⁺ -exchanged clays.....	47
4.4.2. cyclohexene refluxed with Fe ³⁺ -exchanged clays.....	50
CONCLUSION.....	54
REFERENCES.....	55
APPENDIX.....	58

DEDICATION

This piece of work is dedicated to my brother, **Major Abate Terfasa**, who has taken the responsibility of parenthood throughout my high school and undergraduate years but was unfortunate to see the ambitions he had for me.

ACKNOWLEDGEMENTS

I greatly acknowledge my research advisor Dr. Negussie Retta for his expert, patience, consistent and encouraging guidances during the course of this project.

I would like to thank the Ethiopian Institute of Soil Laboratory Service for providing me with the starting material, bentonite(BDH), and for allowing me to use their laboratory and all necessary instruments for the vital part of the work, Dr. Medihin Zewude and Ato Afework Mulgeta for they spared their time in running the GC.

I would like to extend my appreciation to Dr. Ermias Dagne and Ato Teferra Bekele for running the GC and IR respectively, Ato Ahmed Mustefa for his patience and helpful behaviour in providing computer services whenever sought.

My thanks also go to Dr. Mekonen Dilgasa, Dr. Hailemichael Alemu, Dr.V. Marx, Dr. B.S. Chandravanshi, Dr. Girma Moges, Ato Mussie Hagos, W/t Azeb Yigezu, Ato Assefa Sirgawie, Ato Negussie Megersa, Ato Tamiru Ararsa, Ato Tamiru Ayana, Ato Mesfin Janka, Ato Naga Gichle, Ato Teshom Dhaba, Ato Tadesse Abdi, Ato Sahlmichael Deme, Ato Gugsu Mamo, for their moral encouragement and positive attitude toward my success.

I would like to extend my greatest appreciation to W/t Faiza Abdurhaman for her tolerance and consistent moral help throughout my graduate school studies.

I would like to express my gratitude to my brothers Ato Darge Berkessa, Ato Tamene Berkessa and Ato Haile Berkessa for their assistance during my learning.

I would like to acknowledge my roommates Ato Goytom Zerom and Ato Haile Adera for their generous moral help and creating conducive study atmospheres.

LIST OF TABLES

1. 1:1 and 2:1 clay minerals layered clay minerals.....	12
2. Composition and CEC of the five groups of clay minerals.....	14
3. Different smectite group clay minerals obtained by isomorphous substitution in the prototype pyrophyllite or talc structures.....	16
4. The degree of swelling of the clays	36
5. Elemental composition of local clay and drilling mud bentonite.....	37
6. Cation exchange capacity values of unfractionated clays.....	38
7. Exchangeable bases of unfractionated clays.....	40
8. Amounts of exchangeable hydrogen ions of unfractionated clays	41
9. IR spectral interpretations of unfractionated clays.....	42
10. The cation exchange capacities of fractionated clays.....	43
11. Exchangeable hydrogen ions of fractionated clays.....	45
12. Cation exchange capacity values of Fe ³⁺ -exchanged clays.....	46
13. Amounts of exchangeable hydrogen ions of Fe ³⁺ -exchanged clays.....	46
14. Relative retention and percentage of cyclohexanol and refluxed cyclohexanol with Fe ³⁺ -exchanged clays.....	48
15. Relative retention times and percentage compositions cyclohexene and refluxed cyclohexene with three different clays.....	51

LIST OF FIGURES

1. Schematic structures 2:1 and 1:1 layered sheet silicates	11
2. Schematic structure of smectite group clay minerals	15
3. Schematic mechanism of conversion alk-1-ene to alcohol, ether or ester by cation exchanged clays.....	21
4. Schematic mechanism of dehydration of alcohols to alkenes or ether by cation exchanged clays.....	23
5. Schematic mechanism of elimination of H ₂ S from thiols by cation exchanged clays.....	24
6. Schematic mechanism of elimination of NH ₃ from amines by cation exchanged clays.....	25
7. Schematic mechanism of decomposition of esters to alkenes and acids by cation exchanged clays.	26
8. Schematic mechanism of conversion of cyclohexanol to cyclohexene and dicyclohexyl ether by Fe ³⁺ -exchanged clays	49
9. Schematic mechanism of conversion of cyclohexene to cyclohexanol and dicyclohexyl ether by Fe ³⁺ -exchanged clays.....	51

ABBREVIATIONS

PVC	Polyvinylchloride
XRD	X-ray Deffractometry
IR	Infrared
DTA	Differential Thermal Analysis
μm	Micrometer
Å	Angstrom
Mequiv	Milliequivalents
CEC	Cation Exchange Capacity
Td	Tetrahedral
Oh	Octahedral
^1H NMR	Proton Nuclear Magnetic Resonance
FID	flame ionizer detector
GC	gas chromatography
Av.	average
LCS	Local Clay Sample
DMB	Drilling Mud bentonite
BDH-B	Bentonite(BDH)
RT	Retention Time

ABSTRACT

INVESTIGATION OF THE CATALYTIC NATURE OF Fe³⁺-EXCHANGED CLAYS ON CYCLOHEXANOL AND CYCLOHEXENE

BY
BELINA TERFASA

ADVISOR: Dr. NĒGUSSIE RETTA

The investigation of the catalytic nature of cation exchanged clays on some organic reactions was the core objective in this project. Important features of the three clays, local clay, drilling mud bentonite, and bentonite(BDH) with respect to free swelling, exchangeable bases, CEC, acidity measurement, IR spectra have been studied. The study of the catalytic activities of Fe³⁺-exchanged clays(local clay, drilling mud bentonite and BDH-bentonite) was carried out on cyclohexanol and cyclohexene under reflux conditions. As shown by gas chromatographic analysis, the Fe³⁺-exchanged clays were able to convert the substrates into new products.

By using retention time coincidence tests and co-injection peak enhancement technique, one of the products obtained from cyclohexanol with the three Fe³⁺-cation exchanged clays was identified to be cyclohexene. The second product was not identified but suggested to be dicyclohexyl ether. In the case of refluxing cyclohexene, retention time coincidence test reveals that no cyclohexanol was formed as a product. But other unidentified products were formed as shown by the appearance of new peaks. The ferric cation exchanged clays have dehydrated cyclohexanol and could not hydrate cyclohexene. Therefore, the clays may be identified as dehydrating agents.

CHAPTER 1

INTRODUCTION

Catalysis is an important process in a number of chemical reactions, in biological systems as well as in manufacturing industries [1,2]. Chemists have long been interested in minimizing the energy requirements of a particular chemical reaction by seeking suitable catalysts.

Catalysts may be best characterized by defining their properties [3,4].

1. Catalysts do not contribute energy to a reaction, because they remain unchanged at the end of the reaction.
2. Catalysts do not change the equilibrium points of a reversible reactions, as they influence the forward and reverse rates in the same proportions.
3. Catalysts inter into a reaction during a course of the reaction over and over by regenerating themselves so that the catalyst remains unchanged on completion of the reaction, small amount of the catalyst , thus, being able to transform large quantities of a substrate.

The course of a reaction may be altered by the influence of the catalyst on the velocity of the reaction on approaching the equilibrium state. The mechanism by which a catalyst functions depends upon the type of the reaction in which it takes part and the mode of its action is largely chemical. In a catalytic process, the molecules of the reacting substances are converted into an active state in which their configuration undergoes an essential change. The acceleration of a chemical change by a catalyst is, thus, via alternate formation and decomposition of compounds between the catalyst and the substrate(formation of intermediates) is one of the chemical views of the mechanism of catalysis [1,3,4]. The intermediate species are sufficiently labile to decompose readily yielding the reaction product and regenerate the catalyst.

A good catalyst ought not to form a stable addition complex between substrate and the catalyst but ought to enter into an equilibrium with the activated molecule which is shifted as far as possible toward the formation of a free molecule. Powerful catalysts which ionize readily are considered to be open systems while reacting organic substances (molecules) even that are unsaturated belong to the closed systems. When these two systems approach each other the catalyst extends its open and polar character upon the less polar molecule of the reactant leaving them in a state of greater polarity and higher activity. A labile reaction intermediate product is formed as a result of deformation of electron orbitals in the molecule caused by the catalyst. The reacting species are brought into an intermediate state as a result of intermolecular process caused by the catalyst or changes of bonds between the reacting substance and the catalyst, in either transition steps increased activity in the system results.

An ordinary catalysis is a combination of the catalyst with reacting molecules which establishes a favourable orientation of the characteristic trajectories of the electrons, and the catalyst induces the conversion of closed bonds into an open ones. The dislocation of special bonds may indicate the position where the molecule have been activated. Molecules, in order to react, have to pass through an intermediate state characterized by definite difference in enthalpy and energy compared with the average [4].

Basically, catalysts are of two major categories, homogeneous and heterogeneous catalysts [1, 2, 4]. They may have simple chemical structures such as base or acid, they may have intricate structures such as certain metal complexes or they also occur in nature as complex enzymes.

In heterogeneous systems, the catalyst (mostly solids) and the substance to be catalysed are in two different physical states. The catalyst is essentially added to the reaction mixture to facilitate a reaction via adsorption of some or all of the reactant on its surface. On the contrary, true homogeneous catalysts and reacting substances are not separated from each other by a phase boundary at which the catalytic reaction has its seat, both being uniformly distributed in the reaction system. Thus, in the homogeneous system, the catalyst functions in the form of a single molecular entity

which are distributed among the molecules of the reactant showing the same mobility. Such catalysts normally operate in solutions and gases and the catalyst is dissolved in the reaction mixture. Therefore, the rate of homogeneous catalysis is directly proportional to the concentration of the catalyst because the catalyst is maintained in an intimate mixture with the reacting components and is acting by mass. Nevertheless, the rate of the heterogeneous catalysis is directly proportional to the exposed surface area of the catalyst. Even though both kinds of catalysts perform the act of increasing the rate of the chemical reactions by reducing the activation energy required by a particular reaction, yet there are marked differences between homogeneous and heterogeneous catalysts.

1. Separation of the catalyst :

The major disadvantages of homogeneous system is the problem of separation of very expensive catalysts from the reaction product at the end of the reaction. Unless the means of separation are efficient, it will result in a loss of the catalyst which may render the process uneconomic and/or contamination of the products which is unacceptable especially in the case of food stuffs.

The means of separation of homogeneous catalysts from the reaction products is carried out with a very efficient distillation or ion-exchange process. Reaction products with relatively low boiling points such as homogeneous catalysis in Wacker process for the oxidation of ethylene to acetaldehyde (boiling point 20.8 °C) and Monsanto process for the carbonylation of methanol to acetic acid (boiling point 117.9 °C) distillation may be an effective means. However, distillation will not be a practical method for the processes where the substance decomposes before its boiling point in such cases as hydrogenation of soft oils to yield components suitable for the incorporation into margarine (even under reduced pressure). Nevertheless, in heterogeneous catalysis, there are no such complications and separation of the reaction product can easily be achieved by some kind of coarse filtration.

2. Catalyst efficiency:

In heterogeneous systems, the catalytic reaction must necessarily take place via adsorption of the reactants on the surface of the catalyst so that all atoms and molecules of the catalyst not present at the surface remain unused. In contrast, all molecules of the homogeneous catalyst are theoretically available as catalytic centres. Therefore, homogeneous catalysts are potentially more efficient than the heterogeneous ones in terms of the catalyst needed to catalyse a given amount of a reactant.

3. *Catalyst reproducibility:*

Homogeneous catalysts have the advantage over the heterogeneous catalysts of being totally reproducible, because they have definite stoichiometry and structure. But the structure of the surface of a heterogeneous catalyst is heavily dependent on both method of preparation and history subsequent to preparation.

4. *Catalyst Specificity :*

A given homogeneous catalyst will generally have only one type of active site, and, therefore, will often be more specific than a heterogeneous catalyst where several active sites may be present in the form of different surface defects. The specificity of homogeneous catalysts can often selectively be modified by altering the other ligands so as to alter either the electronic nature or the steric requirements of the site. Because of the definite structural composition of homogeneous catalysts, it is much more easier to modify them in order to control the reaction.

5. *Thermal stability :*

The thermal stability of heterogeneous catalysts, such as pure metals and metal oxides is often much higher than that of homogeneous catalysts. Since the rate of most reactions increases with increasing temperature, a high operating temperatures may be an advantage.

6. *Solvent :*

There is no problem in selecting a solvent for heterogeneous catalysts whereas the range of suitable solvents for homogeneous catalysts is often limited by solubility characteristics of the catalyst. In general, the relative importances and advantages of the homogeneous and heterogeneous catalysts can be compared [5].

The homogeneous catalysts are advantageous due to the fact that they are characterized by a well studied and interpreted catalytic activities under milder conditions, high efficiency, reproducibility and possess steric and electronic properties that can frequently be controlled. The heterogeneous catalysts have several advantages including acceptable thermal and mechanical stability, high activity for a wide range of reactions, capacity to use in packed and fluidized beds and ready separation from the reaction products. However, problems encountered with heterogeneous catalysts are design and improvement limits due to frequently ill-defined active sites, limited accessibility and effectiveness of catalytic sites and severe and costly reaction conditions such as high temperature and pressure.

At first insight it might appear that the balance of the advantages of these two types of catalysts would lie with the homogeneous catalysts. Although homogeneous catalysts are desirable because of their high activity and selectivity, separation of the reaction product from the catalyst and/or recovery of the catalyst is inherent problems associated with conventional soluble catalysts. Catalyst recovery is one of the most important parameters for economic and industrial viability [6]. The use of homogeneous catalysts on an industrial scale can lead to a number of practical problems including corrosion and deposition of the catalyst on the walls of the reactor [7]. Thus, recently, considerable research efforts have been expended in developing catalysts that combine advantages of the two extremes. Some of such achievements are the development of supported catalysts. Since homogeneous systems allow much greater selectivity in catalytic reactions, attempts have been made to achieve similar benefits by heterogenizing known homogeneous catalysts by incorporating tertiary phosphine pyridine, thiol or other ligands into polymers like styrene-divinylbenzene as well as supporting complexes like carbon, silica, alumina and ion-exchange resins [8]. A carrier may be useful because it provides a larger contact surface in a more equal distribution of the catalyst. A carrier influences structural and physical

properties of the catalyst deposited on it by preventing sintering and enhancing dispersion [7].

The deposition of the catalyst on a support may amount to an increase in the number of active centres corresponding to an energy level necessary to carry out a particular reaction. The mechanism of action of a carrier in a catalytic reaction with respect to the catalyst which it supports is not at all indifferent support for a catalyst but it produces a deforming action upon the atoms or molecules of the catalysts; polarizes them and brings about a change in their external fields thereby changing their catalytic properties. In a support catalysis, atoms or molecules of the catalyst are subjected to the action of attractive or repulsive (coloumbic forces) and forces of mutual polarization with the support.

The choice of the catalyst support must be in such a way that the carrier must have high deforming influence upon the atoms or molecules of the catalyst deposited on it. In addition to the structural characteristics, amorphous or crystalline, porous or compact, the chemical composition, state of dispersion, physical properties of the surface, contact property, electrical property, mechanical strength, saturation capacity and active sites of the carrier must be differentiated before the choice of the support.

The precipitation of catalytic substances on a carrier goes back to 1823 when Doebereiner first used a spiral platinum wire and later potter's clay as a carrier for a platinum black in an experiment on the behaviour of platinum black toward hydrogen, oxygen, carbon dioxide, ethylene methane, etc.

Clemens Winkler, (1880) stated that porous substances such as pumice, clay, and fibrous substances such as asbestos and cotton are carriers and true contact agents. From this time other example such as silica gel, activated charcoal, Zeolite, silicates, kaolin glass, etc. are successfully applied as a carrier in a catalytic process in a tremendously large number of important chemical reaction.

In addition, other advancements include supported transition metal complexes such as transition metal carbonyls($\text{Cr}(\text{CO})_6$, $\text{Fe}(\text{CO})_5$, etc) which involve the formation of a

chemical bond between the surface of the support and the ligand group involved in the metal complex. In this way, transition metal complexes may be attached to the surface of both organic (polystyrene, polybutadiene, PVC, etc) and inorganic supports (γ - Al_2O_3 , SiO_2 , etc.) solids [5] and used as a heterogeneous catalysts. Furthermore, other development which has recently drawn attention is a use of sheet silicate support catalysis.

Pillaring of clays which was first introduced by Barber and Macleod (1955), induces permanent porosity in smectite clays by probing open the clay layers with tetraalkylammonium ion. Pillaring of clays with metal oxides like nickel, iron, etc. has become the most efficient catalysts in chemical conversions [9,10].

Application of cation-exchanged clay support catalysis in the chemical conversion of novel organic reactions is becoming one of the most important areas of recent research [11].

Thompson is generally credited for being the first person who systematically studied ion-exchange in soils [12,13,14]. In his experiment, he added ammonium sulphate to a column of soil and observed that it was converted to CaSO_4 . He, then concluded that NH_4^+ ions were retained or exchanged for Ca^{2+} ions in the solution. Following Thompson, Way began a detailed study of the ion exchange phenomena and suggested that the exchange process is attributed to the clay fraction of soils and he determined the replacing power of ions to be $\text{Na}^+ < \text{K}^+ < \text{Mg}^{2+} < \text{Ca}^{2+} < \text{NH}_4^+$ and pointed out that this series is irreversible which was later proved to be incorrect by Eichhorn (1958).

Further proof that the active components of soils responsible for ion-exchange are zeolite [4] (anhydrous silicates occurring in natural volcanic rocks constructed from the lattice of SiO_4 and AlO_4) came from Lemberg (1867) and Weigner (1912) who explained that ion-exchange process is an adsorption process and not an ordinary chemical reaction. Later, Hendrick (1930) discovered that inorganic colloidal materials of soil are crystalline and concluded that ion-exchanges are occasioned in the crystal lattice structure of clay minerals and not a simple adsorption.

Ion-exchangers behave as porous networks which carry a surplus electric charge distributed over the surface and through out the pores [15]. The surplus charge on the ion-exchangers is compensated by adsorption of foreign ions of opposite charge.

Ion-exchangers are large molecules, water insoluble materials with cross linked structures composed of ionic groups. Ion-exchange phenomena differs from simple adsorption that it takes place stoichiometrically by releasing ions of like charges into the solution [16]. The two very important requirements of an ion exchanger are insolubility and chemical stability [17].

A resin, a precursor of a cross linked material [18], may exchange cations or anions and consequently be called cation-exchanger or anion-exchanger respectively. A cation-exchanger resin may be defined as a polyvalent anion which has a positive charge as a counter ion whereas anion exchanger resin is defined as a polyvalent cation which has a negative charge as a counter ion. Amongst the two types of exchangers, acid cation exchangers include cross-linked polystyrene with functional groups -OH, -SO₂OH and -CH₂SO₂OH and basic anion exchangers include phenolic resins with functional groups -OH, -NH₂, -NHR, -N(C₂H₅)₂. Cation exchangers also include clays like zeolites, kaolinite, illite, vermiculite and smectites. It was not until the beginning of 20th century that the knowledge of ion exchangers was applied to the development of water softeners [14]. With the advance of various analytical techniques like x-ray diffractometry(XRD), infrared spectroscopy(IR) differential thermal analysis(DTA), etc. detailed features of the clays and their cation exchange behaviour have been uncovered.

Cation-exchange process was applied to the quantitative and qualitative separation of small samples like rare earth ions. Recently, the catalytic application of cation-exchanged clays in general and smectite group clays in particular were used in a number of industrially important reactions specially in the chemical conversion of organic compounds. Polymerization, oligomerization, ether formation, esterification, etc. [4,16,19] have been successively accomplished by using H⁺, Na⁺, Fe²⁺, Fe³⁺, Cu²⁺, Cr²⁺, etc. exchanged clays [1, 20]. Due to this, cation-exchanged clay support catalysis has drawn much attention these days. Therefore, even though extensive work

has been done in this area, there remains a wide range of reactions not studied yet. Thus, the major purpose of the present work is to explore the catalytic effect of cation-exchanged clays on some common organic reactions which have not been studied before.

The general objectives of this project are:

1. to investigate the characteristics and features of clays and cation-exchanged clays,
2. to investigate the catalytic activities of cation-exchanged clays on the conversion of organic compounds particularly cyclohexanol and cyclohexene.

The clay samples used throughout this study are:

1. Local clay sample from *Gidicho Island of Lake Abaya* obtained from Ethiopian Institute of Geological surveys.
2. Drilling mud bentonite obtained from Ethiopian Institute of Geological Surveys which was commercially imported from Christensen Mining products(Utah).
3. Bentonite(BDH)

CHAPTER 2

LITERATURE REVIEW

2.1. COMPOSITION AND STRUCTURE OF CLAY MINERALS

In general terms, clay implies a natural, earthy and fine grained material which develops plasticity when mixed with a limited amount of water [12]. In soil science, the term clay is often used for the soil fraction with an equivalent diameter $< 2\mu\text{m}$ [21]

Fundamentally, clay minerals are complex compounds in which silica is combined with alumina or magnesia and other cations involved both structurally in the crystal framework and in close association with the basic structural units [22]. Chemical analysis of clays show that they are composed essentially of silica (46.52%), alumina(39.53%), and frequently with appreciable quantities of iron, alkali metals and alkaline earth metals[4,13]. The structures of clays are analyzed by x-ray diffractometry(XRD) complemented with infrared spectroscopy (IR) and other spectroscopic instruments.

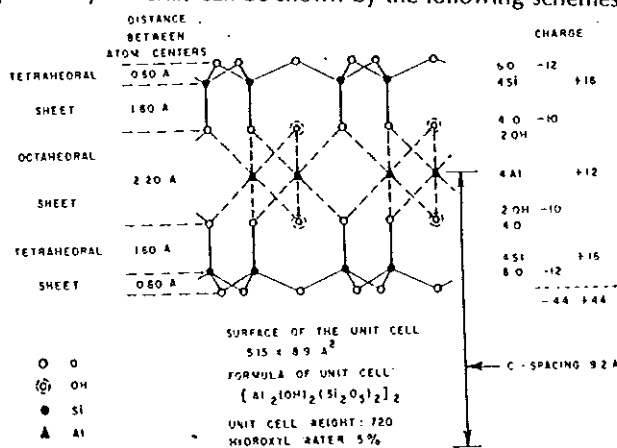
The building structural units of crystalline clay minerals are:

1) Two dimensional array of Si-O tetrahedra in which the silicon atom is centrally placed in relation to four equidistant oxygen atoms. Different silicon-oxygen tetrahedra are arranged into a sheet structure through three of the four oxygen atoms of each tetrahedra with the neighbouring tetrahedra. The oxygen arranged in this framework are called basal oxygens while the fourth oxygen, uncoordinated and pointing away from the sheet is said to be an apical oxygen.

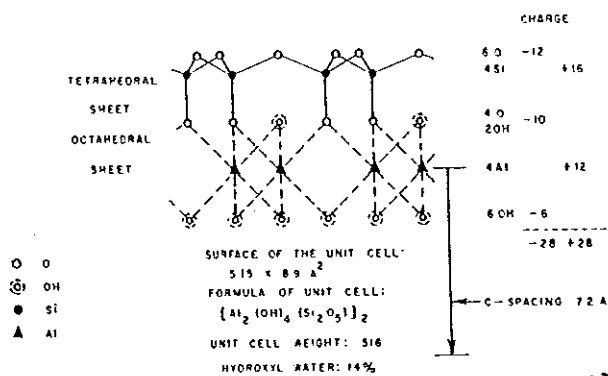
2) The second structural unit of clays is composed of aluminium-oxygen(or hydroxyl) or magnesium-oxygen (or hydroxyl). In this structure, the aluminium and/or magnesium atoms are coordinated with six oxygen atoms or OH groups centred at the six corners of a regular octahedron. The sharing of oxygen atoms by neighbouring octahedrons results in a sheet structure. The oxygen atoms or OH group lie in two

parallel planes with Al or Mg atoms between the planes. The sheet formed by such an arrangement is called an octahedral sheet.

Analogous symmetry and almost identical dimensions between the tetrahedral and octahedral sheets allow the sharing of oxygen atoms between the sheets. The fourth oxygen protruding from the tetrahedral sheet is shared by an octahedral sheet. If the sharing of O-atoms occurs between one silica tetrahedral sheet and one alumina octahedral sheet, it is termed as 1:1 layered clay mineral whereas the sharing of two silica tetrahedral sheet O-atoms between one alumina octahedra, the alumina octahedra being sandwiched between two silica tetrahedra, forms 2:1 layered clay mineral. The combination of one silica tetrahedral sheet and one or two alumina octahedral sheet forms a layer and is a common feature of most clays [2], the structure of these groups of clay minerals can be shown by the following schemes [21].



Atom arrangement in the unit cell of a 2:1 layer mineral (schematic) [21]



Atom arrangement in the unit cell of a 1:1 layer mineral (schematic) [21]

Thus clays are aluminosilicate minerals composed of two dimensional planes of silicon-oxygen tetrahedra and aluminium-oxygen or aluminium-hydroxyl octahedral layered sheets. Based on this, the crystalline clay minerals are subdivided into five groups the Kaolinite group, Smectite(montmorillonite) group, the Illite group, the Chlorite group and the vermiculites [23].

Table 2.1. 1:1 and 2:1 family of layered clay minerals [22]

Chain	Family	Clays
Layer	1:1	kaolinite nactrite dickite halloysite
Layer	2:1	montmorillonite chlorite vermiculite illite nontronite

The distance between a certain plane in a layer and the plane in the next layer is basal spacing or C-spacing used to distinguish between 1:1 layered clays with C-spacing 7.1-7.2Å and 2:1 layered clays with C-spacing atleast 9.2Å in x-ray analysis.

2.2. ION-EXCHANGE PHENOMENA IN SHEET SILICATES.

The major factor that brings about differences among clays is the occupancy of the position of silicon in the silica tetrahedra and aluminium in the alumina tetrahedra by various cationic species. When all the silica tetrahedra central positions are occupied by silicon and all the alumina octahedra central positions are occupied by aluminium, an electrostatically neutral sheet clay with a general chemical formula $Al_4Si_8O_{20}(OH)_4.nH_2O$ [13, 22] is obtained. The neutral 2:1 layered structure of such

clay mineral is termed as pyrophyllite [21].

The isomorphous substitution of other atoms like Mg, Fe, Al, Zn, etc. for silicon in the silica tetrahedra and/or aluminium in alumina octahedra in the prototype pyrophyllite structure will result in clay minerals which are related by common structures and similar physical and chemical properties. The isomorphous substitution of lesser positively charged cations (e.g., Mg^{2+} , Al^{3+}) for higher positively charged cations such as substitution of a divalent Mg^{2+} for a trivalent Al^{3+} in the alumina octahedral sheet and/or Al^{3+} for a tetravalent Si^{4+} in the silica tetrahedral sheet results in an unbalance of electrical charge. The excess negative charge developed over the clay layers as a result of isomorphous substitution is compensated by adsorption of foreign cations on the surface or in the interlayer of the clays. This is the major factor responsible for the cation-cation exchange properties in sheet silicates.

Besides isomorphous substitution, broken bonds around the edges of the silica alumina units would give rise to unsatisfied charges. In silicates, the hydroxyl groups would be attached to silicon of broken tetrahedral units and the hydroxyls could be ionized in a similar fashion as ordinary silicic acid ($-Si-OH + H_2O \rightarrow SiO^- + H_3O^+$) thereby developing a negative charge on the lattice. Further, a negative charge on the lattice can be caused by hydrogens of exposed hydroxyls (which are an integral part of the structure rather than due to broken bonds) may be replaced by cations which are exchangeable. But such hydrogens are not held tightly as compared with hydroxyls associated with broken bonds [13]. Therefore, clay minerals have the property of sorbing certain cations and retain them in an exchangeable state, i.e., the adsorbed cations will be exchangeable for other ions when treated with other cations in a water solution as well as in a nonaqueous environment. Since the exchangeable cations compensate the unbalanced charge over the clay layers, the cation exchange reactions occur stoichiometrically. The total amount of exchangeable ions can be determined analytically [24]. The amount of exchangeable cations expressed in milliequivalents per 100 grams of an air dry clay is cation exchange capacity (CEC) or base exchange capacity. The cation exchange capacity is a measure of the interlamellar charge density. Most of the cation exchange processes are situated at the basal plane surfaces for the exchange due to lattice substitutions (constitutes about 80% in

smectites and vermiculites) while the exchange that takes place around the edges of the clay layers is due to broken bonds. The commonest exchangeable cations in the clays are Ca^{2+} , Mg^{2+} , H^+ , NH_4^+ , and Na^+ . During entry of an ion and exit of another ion, the structural units of the clay is not affected. Depending up on the nature of the clays, different member of sheet clays exhibit different cation exchange capacities that influences their chemical behaviour. Cation exchange phenomena is practically useful in all fields where clay minerals are studied and used, specially in soil science and engineering.

Due to the absence of isomorphous substitution in tetrahedral and octahedral layers, pure pyrophyllite is electrically neutral, thus does not exhibit cation exchange phenomena[12, 21].

The basal spacing of kaolinite, a 1:1 layered clay, does not leave rooms for interlayer molecules and cations, hence does not expand. Therefore, the charge compensating cations reside on its surface, as a result it shows low cation exchange capacity [23, 24, 25]. Sheet clay illite differs from other members by isomorphous substitution of Al^{3+} for Si^{4+} in the silica tetrahedra. The negative charge developed due to this substitution is compensated by the K-ions that strongly bind the layers together and prevent free motion of water and cations, thus it does not swell and as a result has low cation exchange capacity [12, 25]

Table 2.2. Composition and CEC of the five group clay minerals [23].

Mineral	Ideal composition	CEC Mequiv/100g
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_2$	1-10
smectite	$\text{EX}_x[\text{Al}_{2-x}\text{Mg}_x] \langle \text{Si}_4 \rangle \text{O}_{10}(\text{OH})_2 \cdot \text{H}_2\text{O}$	80-150
Illite	$\text{K}_{1-x}[\text{Al}_2] \langle \text{Al}_{1-x}\text{Si}_{3+x} \rangle \text{O}_{10}(\text{OH})_2$	10-40
chlorite	$[\text{Mg},\text{Al}]_3(\text{OH})_6[\text{Mg},\text{Al}]_3 \langle \text{Si},\text{Al}_4 \rangle \text{O}_{10}(\text{OH})_2$	5-30
vermiculite	$\text{EX}_x[\text{Mg}_3] \langle \text{Al}_x\text{Si}_{4-x} \rangle \text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$	100-180

The most common exchangeable cations on smectites are sodium and calcium. But smectites containing other interlayer cations can be prepared by immersing the solid clay into a salt solution containing a desired cation [26].

Table 2.3. Different smectite group clay minerals obtained by isomorphous substitution in the prototype pyrophyllite or talc structure[13,21]

Clay	Td-substitution	Oh- substitution
Pyrophyllite	Si ₈	Al ₄
Talc	Si ₈	Mg ₆
Montmorillonite	Si ₈	Al _{3.34} Mg _{0.66}
Beidellite	Si _{7.33} Al _{0.66}	Al ₄
Nontronite	Si _{7.33} Al _{0.66}	Fe ₄
Saponite	Si _{7.34} Al _{0.66}	Mg ₆
Hectorite	Si ₆	Mg _{5.534} Li _{0.66}
Sauconite	Si _{6.7} Al _{1.3}	Zn _{4.5} (Mg,Al,Fe) _{2-x}

Bentonite, whose chief composition is montmorillonite [25], is mainly characterized by the property of adsorbing water to a greater extent accompanied by a considerable increase in volume and formation of gelatinous mass [27]. Montmorillonite differs from the other member of smectites due to the isomorphous substitution of Mg²⁺ for Al³⁺ in the alumina tetrahedra, this provides it a negative charge on the crystal lattice, which is balanced by adsorption foreign cations. This factor owes it cation exchange behaviour. Due to free motion of water molecules in the interlayer, montmorillonite is distinguished by its exceptional swelling behaviour. This layer swelling is caused by the hydration of interlayer cations which brings about high hydration energy that can overcome the Van der Waal's attractive forces between the layers. Thus when montmorillonite is in contact with water, the water molecules will penetrate into the layers causing the layer to expand like an accordion [21].

The amount of the interlayer water depends upon the nature and concentration of the interlayer cations to be exchanged. For example, Na-montmorillonite takes one layer water and has a C-spacing of 12.5Å and Ca-montmorillonite takes two layers of water molecules resulting in the C-axis spacing of 14.5Å-15Å . This reflects that the amount of the interlayer water molecules is a function of ionic hydration surrounding the exchangeable cations [13, 25].

Due to its variable swelling property, smectite clays can accommodate a wide range organic molecules forming organo-clay complexes. Further, cations in the interlayer or on the surface around edges can easily be exchanged for other cations available in the solution. Because of its high cation exchange capacity, resistance to high temperature treatment [28], montmorillonite has become one of the best clays to be used as cation-exchanged catalyst.

2.2.2. FACTORS AFFECTING CATION EXCHANGE CAPACITY

Ion-exchange is a diffusion process and its rate depends upon the mobility of the ions. When exchange reaction is accompanied by swelling, the change from one stable state interlayer distances to another requires certain activation energy. The replaceability of cations depends upon such factors like experimental conditions, cations involved and the kind of the clay mineral, thus there is no single universal replaceability order. However, cation-exchange capacity is influenced by some important parameters.

1. *Effect of concentration:* The replacement of Ca^{2+} and Mg^{2+} by NH_4^+ was found to increase as concentration of NH_4^+ increases. Since cation exchange is stoichiometric reaction and the laws of mass action would work, this is to be expected. In general, therefore, increasing the concentration of the replacing cation causes greater exchange by the cation.

2. *Nature of the ions:* All factors being constant, the higher the valence of the ion, the greater is its replacing power and the more difficult to displace it when already present on the clay. The nature of ions is manifested by valence in nonhydrated and hydrated conditions, a polarizability and polarizing power. The adsorption affinity to the clays

increases with valency. In ions of the same valence, replacing power tends to increase as the size of the ion increases, the smaller ions are less lightly held than the larger ones. An exception to the effect of ionic size occurs in those ions which have almost correct size and coordinated with the basal oxygen sheet of the layered clay mineral. Potassium has such a characteristic that it is relatively difficult to replace it. Ionic hydration plays an important role in adsorption; is a factor that controls the replaceability of cations. For ions of equal valence, those which are least hydrated have the greatest energy of replacement and are the most difficult to displace when already present on the clay, the less hydrated the ion the more tightly it is held. Thus, lithium, although a very small cation is considered to be highly hydrated and, therefore, has very high hydration size. The low replacing power of Li^+ and its ready replaceability are said to be the consequence of large ionic hydration size. Based on these facts, the replacement series of some cations in a clay layers was shown as $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ [29].

3. *Population of the exchange position*: The ease of release of an ion depends not only on the nature of the ion itself but also up on the nature of the complementary ions filling the remainder of the exchange position, and on the degree to which the replaced ions saturate the exchange spots.

2.3. CATION-EXCHANGED CLAY CATALYSIS

The growing industrial interest in clay catalytic activity in organic reaction is related to the role that clay might have played in the generation of the prebiotic material of certain complexity [21]. It was well known that several members of the sheet silicate family can form interlamellar complexes (intercalates) with a wide range organic molecules [30]. Recently, a good deal of effort has been directed toward the elucidation of the structure and properties of various stable silicate intercalates, so that much is now known about the dependence of charge density of the layered host as well as the size of organic guest and on the degree of the up take of the later. Under favourable circumstances, well-ordered stable organic intercalates are amenable to structural elucidation by IR spectroscopy and X-ray [31].

The interlamellar organo-clay complexes can be prepared by mixing dry clay with a desired organic compound. A wide range of naturally occurring and modified sheet silicates have extensively been used as catalysts in a number of industrially important reactions such as ether formation, dehydration of alcohols, esterification, isomerization, oligomerization, polymerization, oxidation and cracking of hydrocarbons [30]. The clays were first subjected to ion-exchange and it has been found that the interlamellar cations such as Al^{3+} , Fe^{3+} , Cr^{3+} and Cu^{2+} confer significant catalytic properties upon the silicates organic conversion [32]. Frequently the function of the large area of clay catalysts, especially those that were acid washed, were simply to serve as a Bronsted or Lewis acids. The reaction taking place inside the sheet silicate host involves a gradual depletion of reactants that are brought into appropriate juxtaposition in the intercrystallite(interlamellar) region of the intercalate.

It is well known that many neutral reactants are strongly catalysed by Bronsted acids(proton donors) Lewis acids(electron pair acceptors) where catalysis occurs when the conjugate base or acid of the substrate is more labile than the neutral species [33].

The catalytic activities of clays originate either from Bronsted or Lewis sites. Bronsted acidic sites occur in acid treated clays and also created by the polarization and subsequent dissociation of resident water coordinated to the interlamellar metal cations. The Lewis sites, which mostly occur in dry clays are associated with surface features such as in octahedrally coordinated aluminium in the clay [34]. Further oxidizing (e.g., Fe^{2+}) and reducing (e.g., Fe^{3+}) sites are available in the interlamellar or outside on the surfaces of the clay. Bronsted acidity has been shown to be responsible for many processes that include ether, ester and amine formation.

The microenvironment surrounding the exchangeable interlamellar cation in montmorillonites are efficient in bringing about novel organic reactions that proceed with a little thermal activation [35].

2.3.1. Conversion of alkenes to ethers by cation exchanged clay catalysts

The water associated with interlamellar cations reacts under milder conditions with

alk-1-enes giving the corresponding di-(alk-2-yl) ethers [36]. It has been found that hex-1-ene is cleanly converted in the liquid phase either in hexane solution or with self solvent by a certain cation exchanged montmorillonite within a temperature range 44°C to 72°C into an oxygen containing substance, bis-2-hexyl ether. Apart from the specificity of the reaction, the fact that it occurs at such relatively low temperatures is also particularly noteworthy. Based on the initially available water in the interlamellar regions principally as bound to cations ether was produced quantitatively but the yield was variable depending upon the nature of the alkene and reaction conditions. The homologs hept-1-ene, and oct-1-ene behaved in a similar manner on refluxing in n-hexane [30]. The alkene water reaction is a stoichiometric process, involving the coupling of intercalated water with two alkene molecules and ceases when all the water has been consumed.

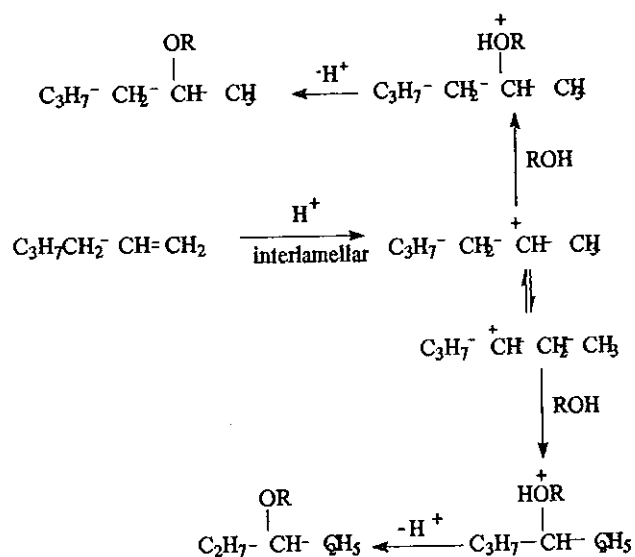
Refluxing of hex-1-ene, hept-1-ene, or oct-1-ene on a copper-exchanged montmorillonite in a solution of n-hexane, a high molecular weight material was produced in each case. A sample formed from hex-1-ene was isolated and preparative gas-liquid chromatography, infrared spectra and ¹H NMR spectra showed it to be an ether; olefinic features were absent. With regard to the spectroscopic evidences, it shows that oxygenated molecules must be derived from water in the clay. Therefore, it is possible to describe the ether formation at least formally as addition of water to alk-1-ene to give alk-1-ol, followed by reaction of alk-1-ol and further alk-1-ene molecule to give ether [37]. Test runs on the activity of related layered structures like collapsed clays or any cation-exchanged clays which are incapable of expanding to intercalate various organic reactants (eg. alkenes) were carried out and found that no product (e.g., ether) was formed. These facts proved that chemical conversion in clay catalysis takes place in the only interlamellar regions. Therefore, intercalation of the substrate is the necessary precondition for the reaction leading to organic conversion. Further, the importance of the structural OH groups were also investigated on synthetic hectorites, $\text{Li}_{0.7}\text{Mg}_{5.3}\text{Si}_8\text{O}_{10}(\text{OH},\text{F})_4 \cdot n\text{H}_2\text{O}$, where the OH group is replaced by F⁻ ions, no difference was observed in behaviour between these two clays. This substantiates the view that the structural OH groups are unimportant in ether production [30].

The <2µm fraction of Cu²⁺-exchanged bentonite (BDH) having cation exchange

100g of an air dry clay was found to be active in converting hex-1-enes. Bentonite (e.g., Hopkin and Williams) was also used to prepare a clay catalyst which is efficient for ether production until all available sites were consumed [32]. After this, other processes like ether and alkene dimerization were also catalysed by the clay.

Reaction of alkenes by cation exchanged clay catalysts

Carboxylic acids [36] have been shown to add readily to alkenes at 100°C to yield esters in a very clean reaction. Ethene and acetic acid, react in the interlamellar regions of Al³⁺-exchanged montmorillonite to yield ethyl acetate as a sole product. Similarly isopropyl acetate is the product from the reaction of propene and acetic acid. However, for hex-1-ene, isomeric products obtained as in the case of the reaction of hex-1-ene with acetic acid in the presence of the Cr³⁺-exchanged montmorillonite at 200°C yield 1-hexylacetate and 30% of 3-hexylacetate. All the reactions proceed via the migration of interlamellar protons produced as a result of ionization of the clay. Mechanistically, conversion of alkenes to alcohols, ethers or esters is suggested in the scheme below (eg. hex-1-ene).



Scheme 2.3.1. Etherification and esterification of alkenes by cation exchanged clay catalysts.

...ntual collapse of the ... added to intercalated ... acting as a protonic ... ic acids or alcohols to ... the preparation of t- ... es that produce highly ... reactions in the sheet

... montmorillonite-k10 ... dec-1-ene at 27°C but ... ization activity of ... ns that the conversion Among the various ... r of Montmorillonite- ... ontmorillonite-K10 > ... lay catalysts. An IR ... t the oligomerization ... of Bronsted acid sites

its

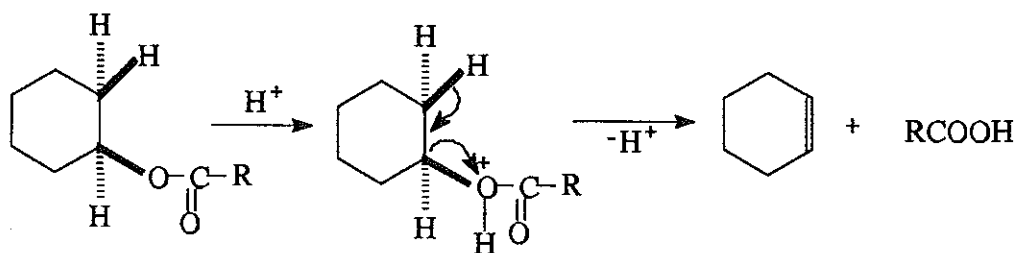
... died and found that ... on of ethanol at 350- ... oduct confirmed the ... rg cation-exchanged ... talyst [40]. Further,

considerations are important with secondary aliphatic amides.

It has been reported [44] that cation exchanged montmorillonite could catalyse the addition of methanol to alkenes, rather than water, though methanol has stronger tendency to displace other intercalated organic compounds might have prevented the hydrocarbon molecules from reaching the catalytic sites. In the event, the reaction proceeded smoothly and more rapidly than sulphuric acid catalysed addition of alcohols to isobutene in solution.

2.3.6. Decomposition of esters by cation exchanged catalysts

Cyclohexylesters [43] such as cyclohexylethanoate, cyclohexylbenzoate, and cyclohexyltri-methylethanoate are known to decompose into cyclohexene and corresponding acids over pyrex or quartz surfaces above 400°C. However, under reflux condition these esters were found to break down efficiently at high rates by using metal ion-exchanged sheet silicate catalysts (e.g., Al^{3+} -montmorillonite) with xylene solvent. This can be shown as follows.



Scheme 3.5. decomposition of esters by cation exchanged clay catalysts

When different ratios of clay catalyst were used, it was found that increasing the catalyst concentration beyond 0.2g in 5cm³ of a 10% of cyclohexylethanoate in xylene

did not increase the rate of disappearance of the ester probably due to mixing problems. When compared with using other catalysts like zeolites, and synthetic hectorites, most of the metal ion-exchanged montmorillonites were found to be most efficient catalysts for the ester break down. Cu^{2+} -exchanged montmorillonite is effective in the polymerisation of ethene where Ni^{2+} -exchanged montmorillonite was found to dimerize ethene to butene. The dimerization activity increased with increasing acidity [45]. Alkylation of benzene and anthracene with 1-dodecene has been accomplished over cation exchanged smectites [46]. Mixed clays Kaolinite, Illite and montmorillonite after mild pretreatment were successfully tested as catalysts in the polymerization of styrene [47].

Product analysis of cation-exchanged catalysis were effected by gas-liquid chromatography-mass spectra (GC-MS), infrared spectroscopy and proton nuclear magnetic resonance (^1H NMR).

All the experimental findings and theoretical treatments rationalize the effectiveness of a particular cation-exchanged sheet silicates in terms of their Bronsted acidity. From the ongoing discussions, it is clear that extensive works have been accomplished in the field of cation-exchanged clay support heterogeneous catalysis. Further, the wide range of investigations carried out so far reveal that much attention has been given to this area. Even though extensive works have been done in this field, there remain a wide range of reactions not studied yet. Therefore, in the foregoing works preliminary studies on basic natures of three clays and their catalytic nature on some organic compounds when they are exchanged with ferric cation will be under taken.

CHAPTER 3

EXPERIMENTAL

3.1. STUDY OF THE WORKING CLAYS

3.1.1. SIEVING

Prior to any investigation, the three clay varieties, Local bentonite, drilling mud bentonite and BDH-bentonite, were sieved by passing them through 200 mesh size sieve to get definite particle size of the clays.

3.1.2 . FREE SWELL TEST

The free swell test of each clay sample was carried out by making use of standard procedure [48].

An air dry powder of each clay was kept in an oven at 65 °C for 24 hours and allowed to cool to room temperature in a desiccator. About 10ml of the dry powder of each clay sample was taken in a 100ml measuring cylinder and made to disperse completely in 50ml of distilled water and more water was added to 100ml mark and kept for 24 hours.

The volume of the swelled sample was read and the degree of swelling(sd) in percentages was calculated by the relation:

$$sd = (V_s \times 100 / V) - 100$$

where: sd = degree of swelling
 V_s = volume of the swelled sample in ml
 V = volume of the sample taken in ml

The results are given in table 4.1.

3.1.3. ELEMENTAL ANALYSIS OF LOCAL CLAY AND DRILLING MUD BENTONITE

The elemental analysis of the two clay samples, the local clay and the drilling mud bentonite, was carried out by fusing the samples into the oxides of the elements and the results were obtained as percentage of their oxides and the results are given in table 4.2.

To obtain information about the mineral composition of the clay samples, x-ray diffraction analysis was used by taking the powder diffraction spectra on a Regaku X-ray diffractometer from 2° to 40°.

3.1.4. DETERMINATION OF CATION- EXCHANGE CAPACITY (CEC)

Cation exchange capacity is an important parameter, because it gives an indication of the type clay mineral present and its capacity to retain cations. There are various methods proposed for cation exchange determination such as ammonium acetate method, sodium acetate method, etc but the ammonium acetate method was adopted because it is the most commonly used [49].

In the ammonium acetate method the clay sample is washed, first with ammonium acetate to displace all available charge compensating cations by ammonium ions, and then with ethanol to make the samples free of excess salt (cations which has not occupied the exchange sites), the adsorbed ammonium is displaced by sodium ion by treating it with sodium chloride solution. The displaced ammonium is distilled and the evolved ammonia is determined

In this experiment, 2g of each clay sample was weighed and put in 250ml conical flask, 75ml of 1M ammonium acetate solution whose pH was adjusted to 7 by adding acetic acid was mixed with equal volume of ethanol and shaken instantly with a shaker. Then the suspensions were closed tightly with a rubber stopper to prevent the escape of ammonium ion in the form of ammonia gas and allowed to stand overnight to replace all available exchangeable cations by NH_4^+ ions.

The next day, the soaked samples were centrifuged and the supernatant liquid was reserved. Each sample was further washed with additional 25ml of ammonium acetate-ethanol mixture by completely stirring to assure the displacement of any available cation on the exchange sites, the volumetric flask containing 100ml of the leachate was removed and kept for the determination of exchangeable bases.

Each sample was, then, washed with 25ml ethanol and the washing was repeated 2 to 3 times to remove excess NH_4^+ ions that has not occupied the exchange site, complete removal of the excess ammonium ions was tested by taking small amount of the supernatant liquid and adding three drops of Nessler's reagent [50] to look for the disappearance of orange-brown precipitate (where, Nessler's reagent, $\text{K}_2[\text{HgI}_4]$, is added to a dilute ammonium salt solution, the liberated ammonia reacts with the reagent to form an orange-brown precipitate). Washing continued until the orange-brown precipitate disappeared.

The remaining precipitate was washed successively with 4- 25ml portions of 10% of sodium chloride solution to displace the ammonium ions on the exchange sites in the interlamellar layer of the clay. The supernatant liquid was collected in a 100ml volumetric flask. This solution contains the NH_4^+ ions that have been occupied the exchange position, thus the amount of the ammonium ions will be the cation exchange capacity of the clay. The amount of the NH_4^+ ions displaced was distilled by Kjeldhal distillation and the evolved ammonia was determined.

The collected 100ml of the leachate was transferred into 500ml Kjeldhal flask and 0.20M H_2SO_4 solution was added to 250ml Erlenmeyer flask receiver on a stand under a condenser tip (with tip just dipping into sulphuric acid solution so as to prevent the escape of NH_3 coming from the distillate). 1N NaOH was added to the component in the Kjeldhal flask and immediately connected to the distillation apparatus again to avoid the escape of ammonia gas and then distilled until the component in the Kjeldhal flask is completely finished.

When the distillation was over, the Erlenmeyer flask receiver was removed from the distiller and titrated against 0.1N NaOH solution, using methyl red as an indicato

until the colour changes from pink to faint yellow.

In this titration process the amount H_2SO_4 left in excess without being neutralized by the evolved ammonia gas from the distiller was determined.

i.e., Milliequivalents of H_2SO_4 = Milliequivalents of NH_3 + Milliequivalents of NaOH.

CEC = Milliequivalents of NH_3 = Milliequivalents of H_2SO_4 - Milliequivalents of NaOH

In the experiment, 2g of standard silica sand was included as a blank, and thus the CEC was calculated simply by the relation:

$$CEC(\text{ mequiv /100gm clay}) = [(b-a) \times N \times 100] / S$$

where: a = volume of 0.1N NaOH consumed for titration of the blank

b = volume of 0.1N NaOH consumed for titration of the sample

N = Normality of NaOH(0.1N)

S = air dry sample weight in gram

The results are provided in table 4.3.

3.1.5. DETERMINATION OF EXCHANGEABLE BASES

The exchangeable bases, Na^+ , K^+ , Mg^{2+} , and Ca^{2+} , were determined while the cation exchange capacity determination was carried out [49]. That is, after the samples were saturated with ammonium ions which displaces all of the exchangeable cations, the leachate was preserved for the determination of the bases. The exchangeable cations were determined:

The amounts of exchangeable K^+ and Na^+ ions were determined by flame emission photometry on Gallencamp Flame Analyser while the amounts of exchangeable Mg^{2+} and Ca^{2+} ions were determined by atomic absorption spectroscopy and the results were calculated in milliequivalents of the cations per 100g of the dry clay and the

results are provided in table 4.4.

3.1.6. DETERMINATION OF EXCHANGEABLE HYDROGEN

The exchangeable hydrogen ions in the clay samples were determined [51] as follows.

0.1gm of each clay samples was taken in 250ml conical flask and to each 100ml of 1N sodium chloride solution was added and the mixture was shaken for 12 hours. After the suspensions were centrifuged, 50ml of the aliquot of each sample was taken and titrated against 0.01N of NaOH. From volumetric titration the amount of H⁺ ions librated was calculated in melliequivalents per 100g and the experimental results are given in table 4.5.

3.1.7. IR SPECTRA OF THE CLAYS

The three clay samples were dried at 60°C in an oven cooled in a desiccator over calcium chloride and the spectrum was taken on Perkin Elmer 1600 Series FT-IR spectrophotometer using KBr pellet [7] and the interpretation is given in table 4.6.

3.2. FRACTIONATION OF THE CLAY SAMPLES

Fractionation of clays is an important process in getting particles of uniform size and properties.

In this experiment, 10g of each clay samples was taken in a respective 500ml conical flask and made to disperse in enough amount of distilled water [35] by shaking for a long period of time, then kept soaked for 24 hours. The drilling mud bentonite (DMB) and BDH bentonite formed a colloid and a dark precipitate while the local clay sample was totally settled forming a clear water layer.

On centrifugation, the DMB and the BDH-bentonite samples were fractionated into three fractions, namely a white colloid, a white gel, and a dark precipitate. The colloid was decanted, the gel was collected carefully and dried in an oven at 100°C,

The Fe³⁺-exchanged clays are characterized in the foregoing experiments.

3.3.1. Cation-exchange Capacity Determination of Fe³⁺-Exchanged Clays.

Each clay sample(0.5g) was taken in 250ml of conical flask and to each sample 50ml of 1M ammonium acetate solution was added and shaken for several times every 15 minutes until the particles were completely dispersed in the solution. The next day, each sample was shaken and centrifuged, the supernatant liquids were collected in a 100ml volumetric flasks; each precipitate was washed with 25ml of additional ammonium acetate solution twice and the aliquot was collected in the corresponding volumetric flask. Each aliquot sample was subjected to atomic absorption spectroscopy to determine the amount of ferric ions that were displaced by the ammonium ions which will represent the cation-exchange capacities of each Fe³⁺-exchanged clay. The results are given in table 4.9.

3.3.2. Determination of the Exchangeable Hydrogen of Fe³⁺-exchanged Clays

The exchangeable hydrogen determination Fe³⁺-exchanged clays was carried with the same procedure as experiment 3.1.6. and the results are given in table 4.10.

3.3.3. IR spectrum of the Fe³⁺-exchanged clays

Fe³⁺-exchanged clays were dried at 100⁰C, cooled in a desiccator to room temperature over CaCl₂, their IR-spectra were taken by FT-IR spectrophotometer as KBr pellets.

3.4. STUDY OF THE CATALYTIC ACTIVITIES OF Fe³⁺-EXCHANGED CLAYS

Cation-exchanged clay support catalysis, like addition of water to alkenes [13,14], elimination of water from alcohols [15], elimination of ammonia from amides [16] and oligomerization of alkenes [17] were mostly carried out under reflux conditions at different temperatures.

3.4.1.Refluxing cylohexanol with Fe³⁺-exchanged clays

To 0.3g of each Fe³⁺-exchanged clays (BDH bentonite, drilling mud bentonite and local clay) in a 50ml round bottomed flask, 3ml of cyclohexanol was added. Then a magnetic stirrer was added to each mixture and fitted to a condenser. After stirring for 2 hours, each hydrocarbon-clay mixture was refluxed for 4 hours at 161-165°C on a paraffin oil bath. The refluxed hydrocarbon-clay mixture was cooled to a room temperature and each sample was separated by centrifugation, then the yellowish supernatant liquid was obtained. To compare the effect of Fe³⁺-exchanged clays, cyclohexanol was also refluxed without the catalyst under the same conditions and all samples were subjected to a gas chromatographic analysis under the following conditions.

Column: capillary SE-54 non polar stationary phase (50mx0.259i.dx0.25 film thick)
Temperature: oven- 40-220°C; Injector- 200°C, FID- 270°C, Program rate 8°C/minute.
Flow rate: H₂-30ml/minute; air-300ml/minute; carrier gas N₂-1.3ml/minute
Sample size: 0.05μL

Instrument: Varian model 3700 Gas Chromatograph

The results of the relative retention times and percentages of the starting material and after reflux with the three clay are given in table 4.11.

3.4.2. Refluxing cyclohexene with Fe³⁺-exchanged clays

0.5g of Fe³⁺-exchanged clay was taken in a respective 50ml round bottomed flask, to each 5ml of cyclohexene was added, after adding a magnetic stirrer, the hydrocarbon clay mixture was fitted to an ether condenser and stirred for 2 hours. While stirring, the colour of the mixture was changed from brown to black. Then the mixture was refluxed for 4 hours on a thermostated water bath at 82-84°C. The hydrocarbon clay mixture was separated by centrifugation. To compare the effect of the Fe³⁺-exchanged clays pure cyclohexene was also refluxed without the clays under the same conditions. The supernatant liquid and cyclohexene refluxed without the catalyst were subjected to GC under the same conditions as experiment 3.4.1. The results of the GC are given in table 4.12.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. UNFRACTIONATED CLAYS.

4.1.1. The free swell test.

Table. 4.1. The free swell test of the clays

Sample	Volume of swelled sample(ml).	Degree of swelling(sd) (%)
Local clay	18.0	80.0
Drilling mud Bentonite	100.0	900.0
BDH-Bentonite	100.0	900.0

A bentonite is characterized by the fact that it may adsorb up to five times its weight of water and increase its volume up to fifteen times of its dry weight. When treated with 18-20 parts of water, such bentonite will form a sol in which the mineral will remain suspended almost indefinitely.

The same degree of swelling of BDH-bentonite and drilling mud bentonite shows that they possess similar interlayer spacings. Due to their high degree of swelling, they show typical nature of bentonites. Compared to the two bentonites, the degree of swelling of the local clay is very low, thus it is difficult to conclude that the local clay belongs to the same group as the two bentonite samples. Basically, bentonite or smectite group clay minerals are distinguished by the expansion of their layers when they become in contact with water [7]. But the local clay sample lacks this quality.

The maximum swelling of the bentonite samples was tried at 130ml and 250ml and observed that the samples became thinner and thinner or their viscosity went on

decreasing and no clear water layer could be obtained. Therefore, the standard procedure described for the free swell test was directly applied.

4.1.2. ELEMENTAL ANALYSIS

Table 4.2. Elemental composition of Local clay (LS) and drilling mud bentonite(DMB) in % of oxides

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	MnO	P ₂ O ₅	TiO ₂
LCS	53.16	17.18	5.42	3.80	3.88	0.32	0.66	<0.01	0.11	0.52
DMB	55.85	17.16	3.08	0.80	1.52	1.44	0.36	<0.01	0.06	0.12

The chemical compositions of hydrous clays show that they are composed of 46.52% silica, 39.53% Al₂O₃, and frequently appreciable quantities of iron, alkalis and alkaline earth metals are also found [9]. The chemical composition of bentonites was shown to be 60.64% SiO₂, 23.26% Al₂O₃, 3.92% Fe₂O₃, 0.59% CaO, 2.19% MgO, and 4.33% Na₂O [10]. The percentage chemical composition by weight of montmorillonite supplied by Boland Base Mineral Ltd was 65.10% SiO₂, 20.40% Al₂O₃, 4.80% Fe₂O₃, 2.11% CaO, 4.40% MgO, 0.30% K₂O and 2.80% Na₂O [5].

The elemental composition of the two clay samples show similar trend with each other and with the reported elemental composition of bentonite and montmorillonite. While speaking the composition of a clay, the geological origin, area from where the sample is collected and the way of preparation of the sample must be taken into account. The discrepancy from the reported literature value may be accounted for by these parameters. Nevertheless, the elemental analysis confirm that the samples under consideration are alumino-silicates.

Even though the elemental analysis of the two clays show that they have almost the same composition, surprisingly their swelling behaviour is completely different. Because of the significant swelling, the drilling mud bentonite can be said that it is composed of large quantities of smectite group clays like montmorillonite and due to its negligible swelling, the local sample may not be regarded as bentonite but it may

be another variety of clays, probably like illite or kaolinite which do not expand to an appreciable extent., despite the fact that the composition of illite is similar to montmorillonite, due to the presence of large sized potassium ion in the interlayer it does not swell.

Untreated x-ray powder diffraction profiles taken from 2° to 40° are similar showing that all the clay samples are qualitatively similar and composed of various types of clay minerals which is shown by the peaks at different angles of irradiation by the x-ray. Different components give different responses corresponding to their interlayer distances.

4.1.3. CATION-EXCHANGE CAPACITY (CEC)

Table 4.3. The experimental cation exchange capacity values of the unfractionated clay varieties.

Sample	Vol. leachate	Vol. NaOH consumed	CEC	Av. CEC
Blank	100ml	30.20	0.00	0.00
Local clay	100ml	16.80	67.00	66.50
	100ml	17.00	66.00	
Drilling mud Bentonite	100ml	19.00	56.00	56.00
	100ml	19.00	56.00	
BDH-Bentonite	100ml	14.20	80.00	79.50
	100ml	14.50	78.50	

The cation-exchange capacity range of smectite clay group is 80-150 milliequivalents

per 100g of the dry clay [9]. Bentonite, whose chief composition is montmorillonite, is a member of smectite group clay mineral. Thus, the CEC of bentonite is in the CEC range of smectite clay minerals. However, from table 4.3 only the CEC value of BDH-bentonite approximately enters into this range, where the remaining clay samples do not enter into the range. This is due to the fact that (as observed from the x-ray diffractometer spectra), the clays are poly component materials that their properties are determined by their components. Therefore, the experimental CEC value will be the contribution of all the components.

The CEC value of the local clay (66.5 mequiv / 100g of dry clay) is greater than the CEC value of the drilling mud bentonite (56 mequiv / 100g of dry clay). This is in agreement with the higher amount of the exchangeable bases like Ca^{2+} (41.12 mequiv. / 100gm) which is very much larger than the drilling mud bentonite and that of BDH-bentonite. Relative to the other clay samples, even though, the local clay has a negligible swelling properties, it possesses higher charge density. Thus, it is reasonable to proceed with the investigation of the catalytic activities the local clay on organic conversions.

During the experiment, washing the clays by percolation was tried several times, but consistent results could not be obtained. Because the nature of the clays were sticky and expanding. Therefore, washing by centrifugation of these clays was found to be effective and gave reproducible results in the determination of CEC.

The relative cation exchange capacities of the three can be ordered as: BDH- Bentonite > Local clay > drilling mud bentonite. This order, thus, represents the order of relative charge density that is embodied in the unfractionated clays. Further, the conversion 1-hexene to di-2-hexyl ether was effected by using Cu^{2+} -exchanged BDH-bentonite with CEC 70 mequiv per 100gm of dry clay [37]. Thus, the use of these clays in the conversion of organic substances like alcohols and alkenes could be promising.

4.1.4. EXCHANGEABLE BASES

The knowledge of exchangeable bases gives a clue to estimate the cation exchange capacity. The total cation exchange capacity has to be greater than the amount of exchangeable bases. Because apart from the exchangeable bases, there can also be other charge compensating cations for which analysis would not be carried out.

Table 4.4. Exchangeable bases of unfractionated clays

Sample	Mequiv / 100gm of clay				Total
	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	
LCS	0.71	0.58	5.71	41.12	48.12
DMB	6.32	0.63	6.16	11.07	24.81
BDH-B	22.35	1.25	5.33	27.59	55.52

As can be seen from this table, the relative values of the exchangeable bases of the clays are in agreement with the relative order of their cation exchange capacities and the values of exchangeable bases is less than the corresponding CEC values of the clays which reveals that other exchangeable cation also contribute to the CEC values

4.1.5. EXCHANGEABLE HYDROGEN IONS

Hydrogens of the exposed hydroxyl groups which are the integral part of the clay structures may be replaced by other cations that might be exchangeable. The determination of exchangeable hydrogens in clays is an equilibrium determination of the proton [H⁺] supplying power of the colloidal material. The quantity of protons removed in the extraction solution is termed as the quantity of exchangeable hydrogen.

The catalytic activities of clays is a result of Lewis or Bronsted acid sites [26], specially when clays are involved in acid catalysis. Thus the knowledge of the nature of clays with respect their acidity is of greater importance while investigating the catalytic activities of clays.

Table 4.5. Amount of exchangeable hydrogens in mequiv / 100 gram of dry clay.

sample	1	2	3	4	Average
LCS	2.0×10^{-2}	2.4×10^{-2}	2.2×10^{-2}	2.0×10^{-2}	2.2×10^{-2}
DMB	1.6×10^{-2}	1.4×10^{-2}	1.4×10^{-4}	1.6×10^{-2}	1.5×10^{-2}
BDH-B	1.2×10^{-2}	1.0×10^{-2}	1.4×10^{-2}	1.2×10^{-2}	1.2×10^{-2}

As can be seen from this table, it is clear that the order of the acidity will be local clay > drilling mud bentonite > BDH-Bentonite. The stronger proton supplying power of the local clay is higher. The maximum acidic site concentration attained by treating Wyoming bentonite with glacial acetic under different temperature and time of treatment was 333 milliequivalents per 100g of the dry clay [53]. The acidities of these untreated clays is an encouraging foundation for using them in chemical conversion of some organic compounds as acid catalysts. In general, the three clay samples are acidic in nature.

4.1.6. Interpretation of the IR spectra of the clay samples

Clay minerals show infrared absorption bands in the frequency range between $3,500\text{cm}^{-1}$ to $3,700\text{cm}^{-1}$ due to the hydroxyl groups which are the integral part of the clay structures attached to aluminium in the alumina octahedra. The variation between this ranges arises from hydroxyl groups shared between atoms isomorphously substituted either for aluminium in the octahedral and/or silicon in the tetrahedral layer of the pyrophyllite structure. The structural OH bands for many clay minerals are narrow and thus can easily be distinguished from broad bands observed for hydrated minerals from 3200cm^{-1} to 3650cm^{-1} which are attributed to the presence of hydrogen bonded water molecules on the surface.

Table 4.6. IR spectra interpretations of the three clays.

Sample	Absorbtion frequency(cm ⁻¹)	Group responsible
LCS	3622.2 3443.1 1646.0 1040.2 521.7 466.8	structural O-H stretching vibration hydrogen bonded O-H stretching of water interstitial water O-H deformation vibration of Si-O Al-O-Si, Si-O-Fe Si-O-Fe, Si-O-Mg vibration
DMB	3630.5 3448.7 1645.9 1046.4 523.8 467.4	structural O-H stretching vibration hydrogen bonded O-H stretching of water Interstitial OH deformation water Si-O vibration Si-O-Al Si-O, Si-O-Fe, Si-O-Mg vibration
BDH-B	3629.9 3446.9 1646.2 1044.5 916.7 524.8 465.6	structural O-H stretching vibration H-bonded O-H stretching of water interstitial water Si-O vibration O-H bending vibrations Si-O-Al Si-O, Si-O-Fe, Si-O-Mg vibration

For free O-H groups, the frequency is around 3,700cm⁻¹, with frequency decreasing under the influence of associations, the decrease being a measure of hydrogen bond. As a general rule, in the layered silicate structures OH groups that are comparatively slightly associated show absorption frequencies of 3,600cm⁻¹ to 3,700cm⁻¹ whereas

the adsorbed water shows absorption band at lower frequencies, $3,400\text{cm}^{-1}$ and another band around $1,640\text{cm}^{-1}$ corresponding to deformation vibration of water. In general, a sample of montmorillonite and nontronite show strong absorption band between 3600cm^{-1} and 3700cm^{-1} , broad band around 3400cm^{-1} and several absorption bands between 1100cm^{-1} to 650cm^{-1} due to lattice vibrations [7].

As can be seen from the table, the IR spectra of the clays are similar showing that there are no significant differences among the bonding systems of the three clays. The shift of some bands may be due to the differences in isomorphous substitution of various cations in the silica tetrahedral and/or in the alumina octahedral layers.

4. 2. Study of fraction of clays considered

4.2.1. The CEC Values of fractionated clays

Table 4.7. CEC values of the fractionated of clay samples

Sample	Vol. NaOH consumed in titration	CEC(meq/100g of clay)	Av.CEC
Blank	28.70	0	0
LCS	22.50	62.00	63.5
	22.20	65.00	
DMB	22.80	59.00	58.00
	23.00	57.00	
BDH-B	20.30	84.00	85.00
	20.10	86.00	

When compared with unfractionated clay samples (table 4.3) a change of the CEC values of the clays after fractionation is observed. The local clay was suspected to

contain some impurities due to the manner of its collection of the sample. Therefore, after washing the sample the CEC was decreased from 66 to 63.50 Meq/100g of dry clay. This shows that some of the components responsible for higher CEC have been washed away while fractionation process.

The CEC values of drilling mud bentonite and BDH-bentonite were increased from 56.00 to 58.00 and from 79.50 to 85.00 respectively on fractionation. The BDH-bentonite enters to the CEC range of smectite group clay minerals to which it belongs. This increment in the CEC values after fractionation reveals that the gel fraction contributes to the higher CEC values while the discarded fraction may not. Therefore, the gel fraction may be regarded as a portion that is composed of components having greater CEC values. In other words this fraction carries higher charge density which can accommodate larger quantity of cations for exchange. Thus, it is promising for the preparation of cation exchanged clay support catalyst for the conversion of organic species. These experimental CEC values are reproducible and reasonable compared with the unfractionated clay samples. The changes in the CEC values of the clays is a result of fractionation which has worn out either the fraction responsible for the decrement or increment of the CEC values. However, the overall relative order of the CEC the clays is maintained.

4.2.2. EXCHANGEABLE HYDROGEN IONS OF FRACTIONATED CLAYS

Table 4.8. Exchangeable hydrogens in Mequiv/ 100g of dry clay

Sample	Experiment				Average
	1	2	3	4	
LCS	1.0×10^{-2}	1.0×10^{-2}	1.0×10^{-2}	1.0×10^{-2}	1.0×10^{-2}
DMB	0.9×10^{-2}	1.0×10^{-2}	1.0×10^{-2}	1.0×10^{-2}	0.96×10^{-2}
BDH-B	1.1×10^{-2}	1.3×10^{-2}	1.0×10^{-2}	1.2×10^{-2}	1.15×10^{-2}

Compared with the unfractionated clays, all the acidity of the clay fractions has

decreased perhaps due to the leaching out of the portions responsible for their acidity and the exchangeable cations that have the power of polarizing the interlayer water and structural OH group to make H⁺ ions available. Nevertheless, the relative acidity order of the clays is maintained.

4.2.3. Interpretation of the IR spectra of the fractionated clay samples

The IR spectrum of each of the fractionated samples shows the same trend of absorption bands except that each frequency of the fractionated sample is slightly shifted to higher frequencies and no major differences were observed after fractionation. The same interpretations given in the table 4.3. can be applied.

The powder X-ray diffraction of local clay and BDH-bentonite was taken under the same conditions as the unfractionated clays and some peaks were observed to diminish may be due to the washing away of some components during fractionation.

4.3. Study of Fe³⁺-exchanged clays

4.3.1. Cation exchange capacities of Fe³⁺-exchanged clays

Table 4.9. CEC values of Fe³⁺-exchanged clay samples as determined by atomic sorbtion spectroscopy.

Sample	vol. of leachate	instrument reading	CEC/100g
LCS	100ml	0.48	1.72
DMB	100ml	0.26	0.93
BDH-B	00ml	0.11	0.39

As can be observed from this table, the CEC values of Fe³⁺-exchanged clays are very small compared with the CEC values of the unexchanged clays samples (Table 4.7). The smaller CEC values obtained may be accounted for due to the inability of NH₄⁺

ions to displace the trivalent iron ions. Because the Fe^{3+} cations may be held strongly to the negatively charged clay layers and the ionic hydration of the ferric cation is higher than that makes it difficult to displace NH_4^+ . As a general rule, it is difficult to displace cations of higher positive charge with cations of lower positive charge [12].

4.3.2. EXCHANGEABLE HYDROGEN IONS OF Fe^{3+} -EXCHANGED CLAYS

Table 4.10. Exchangeable hydrogen ions of Fe^{3+} -exchanged clays in mequiv/100g of the dry clay

Sample	V. extract	N.extract	meq./0.1g	meq/100g
LCS	100ml	2.0×10^{-2}	1.0×10^{-5}	1.0×10^{-2}
	100ml	2.4×10^{-2}	1.2×10^{-5}	1.2×10^{-2}
DMB	100ml	5.0×10^{-2}	2.5×10^{-5}	2.5×10^{-2}
	100ml	4.0×10^{-2}	2.0×10^{-5}	2.0×10^{-2}
BDH-B	100ml	6.0×10^{-2}	3.0×10^{-5}	3.0×10^{-2}
	100ml	7.0×10^{-2}	3.5×10^{-5}	3.5×10^{-2}

Compared to the amount of the exchangeable hydrogen ions of the unexchanged fractionated clays, the corresponding individual acidity of all Fe^{3+} -exchanged clays has increased which may be related to the polarizing effect of the triply charged ferric cation on the interlayer water. Thus, the Fe^{3+} -exchanged clay samples are generally acidic which is the basic requirement for the clays to be used as acidic catalysts.

Compared to the unfractionated local clay, the amount of the exchangeable hydrogen ions of the Fe^{3+} -exchanged was decreased while increment in both drilling mud and BDH-bentonite was observed. This may be related to the swelling nature of the clays that local clay has the least degree of swelling meaning it accommodate the least amount of polarizable water molecules to be dissociated by the ferric cation. But the other two clays have high and similar degree of swelling that they can accommodate larger amounts of polarizable water molecules to be dissociated by the ferric cation.

The IR spectral studies of cation exchanged clays taken by using a KBr pellet shows that there are no qualitatively significant differences among Fe³⁺-exchanged clays and the unfractionated and fractionated clays. According to Farmer and Russel [13], absorption patterns are not affected by changing interlayer cations and is only slightly changed by changing the amount of interlayer water.

4.4. GAS CHROMATOGRAPHIC ANALYSIS OF REFLUXED CYCLOXANOL AND CYCLOHEXENE WITH Fe³⁺-EXCHANGED CLAYS

4.4.1. Cyclohexanol refluxed with Fe³⁺-exchanged clays

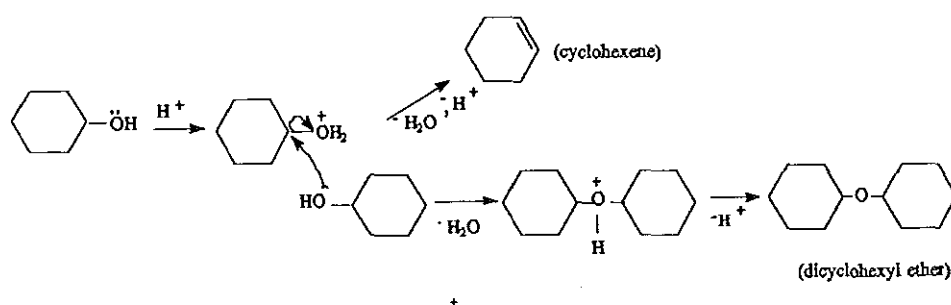
Table.4.11. Relative retention times(RT in minutes) and percentage(%) of starting cyclohexanol and after refluxed with three different Fe³⁺-exchanged clays

cyclohexanol		Cyclohexanol with BDH-bentonite		Cylohexanol with DM-bentonite		Cyclohexanol with Local clay	
RT	%	RT	%	RT	%	RT	%
—	—	1.21	18.73	1.47	18.04	1.62	25.04
4.33	94.59	3.80	70.16	4.77	72.92	4.64	61.80
6.19	1.43	5.65	1.61	6.40	1.41	6.59	1.54
—	—	11.69	4.73	12.77	3.34	12.91	5.31
13.64	1.21	12.94	1.65	13.92	1.41	14.10	2.22

The catalytic action of Fe³⁺-exchanged clay samples is observed in the decrease in the percentage of the starting material and the appearance of new peaks which were originally absent in the pure cyclohexanol chromatogram. The two new pairs of peaks appeared in all the three clays have about the same retention times (1.21 and 11.69 minutes for the BDH-bentonite, 1.47 and 12.77 minutes for the drilling mud bentonite and 1.62 and 12.91 minutes for the local clay). This probably shows that the clays have formed the same reaction products, but produced different percentages(18.37% for BDH-bentonite, 18.03% for drilling bentonite and 25.04% for local clay).

BDH-bentonite and the drilling mud bentonite showed equal degree of swelling (900% from table 4.1) but possess different CEC values and acidities throughout, nevertheless, both have yielded almost equal amounts of the reaction product in the first case (18.37% and 18.03% respectively) which shows that the interlayer spacings may play a major role. But the local clay differs from the two bentonites specially in its degree of swelling low (80%, table 4.1), however, it has produced greater yield compared to the other clay samples. The parameter affecting is probably the interlayer spacing. The two clays with the same degree of swelling gave almost equal amounts of product while the local clay with the least degree of swelling and the highest CEC value after exchanged with ferric cation yielded the greatest amount. Therefore, the highest yield obtained by the local clay may be the combined effect of the two factors. The size of the organic guest may exactly fit into the interlayer spacing of the local clay. Besides, the higher CEC of Fe^{3+} -exchanged local clay may enhance greater polarization of cyclohexanol molecules so that they will be more labile for conversion. But in the other clays the larger swelling nature of the clays provided free entry and exit for larger quantities of cyclohexanol molecules without being catalysed.

Cyclohexanol undergoes general reactions of secondary alcohols [54], and in acidic media dehydration and formation of ether takes place. From the catalytic reaction mechanism of cation-exchanged clay catalysis of alcohols, the major expected products are alkenes and ethers [41], thus the expected products of refluxing cyclohexanol with cation-exchanged clays are cyclohexene and dicyclohexyl ether. The mechanism of dehydration of cyclohexanol to cyclohexene and the production of dicyclohexyl ether can be depicted by the following reaction scheme.



Scheme 4.9.1. Conversion of cyclohexanol into cyclohexene dicyclohexyl ether by cation exchanged clays

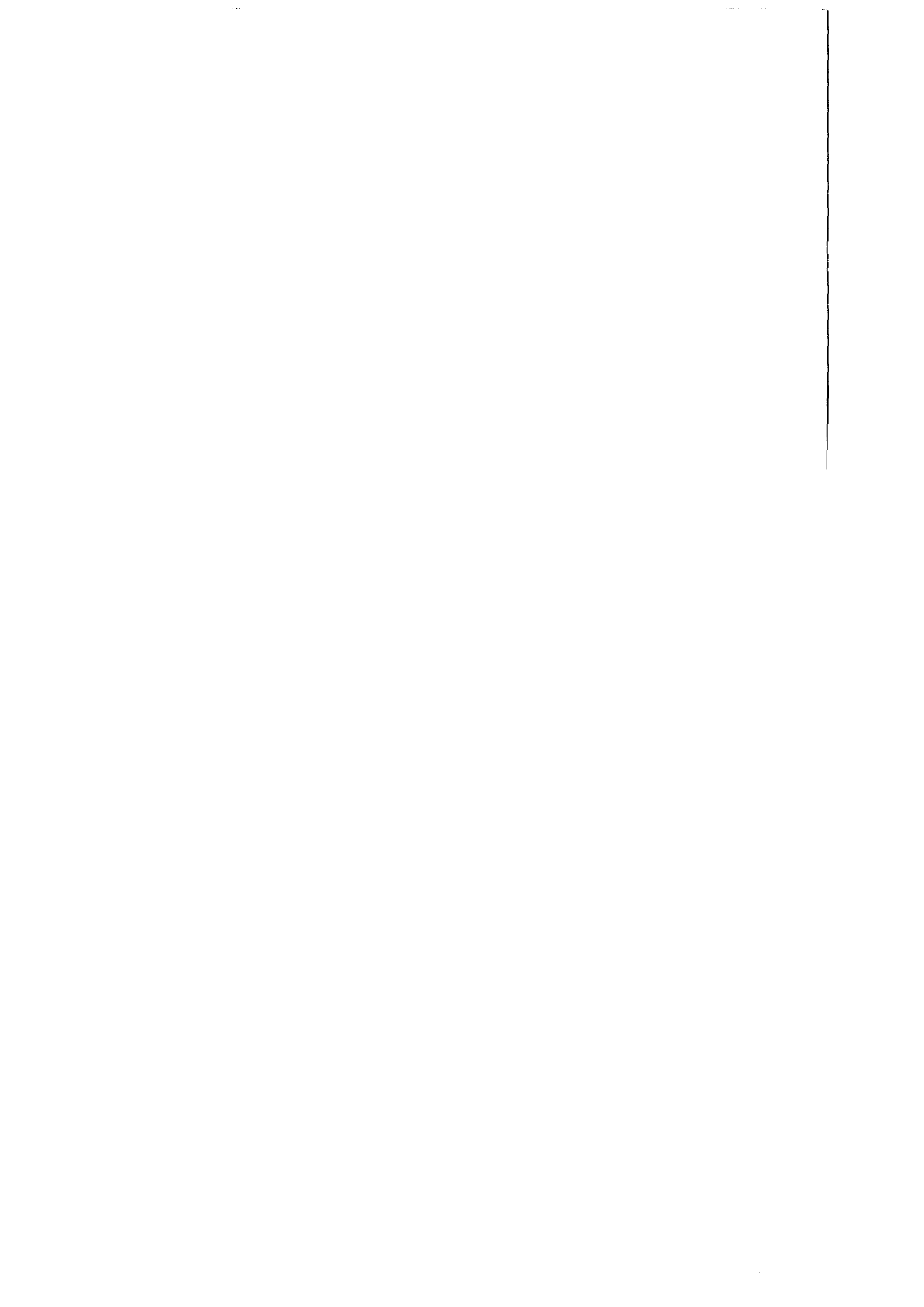
In order to get primary confirmation about the new peaks after refluxing cyclohexanol, retention time coincidence was applied by running the chromatogram of pure cyclohexene under the same chromatographic conditions as the refluxed samples. The major peak obtained with a retention time 1.57 minutes was around the same retention times of the new peaks appeared for the refluxed cyclohexanol with the three clays. Therefore, from this it is possible to tentatively conclude that the new peaks appeared with a retention time of cyclohexene in each case may correspond to the cyclohexene produced as a result of the catalytic action of the Fe³⁺-exchanged clays. Furthermore, to confirm the peaks were exactly cyclohexene, peak enhancement technique was applied by injecting 1:4 ratio by volume pure cyclohexene with the refluxed cyclohexanol samples. The expected peaks for the three samples were enhanced and the percentages of each peak was increased (from 1.73% to 29.67%, 1.73% to 29.67% and 1.73% to 29.67% respectively). Hence, it can be concluded that the new peaks are cyclohexene.

The second new peak of the refluxed cyclohexanol could not be predicted. As the external standard dicyclohexyl ether was unavailable, retention time coincidence and peak enhancement method could not be applied to identify the peak.

Refluxing pure cyclohexanol without Fe³⁺-exchanged clays under the same conditions showed no new peaks in the chromatogram. This shows that the appearance of new peaks is a result of the catalytic action of iron(III) ion exchanged clay and not the effect of cyclohexanol.

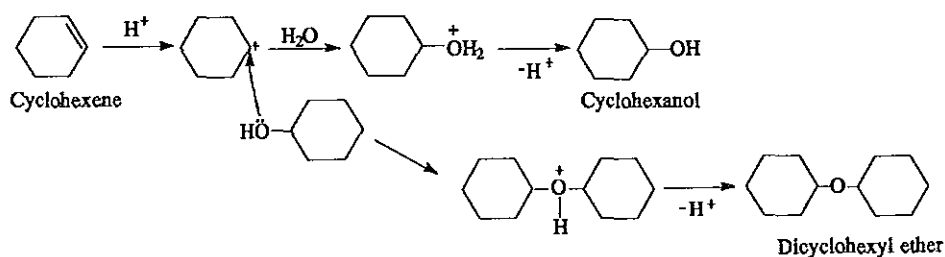
4.4.2. Cyclohexene refluxed with Fe³⁺-exchanged clays

Table 4.9.2. Relative retention times (RT in minutes) and percentages (%) of major peaks of cyclohexene refluxed with three Fe³⁺-exchanged clays



Cyclohexene		Cyclohexene with BDH-B		Cyclohexene with DMB		Cyclohexene with LCS	
RT	%	RT	%	RT	%	RT	%
1.57	96.22	2.17	76.03	1.70	91.37	1.53	94.65
-	-	12.29	0.63	12.73	3.65	12.01	0.15
-	-	17.64	1.66	-	-	-	-
-	-	18.37	2.14	-	-	-	-
-	-	21.35	15.22	-	-	-	-
-	-	22.00	3.94	22.31	1.21	21.89	2.26

The decrease in of the percentages of pure cyclohexanol and the appearance of new peaks after refluxing reveals that some changes have occurred to the starting material. Mechanistically, the expected reaction products of alkene (e.g., cyclohexene) from the catalysis of cation-exchanged clays cyclohexanol are noted in other reports [40]. For cyclohexene, the clay interlamellar reactions can be shown as follows.



Scheme 4.9.2. Conversion of cyclohexene into cyclohexanol and dicyclohexyl ether by cation exchanged clays

That is cyclohexene is first protonated and the electrophilic carbocation formed will react with interlamellar water to produce cyclohexanol. In the presence of excess cyclohexene, the produced cyclohexanol may react with the protonated cyclohexene and produce cyclohexyl ether.

When the chromatogram of the refluxed cyclohexene is compared with that of the pure cyclohexanol taken under the same conditions, the absence of a peak around 4.33 minutes may preclude the formation of cyclohexanol as a reaction product.

After refluxing cyclohexene with the three Fe^{3+} -exchanged clays, the peaks with retention times around 12 and 22 minutes predominate the new chromatogram in all cases. The percentage conversion is pronounced in BDH-bentonite. This may show that they have converted cyclohexene in a similar way and the BDH-bentonite may be efficient in cyclohexene conversion.

When cyclohexanol was refluxed with Fe^{3+} -exchanged clays (section 4.9.1.), it was suggested that the clays dehydrated cyclohexanol to yield cyclohexene. But the reverse process could not take place, i.e., from the retention time coincidence refluxing cyclohexene did not produce cyclohexanol. This is because the Fe^{3+} -exchanged clays used in both experiments were the same. The ability of the clays to dehydrate cyclohexanol and the inability to hydrate cyclohexene shows that these clays can serve as a dehydrating catalysts. These features of the clays may result from the drying conditions and storing in a desiccator over calcium chloride that water might have been removed from the clays to a greater extent. Besides, the presence of triply charged ferric cation will act as a Lewis acid and will strongly be coordinated to the lone pair of the interlamellar water molecules. Therefore, the scarcity of interlamellar water and the affinity of the ferric cation for water molecules may be the responsible factors for the dehydration of cyclohexanol to cyclohexene and inability of the Fe^{3+} -exchanged clays to hydrate cyclohexene to cyclohexanol.

Refluxing pure cyclohexene without the Fe^{3+} -exchanged clay catalysts under the same conditions as refluxing cyclohexene with the catalysts was also undertaken. The GC analysis of the cyclohexene refluxed without the catalyst showed no appearance of

new peaks, implying heating alone had no effect in the conversion of cyclohexene. Hence, the conversion of cyclohexene to other products is only the result of the catalytic effect Fe^{3+} -exchanged clays.

CONCLUSION

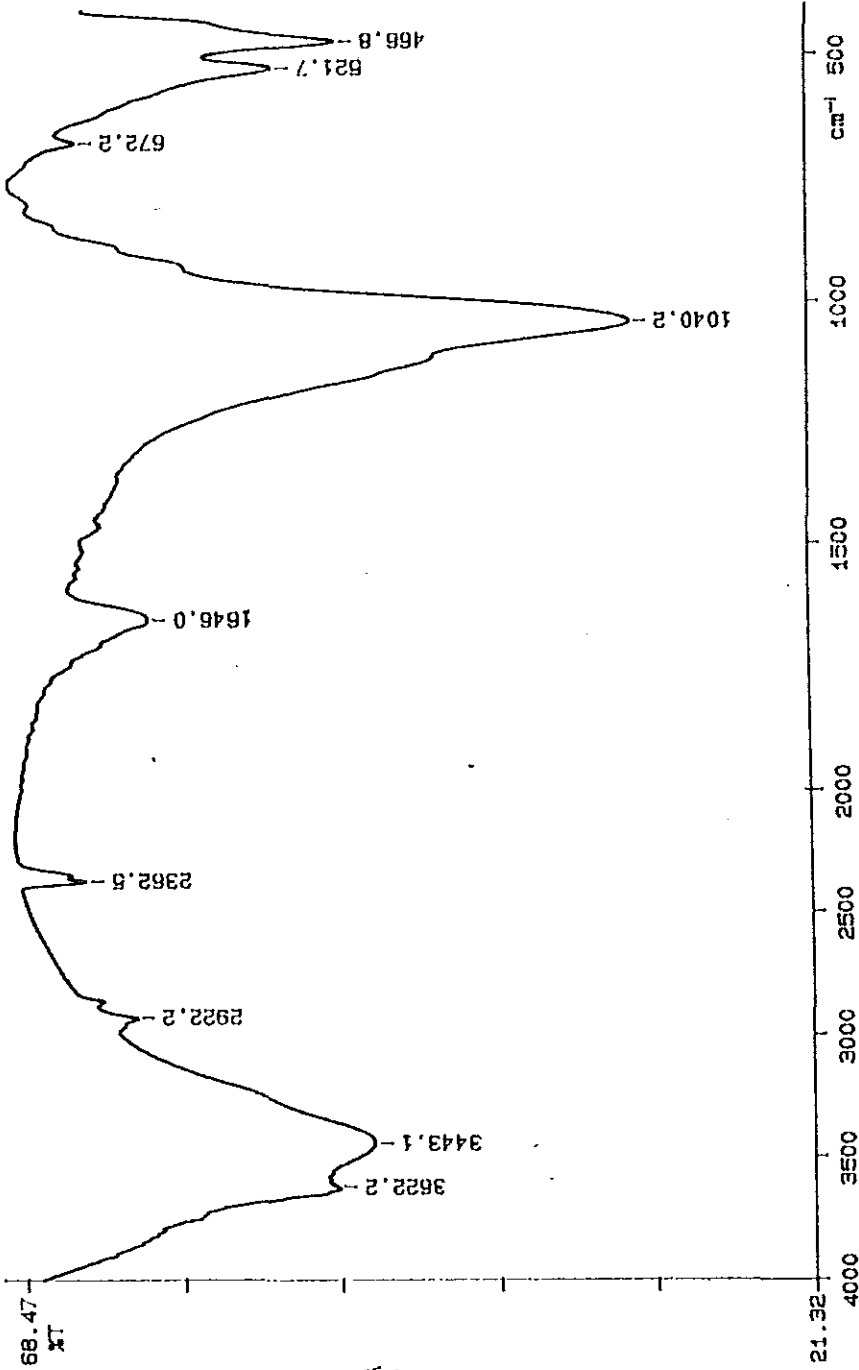
By using three ferric cation exchanged clay varieties, local clay, drilling mud bentonite and bentonite(BDH), on the bases retention time coincidence conversion of cyclohexanol into cyclohexene and unidentified compound has been achieved. However, the reverse process has not occurred which reveals that the Fe^{3+} -exchanged clays under this particular preparation and reaction conditions facilitated protonic dehydration of the cyclohexanol rather than hydration of cyclohexene. Therefore, Fe^{3+} -exchanged clays can be used for the dehydration of alcohols. As can be seen from the ongoing work the importance of charge density, amount of water in the clay and the cation used are important parameters in cation exchanged clay catalysis.

REFERENCES

1. Hertley, F. R., *Advan. Organometal. Chem.* 1977, 189
2. Ford, W. T.; Chandran, R.; Turk, H., *Pure and appl. Chem.*, 1988, **60**(3), 395
3. Laidler, K. J., *Chemical Kinetics*, Tata, McGraw-Hill Publ. Company Ltd., New Delhi, 1980, P. 434
4. Berkman, S.; Morrel, J. C.; Egloff, G., *Catalysis*, Reinhold Publ. Company, New York, 1978, p. 450
5. Bailey, D. C.; Lenger, S. H., *Chem. Rev.*, 1981, **81**(2), 108
6. Chaudary, B. M.; Kumar, K. R; Kantam, M. L., *J. Catal.*, 1991, **130**, 41
7. Allum, K. G.; Hancock, R. D.; Howell, I. V., *J. Organometal. Chem.*, 1975, **87**, 189
8. Cotton, F. A.; Wilkson, G., *Advanced Inorganic Chemistry*, A Wiley-Interscience publication, JohnWiley and Sons, New York, 1988, P. 1225
9. Righter, E. G.; Tzou, M. S; Pinnava, T. J., *J. Catal.*, 1991, **130**, 29
10. Hraba, S. M.; Komarneni, S.; Mallaa, P. J.; Srikanth, V.; Roy, R., *J. Catal.*, 1992, **131**, 4614
11. Pillai, S. M.; Raviranathan, M., *J. Chem. Soc., Chem. Commun.*, 1994, 1813
12. Kelley, W. P., *Cation Exchange in Soils*, Reinhold Publ. Corporation, New York, 1950, p. 1
13. Grim, R. E., *Clay Mineralogy*, McGraw-Hill Book Company, New York, 1968, P. 69
14. Clearfield, A., *Chem., Rev.*, 1988, **88**, 125
15. Strivastava, V. K., Strivastava, K. K., *Introduction to Chromatography-Theory and Practice*, S. Chand, Company Ltd., New Delhi, 1981, P. 70
16. Inczedy, J., *Analytical Application of Ion Exchange*, Pergmon press, London, 1966, P. 5
17. Sammuel, O., *Ion Exchange in Analytical Chemistry*, John Wiley and Sons Inc., New York, 1954, P. 54
18. Saunders, K. J., *Organic Polymer Chemisry*, Champan and Hall, London, New York, 1988, Second Edition, P. 1
19. Sato, T.; Dakka, J.; Sheldon, R. A., *J. Chem. Soc., Chem. Commun.*, 1994, 1887
20. Kojima, M.; Hartford, R.; O'Conner, C. T., *J. Catal.*, 1991, **128**, 487

- Purnell, H., *J. Chem. Soc., Chem. Commun.*, 1981, 9
44. Adams, J. A.; Bylina, A.; Graham, S. H., *J. Chem.Soc., Chem. Commun.*, 1980, 1003
45. Sohn; Rack, J.; Hyem; Bae; *Chem. Abst.*, 1984, **98**, 17104
46. Striddle; George, E., *Chem. Abst.*, 1979, **86**, 551406
47. Michaelson; Robert, C.; *Chem. Abst.*, 1987, **107**, 200937a
48. Knoth, M., Ethiopian Institute of Geological Surveys Laboratory Manual for Physical tests of Minerals, Addis Ababa, 1986, P. 1
49. Mulgeta, H., National Soil Laboratory Service: Notes On Instrumental Methods of Chemical Analysis, Addis Ababa, 1994, p.5
50. Vogel, Quantitative Inorganic Analysis, London and New York, 1978, P. 730
51. De, A. K., Chowdury, K. J., *J. Chrom.*, 1975, **101**, 63
52. Frenckel, H.; Meiri, A., Soil Salinity, Van Nostrand, Reinhold Company, New York, 1985, P. 185
53. Theodrcharis, C. R.; s'Jacob, K. J.; Gray, A., *J. Chem. Soc., Farad. Trans.*, 1988, **84**(5), 1509
54. Finar, I. L., Organic Chemistry, English language Book society, sixth edition, England, 1986, p. 547

PERKIN ELMER

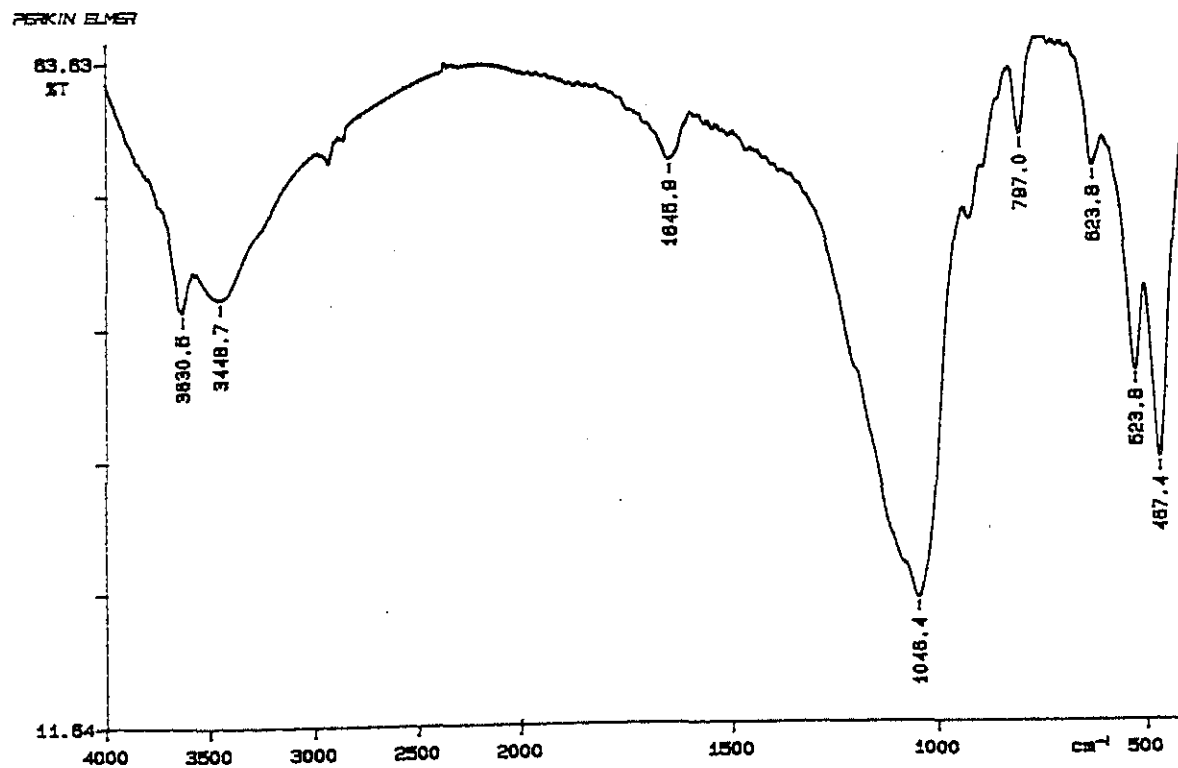


57

Appendix: 1. IR Spectra of unfractionated
Local clay.

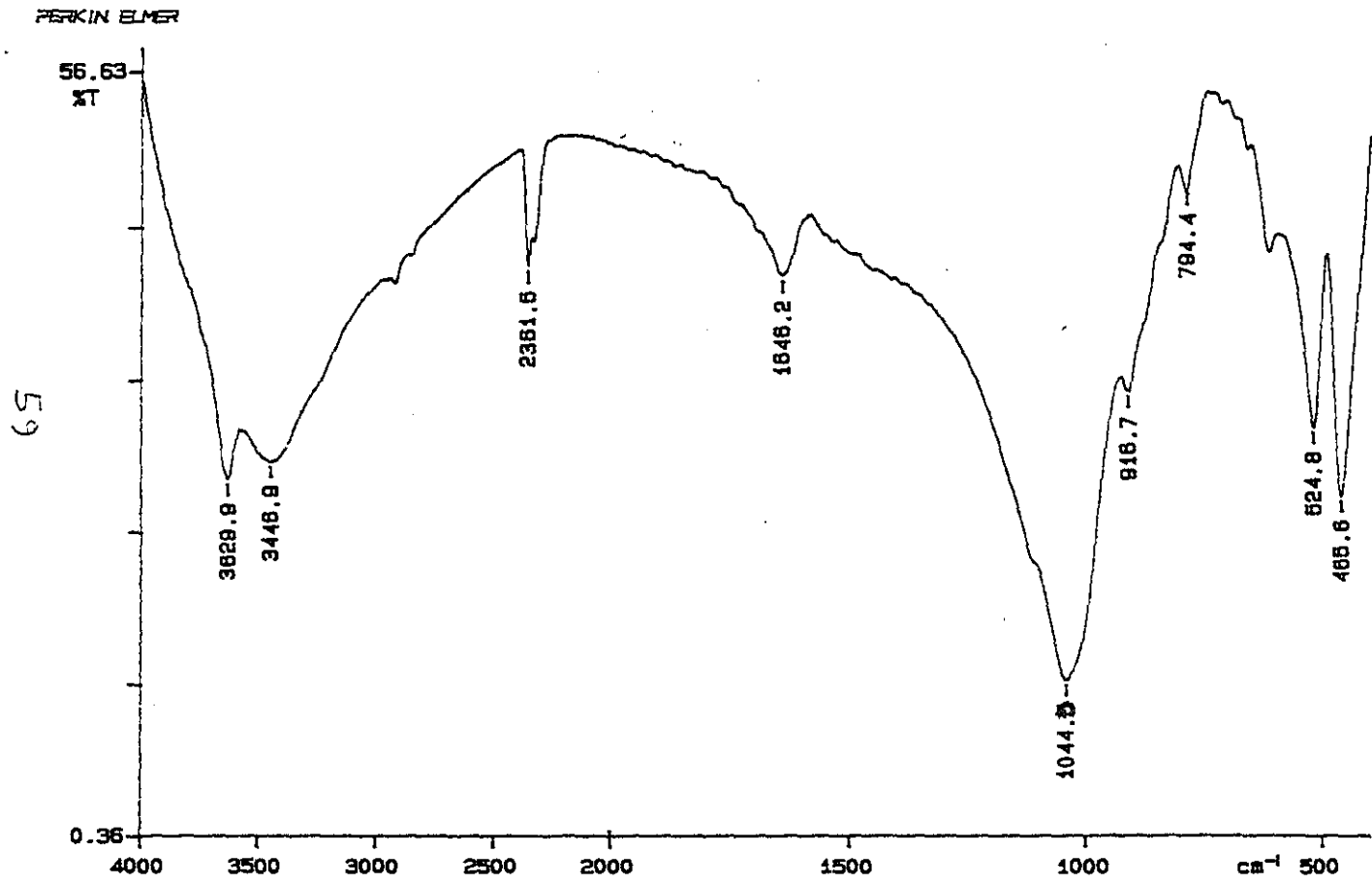
Unfractionated local clay sample

85



95/03/08 07:06 Kidane
Y: 4 scans, 4.0cm-1, flat, smooth
CB
Unfractionated DMB

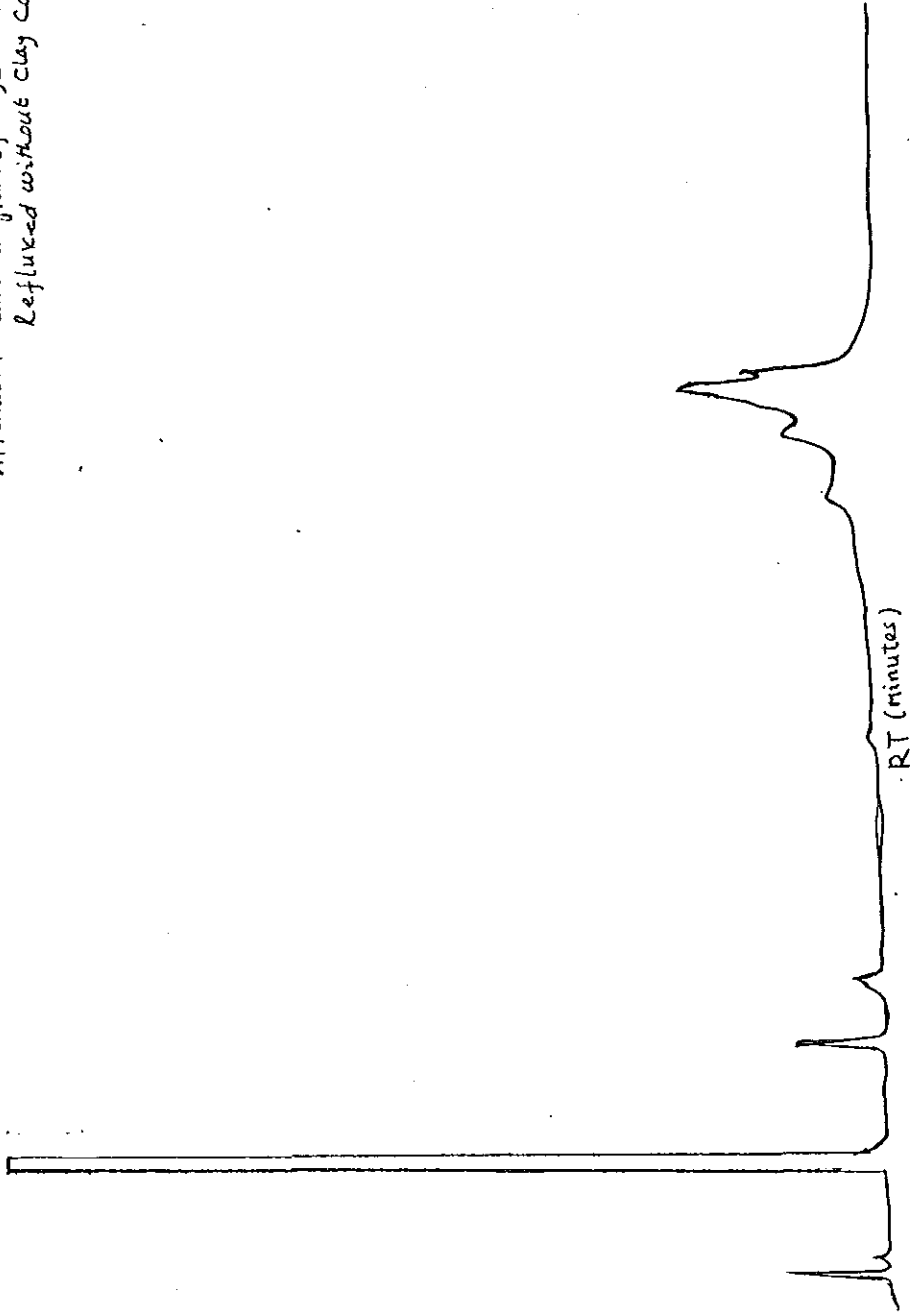
Appendix 2: IR spectra of unfractionated
Drilling Mud Bentonite



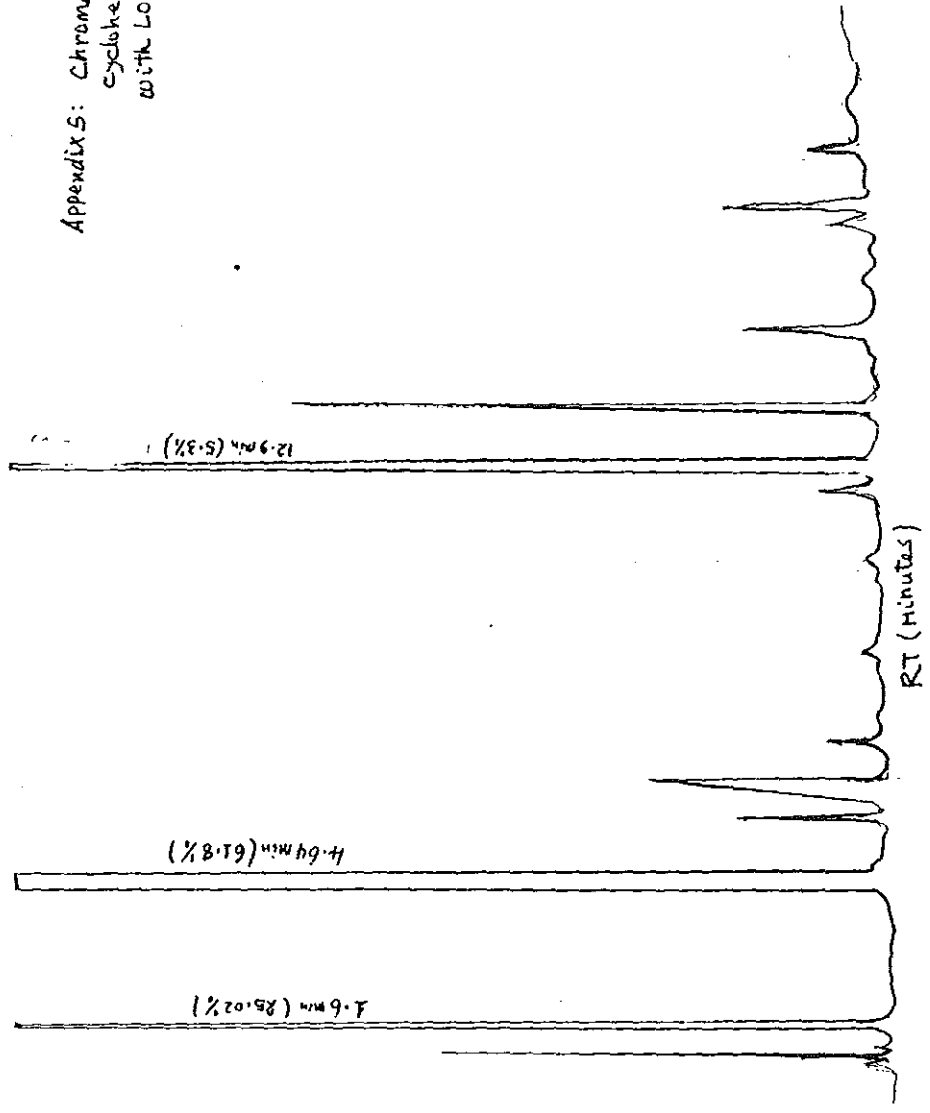
95/03/08 07:27 Kidane
Z: 4 scans, 4.0cm⁻¹, flat, smooth
BDH B
Unfractionated BDH-Bentonite

Appendix 3: IR spectra of Bentonite (BDH)

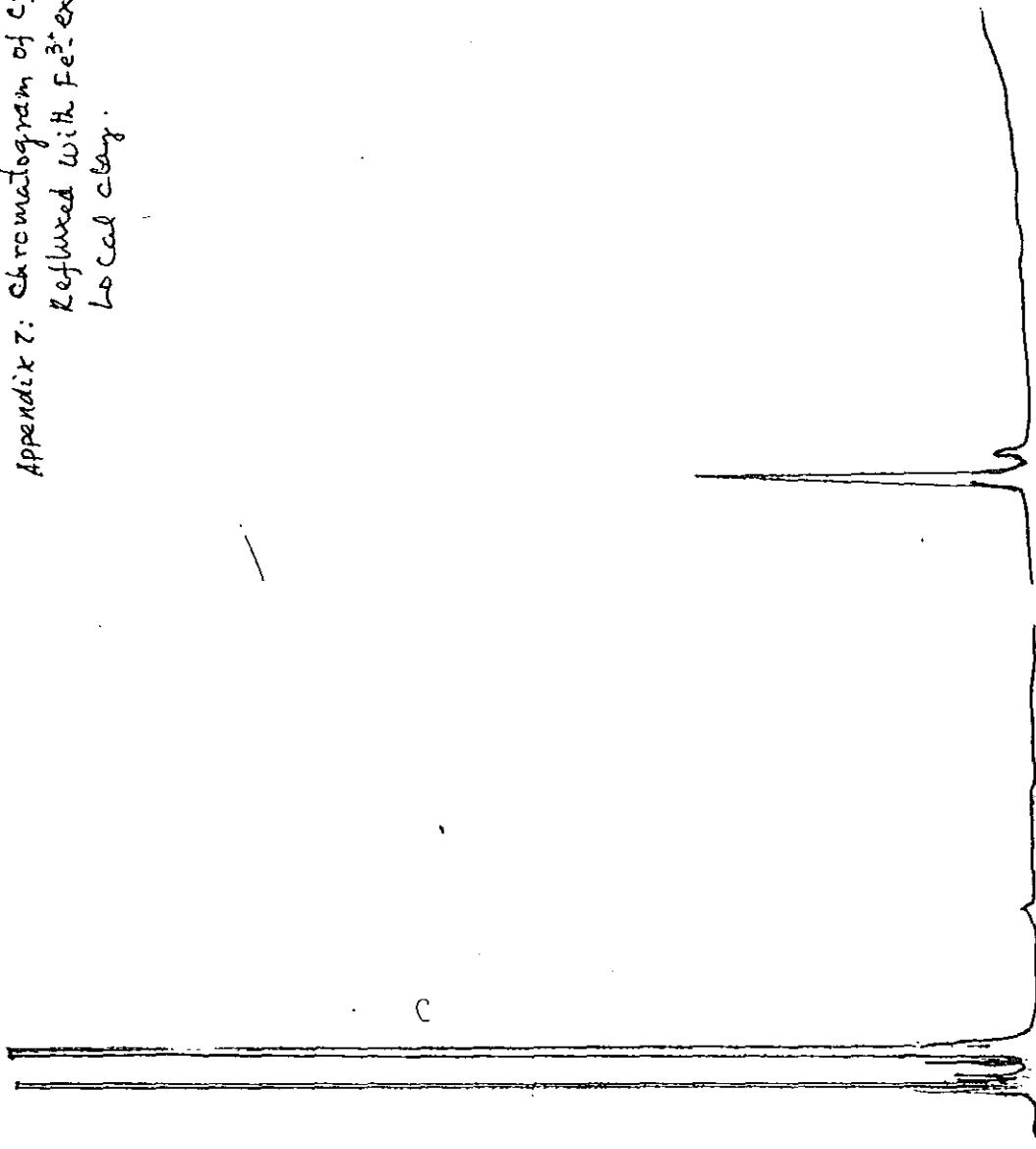
Appendix 4: Chromatogram of Cyclohexanol
Refluxed without Clay Catalyst



Appendix 5: Chromatogram of
Cyclohexane refluxed
with Local Clay.



Appendix 7: Chromatogram of Cyclohexene
Refluxed with Fe^{3+} exchanged
Local clay.

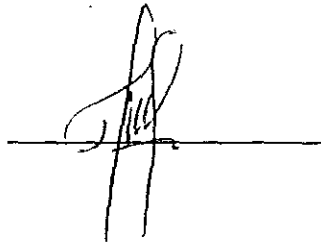


DECLARATION

I, the undersigned, declare that this thesis is my work and that all source of materials used for the thesis have been duly acknowledged.

Name : Belina Terfasa

Signature:



Place and date of submission: Chemistry Department
Addis Ababa University
June, 1995

This thesis has been submitted for examination with my approval as a university advisor.

Dr. Negussie Retta

Signature

