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Synthesis of clay-based catalysts for bioethanol conversion

By

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Declaration

I, Juvet Malonda Shabani, declare that the contents of this dissertation/thesis represent my own unaided work, and that the dissertation/thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

Signed **Date**

Abstract

For decades, clays have been applicable as commercial catalysts mostly for cracking in petroleum industries. Clays are also used for development of useful catalysts for various other industrial applications. Hence, this work was aimed to synthesize clay-based catalysts from clay minerals (Kaolin, bentonite and talc) that will be active for the conversion of bioethanol to fuel hydrocarbons.

Catalyst characterisation techniques employed on the samples produced in this work include the Energy Dispersive Spectroscopy (EDS), Scanning Electron Microscopy (SEM) and the X-Ray Diffraction pattern (XRD). All catalytic reactions were carried out in a fixed bed reactor (at fixed reaction condition of 6 hour and 350 ^{0}C) and corresponding reaction products (liquid and gaseous) were analysed through a Gas Chromatograph- Flame Ionisation Detector (GC-FID) and Gas Chromatograph Mass Spectrometer (GC/MS).

The activity of clays in their non-modified state was studied and they were all found active for bioethanol conversion to hydrocarbons. Bentonite was the most active catalyst with bioethanol of 84.95 % and this through subsequent beneficiation and acid-modification approach, led to increased bioethanol conversion of 87.3 %. EDS/SEM characterisation of the catalyst in line to the above modification and increased catalyst activity, revealed that the structural morphology of bentonite and the concentration of basic structural elements (in terms of Si/Al ratio) was increased.

Zeolite catalyst was then successfully produced from kaolin clay by hydrothermal synthesis and this sample through XRD data, resulted in the ZSM-5 phase by by 86.92 %. The morphology of the produced clay-based zeolite as given through SEM results was dominantly cuboidal to rectangular crystal units, and a small proportion of spherical crystal units. The above results are closely comparable to those of zeolite catalysts in the literature, as well as to the yardstick commercial zeolite used for comparison in this work (This instead resulted in the ZSM-5 phase by 87.58 %). The EDS results revealed that the Si/Al ratio of the produced zeolite was 23; of which this catalyst was developed from kaolin clay mineral of Si/Al ratio of 3.6. In accordance to the above outcomes, the clay-based zeolite (H-ZeoClay) among the clay-based catalysts produced and the yardstick commercial zeolite, led to highest activity of 99.91 % bioethanol conversion. The yardstick commercial zeolite comparably led to 99.95 % bioethanol conversion. Highest and comparable distribution and selectivity of hydrocarbons (in both liquid and gas product) by both the produced clay-based zeolite and commercial zeolite, served as additional and supportive evidence in confirming the identity of clay-based zeolite as a zeolite catalyst. Increase in reaction temperature (From 350 to 400 ^oC) in further experiment over the clay-based zeolite, resulted even further to 99.96 % bioethanol conversion. In further experiments, the produced zeolite was promoted with transition metal elements to further assess for catalytic performance. Thus catalyst impregnation with Nickel led to increased and highest activity of 99.99 % bioethanol conversion. This resultant sample was most possibly and relatively observed as the least porous.

Clay-based catalysts for bioethanol conversion reactions were found dominantly selective to gaseous product as compared to liquid product. In this work, the produced clay-based and commercial zeolite catalysts comparably proved to result to highest hydrocarbons distribution in both liquid and gaseous product; followed by the Nickel promoted catalyst.The overall decreasing order of selectivity of gaseous hydrocarbons by clay-based catalysts includes light olefins (C_3-C_5), gaseous diethyl ether and light paraffins. This order for liquid hydrocarbons includes diethyl ether, toluene, xylene, benzene, methanol and butanol. Iron (Fe) promoted catalyst was found to be the most selective to light olefins hydrocarbons in this work. Bentonite catalyst in non-modified state was the most selective to diethyl ether in the gas product, as well as to methanol and butanol in the liquid product.

The optimum reaction conditions for bioethanol conversion over clay-based catalysts were 6 hours at alternatively 350 ^oC and 400 ^oC. Reaction temperature of 350 ^oC was the most favourable when employing non-zeolite clay-based catalysts (Non-modified and modified clays). The activity of clay-based zeolite on the other hand, was relatively more favoured at 400 ^oC, and this would be similarly recommended for metal promoted clay-based zeolites.

Developing clay-based zeolites through hydrothermal synthesis for bioethanol conversion, was observed and is recommended as the best approach towards obtaining high value, in the gasoline-range. Other methods of catalyst promotion with metal elements, such as the commonly ion exchange method in literature, could be deemed for improved catalytic performance.

The application of clay materials from their very non-modified state for bioethanol conversion, followed by their modifications and utility for zeolite production, have been to the best of author's knowledge inthis work. Clays materials have therefore been found useful in the development of catalysts; clay-based zeolite catalysts has proven as alternative and potential means to substitute the use of high costly commercial zeolite for bioethanol conversion.

Dedication

To Melanie Smuts, Magdaleen Smuts, Stuart Du Noon, Julien grieve.

My beloved father and family in DRC

Alex Van Ster and Family

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Keywords and concepts

Catalytic conversion of bioethanol; clay materials; zeolites, clay-based catalysts; hydrocarbons; acid activation, promotion ; Kaolin, clay beneficiation and acid-modification; produced catalyst H-ZeoClay; light olefins; light parraffins ; liquid and gas product hydrocarbons; etc..

Nomenclature

CIA (UCT): Centre for Imaging and Analysis at the University of Cape Town
Cr / Bentonite: Bentonite clay supported over Chromium metal.
FoM: Figure of Match (FoM)
SEM: Scanning Electron Microscope
Si/Al ratio: Silicon to Aluminium ratio of the catalyst. Also refered as the ratio of major element composition
SiO_2/Al_2O_3: Silica to Alumina ratio of the catalysts.
TOS (Time on Stream): Time on Stream is basically the reaction or conversion time of ethanol over the catalyst, this which is continuously fed or as continuous flow system.
TPAOH or/and **TPABr:** Tetrapropylammonium hydroxide (TPAOH) and Tetrapropylammonium bromine (TPABr).
WHSV (Weight Hourly Space Velocity): WHSV denotes the quotient of the mass flow rate of the reactants divided by the mass of the catalyst in the reactor. WHSV = Mass Flow/Catalyst mass
XRD: X-ray Diffraction pattern
XRF: X-ray fluorescence spectrometer
ZSM-5: Zeolite Socony Mobil-5

Nomeclature for catalyst and hydrocarbons products

Non-Zeolite clay-based catalyst	Clay-based zeolite catalysts
N.B: Non-modified bentonite catalyst **B.B:** Modified Beneficiated Bentonite catalyst **$B.B_{1M}$:** Acid modified bentonite catalyst	**$M.K_2$:** Metakaolin, intermediate during the preparation of H-ZeoClay **ZeoClay:** Clay-based zeolite catalyst (Non-protonated) **H-ZeoClay:** Clay-based Zeolite catalyst (Protonated) **H-ZeoCOM:** Commercial zeolite catalyst (Protonated) **H-ZeoClay (400 ^oC):** Clay-based zeolite catalyst evaluated at 400 ^0C
Conversion and hydrocarbon products	**Promoted clay-based zeolite catalysts**
EtOH conv.: Bioethanol conversion **EtOH:** Ethanol (Unreacted in the liquid product) **BuOH:** Butanol in the liquid product **MeOH:** Methanol in the liquid product	**H-ZeoClay (Fe)**: Iron promoted/impregnated clay-based zeolite catalyst **H-ZeoClay (Ni)**: Nickel promoted/impregnated clay-based zeolite. **H-ZeoClay (Co):** Cobalt promoted/impregnated clay-based zeolite catalyst

Glossary

Acidic activation: Beneficiation or promotion of a catalyst by thermally blending it with acid
Acid-modified clay: This refers the natural clays modified with sulphuric acid. They are abbreviated such as B.$B_{1M,}$ meaning the particular clay (bentonite) catalyst has been modified with sulphuric acid (H_2SO_4) of certain molarity – which mostly of 1 M in this work. Others include Talc (B.T_{1M}) and acid-modified Kaolin (B.K_{1M}).

Alkyl aromatics: This can be defined as the sum of C_6 – C_{10} aromatics and are produced through the process of alkylation.
Alumination: an enrichment of a catalyst by increasing its aluminum content
Basicity: Basic strength of a catalyst.
Beneficiated catalyst:

- In relative to non-modified clay catalyst, this is the lowest distributed catalyst fraction (<53 µm) from the particle distibution of the non-modified catalyst, which is turn was subjected to aqueus suspension and settling for a period of time, followed by drying.
- The catalyst obtained as a result of beneficiation of the non-modified natural clay catalyst. Also mentioned in this work as the catalyst obtained prior acid modification
- Non acid-modified or activated catalyst when discussing the effect of acid-modification on clay-based catalyst.
- These with corresponding abbreviations include beneficiated Bentonite (B.B), and beneficiated Kaolin (B.K_1) and beneficiated Talc (B.T).

Beneficiation followed by acid-modification: Both beneficiation and acid-modification
Benign: A material or catalyst which by application is environmental unharmful or friendly.
Benzene or Toluene in the liquid product: These are also referred as liquid Benzene and liquid toluene as respectively

Benzene and toluene in the vaporised form in the gas product: This can also be referred as Gaseous Benzene and Gaseous toluene.

Catalyst: Also referred as sample in the context were the material was analyzed.
Catalyst activity, stability and stability: These are more likely to be assessed using the optimum clay-based catalyst.
Catalyst developed from clay: This is mainly the produced catalyst (HZeoClay), unlike beneficiated and acid-modified catalysts from natural clay material or catalyst in this work.

Catalyst hinders the selectivity: Reduces the selectivity of the catalyst / result to this catalyst to be less selective.
Catalytic reaction test: This also refered as Catalyst(s) evaluation test

Clay-based catalyst: Catalyst developed from the given natural clays (and which will be active for the conversion of bioethanol) . In this work, this also refers to any catalyst developed from clay materials, which is either the non-modified, beneficiated, acid modified or the clay-based zeolite.

Clay-based Zeolite: This is the Zeolite catalyst synthesised from clay material in this work; abbreviated as H-ZeoClay (See H-ZeoClay at Nomenclature)

Clay catalyst in the raw form: This is a non-modified clay catalyst.

Clay-derived catalyst: The catalyst with close enough similar characteristics to zeolite; that which is anticipated to be developed from clay. The choice of the clay for this regards is likely to depend on the Si/Al ratio results by EDS. Kaolin and Bentonite are most like to be used for this purpose as supported by their existing application in literature.

Clay-derived zeolite: This is the zeolite anticipated to be produced from clay material, preferably kaolin in this work. It is also refers as clay-based zeolite.

Clay fraction: clay sample collected in cut as a result of screening.

Clay particles: Also referred as Crystal units that make up the clay sample

Commercial zeolite catalyst: This catalyst was obtained from Zeolyst and abbreviated as ZeoCOM in this work.

Components distribution: Also referred as molecular distribution or hydrocarbons distribution in either gas or liquid product.

Conventional methods of petroleum production: Conventional methods of petroleum production are catalytic processes which use fossil fuel petroleum feedstocks (e.g crude) for the production of petrochemical product. Non-commercial methods use non-fossil fuel feedstocks (e.g Biomass) to produce petrochemical product.

Crude clays: Significant mineralogical impurities

Cuboid: The geomrety of catalyst particles bounded by six quadrilateral faces.

Cycloparaffins: Also referred as Naphthenes

Developed clay-based catalyst: Mainly referred as the synthesized and also the produced clay-based catalyst; H-ZeoClay and ZeoClay respectively. In objective 2 of this work, this is referred as the modified clay-based catalyst.

Different / several methods: Different ways.

Enhanced catalytic performance: Catalyst Activity

Fractionation: Refining

Gasoline-range hydrocarbons: Mixture of hydrocarbons molecules in the range C_6-C_{10}.

Gaseous hydrocarbons: These refer to hydrocarbons products in the gas stream, such as gaseous Olefins or gaseous paraffins, as also refered as light olefins or parraffins in the carbon range between C_3–C_6 in this work. These consist of straight-chained and branched-chained olefins or parraffins (Isomers). Gaseous hydrocarbon for hydrocarbons other than olefins or parraffins (e.g Gaseous

Diethyl ether or gasesiou benzene), refers to the non-condensate vaporised form of the mentioned hydrocarbons

H-Form of catalyst: The protonated form of a catalyst commonly used on zeolite catalyst protonated with a Hydrogen source compound such Ammonium Chloride.

Hydrothermal: When the crystal growth is carried out in aqueous solution above or near 375 K

Higher hydrocarbons: Long-chain molecules of carbon and hydrogen, also refer to as heavier hydrocarbons in this work

Integrated catalysts sample: The measure of closeness or how close the particles of a catalyst are relative to another. Integrated catalyst sample is therefore a catalyst sample with particles closely together. This serves for porosity measurement of the catalyst.

Interlamellar: an armor made of small plates

Ion exchange property: Ability to transfer or receive Irons .

Light olefins: See Gaseous Olefins. In common Chemistry, this is often defined as the sum of ethylene and propylene. See **Olefins (C3-C6)**

Liquid product: Also referred as the liquid aqueous fraction from the reaction

Liquid product: Organic and aqueous product. These two fractions are likely to settle in separate phases.

Metal Promoted catalyst: In this work this is referred to a clay-based catalyst, specifically the produced catalyst, which has been promoted through the impregnation method by a metal element such as Iron (Fe); Nickel (Ni) or Cobalt (Co)-promoted catalyst

Method: Way or an approach used to synthesize or develop a clay-based catalyst.

Modification approach: A method applied to modify a clay or a clay-based catalyst, such as clay beneficiation, acid modidifcation, etc..

Modification technique: Modification approach.

Morpholgy of particle: Also refered as Shape of the particle.

Natural clay: Clay catalyst in the non-modified state.

Non-beneficiated catalyst (e.g N.B; N.K_1): natural non-modified clay catalyst

Non-protonated clay-based Zeolite: See ZeoClay at Nomenclature.

Non-zeolite clay-based catalyst: This refers to Non-modified, beneficiated and acid modified catalyst in this work (e.g N.B; B.B and B.B_{1M}). See Clay-based Zeolite, H-ZeoClay.

Olefins (C3-C6): These consist of both straight-chained and IsoOlefins hydrocarbons.

Optimum (clay-based) catalyst: The (clay) catalyst which results to optimum conversion, product distribution and selectvity. Catalyst leading to the most optimum result in this work.

Overall effect of beneficiation and acid modification:

- The modified clay-based catalyst that was first subjected to beneficiation, (then later) followed by acid-modification
- The clay catalyst resulting from both beneficiated or acid-modified approach

- Catalyst resulting from beneficiation followed by acid-modification Catalyst resulting from the overall effect of both beneficiation and acid modification

Paraffins (C3-C6): These consist of both straight-chained and Isoparaffins hydrocarbons
Particle size: Crystal size or size of the crystal unit(s) that make up the catalyst's sample
Pentagonal cuboid particles: Pentagonal prism; Penta/Heptahedro shape (Pentagonal heptahedron
Performance: Refers to how active a catalyst in the conversion of ethanol.
Petrochemical products: Petroleum-derived products.
Porosity: Also referred to as structural porosity of the catalyst sample. For actual measurement through BET Characterisation, porosity is rather referred as pore volumes of the sample constituting a catalyst.
Potential: Active catalyst.
Precatalyst: The recipient catalyst that is being promoted.
Produced catalyst: Also known as the pronotonated form of the producedd catalyst and abbrevioated as H-ZeoClay.
Promoted clay-based catalyst: These are the produced the clay-based catalysts impregnated with metal element in this work. These Include Fe; Ni and Co-imprgantaed catalyst and respectively abbreviated as H-ZeoClay (Fe) or (H-ZeoClay + Fe), H-ZeoClay (Ni) and H-ZeoClay (Co).

Raw clay: This refers to non-modified clay obtained in their very natural state, such as Talc (N.T), Bentonite (N.B) and three various kaolin clay ($N.K_1$; $N.K_2$ and $N.K_3$)
Reaction conditions: Most likely set for 6 hours reaction time at the temperature of 350 ^{0}C for feed rate of 2 h^{-1} (WHSV).
Rectangular hexahedron Shape: Rectangular cuboidal shape
Selectivity of olefins: Concentration of olefins
Si : Silicon element in the clay or clay catalyst

Single stage catalytic system: In this work, this refers to a non-conventional system that is lower energy requiring (Than conventional processes) and compensate for chain reactions through an appropriate design and single catalytic system.
Sieve shaker: Sieve shaking machine used to screen the clay catalyst for size distribution.

Thermal treatment: Calcination.
XRD results : This the XRD data of the analysed catalysts. The results are denoted as a pattern and relatively as XRD Figure of Match (FoM). E.g XRD results to confirm; specifically means ''XRD Figure of Match to confirm ''.

Zeolite-based catalysts: This refers to catalysts with a zeolite based, a zeolite-supported or modified catalyst (mainly with other substances)

1. Introduction

1.1 Background

Catalysis plays a vital role in our day to day activities and has been an increasingly very powerful tool in chemical engineering production. Catalysts are often referred as workhorses of chemical transformations in the industry as catalytic processes are derivative of more than 80 % of chemical industrial products (Chorkendorff et al., 2007).

For decades, the use of catalysts has been more dispensable and abundant in the production of fuels as compared to other chemical industries. These days, the production of fuels is very much connected to the type of catalyst used. Energy derived from fuels continues to play a very important role in our lives and most catalysts or catalyst supports used for fuel production have very similar properties as those of clays (Miliken, 1991) .

The industrial uses of clays as catalysts dates from the early thirties (20th century), whereby these were used for the cracking of petroleum crude oil and encopassed about 40 % among the cracking catalysts (Milliken et al.,1950; Robertson et al.,1991; Eman, 2013). Although the modern history of petroleum production dates from early 18th century, the application of clay minerals for petroleum catalysis was only introduced in about 1931-1936 (Houdry et al., 1938).

Petroleum production is one of the largest chemical industries and has contributed to the dominant chemical products in the global market, the petrochemical products (Maugeri, 2006; EIA Data, 2006).

1.2 Problem statement

For more than three centuries, fossil fuels have been the main raw materials for conventional petroleum production and these methods have largely posed environmental threats and concerns with regards to global warming and environmental pollution. Moreover, the relevance of using fossil fuels is limited in the near future due their increasingly depletion from global natural reserves and lack of availability (IEA, 2012).

Alternative to conventional methods of fuel production, non-conventional methods have been introduced in order to overcome these challenges, of which biomass conversion to fuels seems to be the most potential non-conventional method (Corma et al., 2007). This method produces fuels that have proven to possess same properties as those from fossil fuel technologies, with the advantages of being transformable to meet their target needs, and reduce dependency on crude oil derived fuels.

Most non- conventional processes of biomass transformation to hydrocarbons have been observed to be catalytic processes (Rinaldi et al., 2009). Hence this as a problem identified , inevitably imposes additional implication on the overal cost of an non-conventional process due to high cost of catalysts mainly obtained from commercial suppliers.

1.3 Motivation / Rationale

Catalysis is a great area of interest in petrochemical production, of which clay catalysts have been for long applicable in both conventional and non-conventional methods of production (Eman, 2013 & Widjaya et al., 2012). Unlike conventional methods, most non-conventional methods (that use non-fossil fuel feedstocks) of petrochemical production are non-complex catalytic systems and hence would operate on lower energy cost. Accordingly, the direct conversion of bioethanol to hydrocarbons fuels can be achieved through such systems by developing suitable catalysts from clay materials. In recent years, zeolites have been predominant and prominent catalysts for the conversion of ethanol to hydrocarbons (Rownaghi, 2011). However, most zeolite catalysts are obtained commercially and are expensive due to high cost of chemicals required for their synthesis (Musyoka et al., 2014; Mezni et al., 2011; Wang et al., 2007). In consideration to reduce cost in this regard, introducing clays as starting materials for zeolite synthesis could lead to about 5 times cheaper than zeolites based on the average prices from major global suppliers of chemicals (Musyoka et al., 2014; Wang et al., 2007). More over, clay materials are more abundant in nature, and also possess promising catalytic properties (Emam, 2013). Clays can therefore serve as cheap raw materials for the synthesis of potential and valuable catalysts (clay-based catalysts) required for the conversion of bioethanol (Zhou, 2011:85, Widjaya et al., 2012 & Emam, 2013:360).

Synthetic biofuels produced through conventional methods are renewable and have higher environmental benefits than fossil based fuels. Clays are non-toxic materials and developing clay-based heterogeneous catalysts is also directed to applications in green catalysis (Zhou et al., 2011). Henceforth, production of petrochemicals through conventional method (biomass feedstock) over a clay-based catalysts, is of great advantage in lining with the

South African National and CPUT's recognition, embracement and policy of Green Technology (ASSAf, 2014:79; CPUT RTI Blue print, 2013; Kettha, 2009).

Biomass derived-products are hydrocarbon-based and the latter are basic constituents of important petrochemicals products in the market: Such as rubber, paints; and (are also a potential source of) high value hydrocarbons, such as gasoline and diesel-range hydrocarbons, as well as combustible gases.

Over the past years, the market demand of these products (more particularly transportation fuels) has risen (Emam, 2013 & Rownaghi et al., 2011:37). This calls for the necessity of increase in hydrocarbons production by alternative routes, in order to compensate to this ever rising demand and related costs. This in turn will also compensate to the need for increased energy security. Further on, the pursue to biofuel production in this work is in line to the proposal issued by the South African Government regarding making biofuels an important part of the country's energy supply (Blanchard et al., 2011). This in turn will serve among one of the important route to mitigate the effects of energy crisis.

1.4 Aim and objectives of the research

The ultimate goal of this project is to synthesise clay-based catalysts that are active in conversion of bioethanol.

In respect to the above, the properties of zeolites are referenced so as to reflect the required catalytic properties of clays for the conversion of bioethanol. This is due to the fact that clay materials possess many catalytic properties similar to those obtained in zeolites. However for clays, these properties may not exactly reflect what is required for bioethanol conversion or what is needed for a particular zeolite catalyst. As a result, there may be need to modify the clays to meet their required catalytic properties. Various modification techniques on clay minerals are therefore investigated in this work so as to achieve the above.

The set objectives for the aforementioned aim are outlined as follows:

- Investigate the effect of clay beneficiation and treatment on catalyst composition and morphology.
- Produce catalysts from various clays (Bentonite and kaolin).
- Study the activity of various clays on bioethanol conversion.

- Carry out comparative studies of bioethanol conversion over clay-based catalyst and other synthesised zeolites
- Investigate the effect of promotion on clay-based catalysts.
- Determine the optimum operating conditions for ethanol conversion process over clay-based catalysts.
- Assess and improve the catalyst activity, stability and selectivity during the conversion of bioethanol.

1.5 Importance of the research

In the open literature, not so much information is available on the conversion of bioethanol over clay-based catalysts

This work will therefore be of academic significance as it adds knowledge to the application of clays in conversion of bioethanol.

The abundant availability of clays could go a long way in boosting economic growth if utilised in the production of valuable catalysts. For this purpose, this research will be a ladder towards deriving techniques for utilisation of locally available cheap raw materials (clays), as well as their application in synthetic fuel production. The above is in line with the expected research output of developing a catalyst with potentials of producing gasoline from bioethanol.

Furthermore, this research is important in proposing a pilot plant set-up for the conversion of bioethanol, which eventually could lead to the realisation of the process in larger scales.

1.6 Research questions

- What are the potentials of using clays as a catalysts in ethanol conversion?
- What will be the comparative properties and performance of clays and modified clays in bioethanol conversion?
- How can the properties of ZSM-5 determine its performance as a catalyst in bioethanol conversion?
- How will modified clay catalysts compare to zeolites in bioethanol conversion?
- Will the catalytic properties and performance of ZSM-5 synthesised from clay be similar or close comparable to that of commercial ZSM-5 catalyst?

1.7 Thesis Format

Clays are well-known catalysts in diverse applications, however not all in their natural states, can be employed as active catalyst for the conversion of ethanol. There may therefore be need to alter natural clays to have various catalytic propertiess so as to respectively obtain a diverse species of hydrocarbons through bioethanol conversion.

Prior to modification however, the screening of the clay species in their natural non-modified state will be carried out so as to assess for their activity in the conversion of bioethanol. This thesis comprises 5 Chapters. Following introduction, Chapter 2 covers the literature reviews, of which the first section reviews on buoethnaol in energy and fuel and on the use of bioethanol as a feedstock for fuel production. The middle section discusses the catalytic properties of clays by referencing certain of these properties to zeolites. The later section to the above discusses the modification approaches to clays and the production of a valuable catalyst (Zeolite in anticipation) from clay by hydrothermal synthesis.

Chapter 3 reports on the materials and equipment required for catalyst preparation, as well as the experimental procedure adopted for catalysts preparation. Characterisation techniques required for the prepared catalysts are further listed in the middle section of chapter 3. The equipment and actual exeprimental procedure for the application of the prepared clay-based catalysts on bioethanol conversion are latter reported in chapter 3.

Chapter 4 reports on the findings and discussion of the thesis, whereby the catalytic properties and corresponding performance of the various produced catalysts, are assessed and compared in accordance to various modifications and development employed for their preparation. Further findings and discussion report on effect of metal promotion on catalytic performance of clay-based catalysts, effect of operating conditions and finally on assessment of product selectivity and distribution by clay-based catalysts.

Chapter 5 reports on the research conclusion by identifying the most optimum clay catalytic development approach for bioethanol conversion activity. This is then followed by research recommendations for future pursue.

2. Literature Review

Catalytic conversion of bioethanol is a potential method reported and observed to have synthesised various hydrocarbon molecules (Widjaya et al., 2012:75 & Inaba et al., 2006) and, is recently a famous area of focus. It is a cost effective synthesis method in which liquid ethanol feed is favourably contacted onto heterogeneous solid catalyst, most commonly in a fixed bed reactor (Viswanadham, 2012:300). A catalytic conversion process that makes use of a suitable and a well-high moisture resistant catalyst, reduces the common challenge of catalyst deactivation (Widjaya et al., 2012:66); especially in regards to liquid feedstock such as bioethanol, which often (if not purified for the purpose) contains high moisture content as among the causes to catalyst deactivation in the reaction medium (Gayubo et al., 2004:1640). The above mentioned catalytic process is therefore promising when using bioethanol feedstock, for which iregardless of the moisture or water content , can still make the overall process more economic by eliminating any prior costs required for water removal in the feed (Widjaya et al., 2012:65-6).

In addition to any suitable catalyst (as mentioned above) for a biomass catalytic process, Gayubo et al. (2004) mentions other factors than can as well be considered or assessed for the overall performance or activity of the catalysts. These include the feed's space velocity, reaction time (reaction time on stream), reaction temperature and coke formation due thermal impact on the catalyst. All the above constitute the parameters for a catalytic system and are further discussed in regards to zeolite and clay-based catalysts in various section of the literature

Zeolite catalysts are predominant for the conversion of ethanol to hydrocarbons. Clay minerals possess several catalytic properties and this is proven in account of their commercial application as catalysts and catalyst supports in conventional petroleum processes (Eman, 2013:360). It has been noted in several reports (Madera et al.,1987:424; Madeira et al., 2012:171 & Widyaya et al., 2012, etc.) that most clays contain similar basic elements as zeolites and are active catalysts in the conversion of ethanol or bioethanol.

2.1 Energy and bioethanol fuel

Fossil fuel sources have long been used for the production of conventional fuels and have chiefly catered to energy need in areas such as transportation, industry, etc. There is however decrease expected in the use of fossil fuel sources due to their current on-going and forecasted depletion, the environmental pollution they pose while being processed and hence the likeliness of energy crisis if fossil fuels continue to be the main dependent sources of energy.

For long dates, ethanol has been secondarily derived from fossil fuel sources (Greener industry, 2015). Ethanol is a short chain alcohol commonly found in alcoholic beverages (Chang et al.,1976). In most ethanol richly producing countries, ethanol is used as motorfuel or fuel additive for gasoline to improve the quality of gasoline fuel. This however has been set with limitations due to high vapour pressure and volatility of ethanol when blended with gasoline (Viswanadham et al., 2012). Hence the need to directly convert ethanol to gasoline has been pursued by many researchers.

In the recent past, ethanol has gained popularity of being primarily and easily obtained from biomass sources, this ethanol is usually refered to as bioethanol. Bioethanol is one of the main biomass resources produced by fermentation and is the most commonly employed alcohol feedstock for catalytic production of hydrocarbons or biofuels (Inaba et al., 2012:136).

Bioethanol is a better substitute to conventional ethanol from environmental and economic perspective. Bioethanol is a renewable (Produced from agricultural renewable resources) and sustainable feedstock for fuel production and thereby reduces total dependence from that of fossil fuel sources and petroleum-based alcohols.

Non-biomass or synthetic ethanol is mostly produced from the non-renewable fossil fuel sources, such as ethylene which undergoes hydration process for the purpose (Hidzir et al., 2014). Producing ethanol through the above fossil fuel-based ethylene route, is promisingly not sustainable in the near future due to on going depletion and environmental pollution caused in processing fossil fuel sources (IEA, 2012). Therefore, production of ethanol from biomass serves as alternative, sustainable and environmental friendly sources (CropEnergies, 2016). Moreover, bioethanol produced by fermentation, is the world’s most produced form of ethanol (Greener industry, 2015).

In comparison to methanol, bioethanol is a better substitute based on cost, performance and environmental consideration. Bioethanol is less toxic than methanol (Priyanka, 2010) and is a cost effective feedstock in processes where gasoline is produced (Widjay et al., 2012). This very ethanol which is transformable to gasoline, is a well known oxygenate or could be used as additive to improve the quality of gasoline when these two are blended (Viswanadham et al., 2012).

It is evident that the conversion of bioethanol to various hydrocarbon products over active catalysts is considerably significant and can be viable especially in agriculturally rich or petroleum poor economies. For example in countries like Brazil, this approach is attractive because of the country's large reserve of sugar cane renewable biomass to produce bioethanol (Machado et al., 2005:2064). Likewise in South Africa, sugar cane and maize are major and the two most valuable produced crops which can serve as biomass sources for the production of bioethanol (Directorate statistics and Economic analysis, 2011:4 & Growth Energy, 2014).

2.1.1 Convenience of using bioethanol feedstock for catalytic conversion

Bioethanol is promising feedstock and transformable to hydrocarbon fuels by catalysis (Viswanadham et al., 2012:298). This however in its raw state, often contains a lot of moisture (>15 %) and may therefore be regarded as ethanol-water mixture. Many researchers have revealed that such high water content in the feed often triggers faster deactivation of zeolite catalysts during conversion (Viswanadham et al., 2012).

Clays generally are highly water-absorbing materials from which clay-based catalysts are developed. These therefore as catalysts are presumed to be highly resistant to moisture contents in bioethanol feed when subjected to appropriate modifications. For example, it was revealed through Widjaya et al. (2012) that bentonite catalyst pillared with chromium metal became highly resistant to water content during the conversion of bioethanol. Hence the conversion of bioethanol over a clay-based catalytic process is suitably promising.

If assumed that bioethanol in its raw state may require further purification for water removal, this then supplied at commercial standard can be obtained in high purity as the non-biomass derived ethanol. Hence ethanol derived from the two mentioned sources will be very much similar in application, provided that these are processed over a suitably designed catalysts (Widjaya et al., 2012:66-7). Similar catalytic behaviour and results have been observed when bioethanol is reacted over zeolite catalyst as compared to ethanol in other reviews (Widyaya et al.2012; Inaba et al., 2006). Therefore from technical perpectives, bioethanol feed possess same properties as ethanol in respect to their transformation to hydrocarbons over zeolite and likely over clay-based catalysts. For this reason in this work, the use of bioethanol is made reference to the predominent conventional ethanol feed in regard to their transformation over clay-based or zeolite catalysts.

2.2 Clay-based catalysts for bioethanol conversion

It has been observed from various literature that the nature and properties of a catalyst have effect on their performance in a catalytic system (Hoang et al. 2010:26). This similarly applies to zeolites catalyst in the conversion of ethanol (Inaba et al., 2005:135), as it would for ethanol conversion over clay-based catalysts. For example, reduction in particle size of zeolite as reported by Viswanadham et al. (2010), resulted to increased ethanol conversion and enhaced selectivity of gasoline-range hydrocarbons. The use of H-ZSM-5 over HY zeolite (as by nature of catalyst) on ethanol conversion as reported by inaba et al., (2005), leads to exclusive formation of aromatic hydrocarbons. Additional factors in the conversion of ethanol such as purity of the ethanol feedstock (Widyaya et al., 2012) and operating reaction conditions (Reaction temperature and time), are known for significant effect on catalytic performance (Viswanadham et al., 2012:303).

Among the above mentioned, the choice of the catalyst is of major significance in the design of a reaction system (Lee et al., 2009: 64). A catalyst by primary definition, entails a substance that speeds up a chemical reaction in reaction mechanism and can be regenerated from a reaction mixture (Hagen, 2006). There are however various other factors to consider when employing a catalyst to a reaction system.

Potential catalysts, predominantly zeolites, have therefore been identified as active catalysts in the conversion of ethanol to oxygenates or olefins. Some zeolites however, are stable and selective to further the above reaction path by converting the latter (intermediates) product to higher hydrocarbons molecules, such as gasoline-range hydrocarbons. This latter conversion is usually refered as oligomerization and aromatization of the intermediates molecules.

The use of clay-based catalysts in the conversion of bioethanol to hydrocarbons has been recently introduced and this is made reference to their long term successful catatytic activity and prominence in petroleum refining processes (Eman, 2013). Clay-based catalysts are also applied for the conversion of bioethnaol in reference to the predominant zeolite catalysts (Widyaya et al., 2012).

2.2.1 The properties of clays for catalysis

Clays have long been known for catalytic applications mostly in petroleum industry. These are widely available materials which occur in nature and can therefore be obtained at cheaper cost – Clays however, may only require certain modifications prior to their use as catalysts in reaction processes.

Most clays possess catalytic properties and these can be modified to meet various catalytic activities. These however, depends on the product selectivity targeted for in the reaction. For example, kaolin and bentonite (Montmorillonite) are well-known commercial catalysts and catalysts supports in petroleum refinery processes. Several researchers have reported on the above clays, including some few others, as active catalysts for the conversion of alcohol (ethanol) to olefins (Widjaya et al., 2012, Eman 2013:360 & Corma et al.,1987:423-433).

Clay minerals possess surface properties and peculiar structural features which make them useful catalysts in various applications (Milliken,1950:314). The surface properties include their generic high surface area, surface chemistry and surface charge. Moreover, clays have small particle sizes that are suitable for use in catalysis (Eman, 2013:359-360). On standard particle size, clay particles are considered to be less than two micrometres - It is only rarely that their equivalent size exceeds 2 µm.

Clays generally are described as flat, hexagonal, and thin (Art 186, 2014 & Heckroodt, 1991). They have anisometric morphology and possesses a crystalline structure which can be modified in a controlled way. In regards to this, clays are refered as assemblies of tetrahedral layers of silicate units and octahedral layers of aluminates units, which result in them having a planar sheets structure (Igbokwe et al., 2011). In terms of composition, the structure of clay can be refered as silica-aluminium heterogeneous structure.

Most clay minerals are acidic in nature and posses a variable basal spacing. As a result to this, clays possess a tuneable acidic property (Igbokwe et al., 2011) and exhibit ion exchange ability (or capacity). The latter is as a result of electrostatic charges on the surface of the particles and is generally expressed in terms of milli-equivalents (meq) per 100 grams of material (Heckroodt, 1991:345).

Most clays possess adsoptive, binding and swelling properties which allow them to selectively adsorb molecules when used as catalysts. For example, the swelling property of clays allow them to adsorb water in between their layers and this is usually referred as water-tight properties. Sodium bentonite clay, the high-swelling form of smectite, can adsorb up to eighteen layers of water molecules between their layers (Yahiaoui et al., 2003). Alternatively, clays can allow certain molecules to pass through their pores or layers. The above properties qualify clays as potential catalysts or catalyst supports in various applications (in reference to Petroleum production by Eman, 2013:356), and as well as suitable catalysts for the conversion of bioethanol.

Clay materials are much comparable to zeolites (size, compositions, structure, etc.), with the advantage that clays occur more abundantly in nature (have several natural deposits), are obtained at cheaper cost and may be utilised as catalysts without or little modification of their natural state. Further on, clays have similar basic components as zeolites and can serve as cheaper raw materials for the synthesis of zeolite. Clay can be modified to zeolites as reported by several researchers (Mezni et., 2011; Silva et al., 2013:85, etc.).

Conventional zeolites being the predominant catalysts for the conversion of ethanol to hydrocarbons, have much work reported on them. In the open literature of clay or clay-based catalysts on the other hand, a relatively little work has been reported in regard to their application in ethanol conversion (Madeira et al., 2012; Widjaya et al., 2012; Inaba et al., 2006; etc.).

2.2.2 Classification and properties of clay minerals

Most clays minerals are formed by the transformation of primary silicates or volcanic glass as a result of hydrothermal or normal weathering processes (Heckroodt, 1991:347). "Clay minerals" as referred (Emam, 2013:358), are hydrous phylosilicates of aluminium or/and magnesium that mainly contain cations in their crystalline structure and most likely a variable amounts of certain metal elements or their oxides (Such as iron, nickel, chromium). Like zeolites, clays can be as well refered as alluminosilicate materials and geologically occurs as natural deposits (Chatawong et al., 2013).

Various academic sources have reported the classification of clay minerals into eight categories (Hillier, 2003; Heckroodt, 1991:344). However, the four major and main catagories includes the kaolinite, smectite, illite, and chlorite (Heckroodt, 1991:344 & Mineral Gallery, 2006).

Table 2.1: Classification of clay minerals and corresponding clays species (Hillier, 2003; Heckroodt, 1991)

Layer type	Group	Subgroup	Species
1:1	Kaolinite-serpentine	Kaolinite Serpentine	**Kaolinite**
2:1	Pyrophyllite-talc	Pyrophyllite-talc	**Talc**, Pyrophyllite
	Smectite	Dioctahedral smectite. Trioctahedral smectite	**Montmorrilonite**, Saponite, Hectorite, Nontrotite
	Mica	Dioctahedral mica. Trioctahedral mica	Muscovite, Illite , celadonite
	Vermiculite	Dioctahedral Vermiculite. Trioctahedral Vermiculite	Dioctahedral vermiculite, Trioctahedral vermiculite
	Brittle mica		Margarite, anandite
	Chlorite	Dioctahedral chlorite. Di-trioctahedral chlorite Tri-trioctahedral chlorite	Donbassite, Sudoite
2:1 Inverted ribbons	Polygorskite-sepiolite	Polygorskite Sepiolite	Sepiolite, Palygorskite

NB: In the above table, clay species used in this work are highlighted.

From the studies on clay occurrences in Africa, Ekosse (2010:218) reported that kaolinite, illite and smectite as respectively, are the most frequent occurring clay minerals in Africa. Kaolinite and smectite group of clays are the most dominants in broad applications (Mineral Gallery, 2007). Kaolin and montmorrilonite clay have been so farthe most important clays used in the manufacturing of catalysts and both clay types as respectively, are classified under the kaolinite and smectite group of clays (Eman, 2013:356).

There are approximately thirty different types of clay species (pure clays) that are classified within the four groups of clay categories. Most clay soils come naturally as mixtures of the different types, along with other weathered minerals. In this regard, most naturally occurring clays can also be described as fine-grained soils that combine one or more clay minerals with traces of metal oxides and organic matter (Grim et al., 2012).

There may therefore be need to modify the natural soil (Crude) clays to meet their required values for use as catalysts.

The properties of certain clay minerals, among those listed and highlighted in Table 2.1 , are reported and described in respect to the relevance of the clays as catalysts in the conversion of ethanol.

2.2.2.1 Bentonite clay

The term bentonite was broadened to include all clays that are produced by the alteration of volcanic ash in situ. Bentonite is essentially impure clay that is largely composed of smectite of which particularly, the hydrous magnesium-calcium-aluminum silicate; refer as montmorillonite (Grim et al., 2012). Like natural zeolites materials, bentonite clays are composed of very fine particles and are derived usually from volcanic ash. In this regards therefore, natural occurring zeolites can be regarded as parent to clay materials since these also occur naturally where volcanic rocks and ash layers react with alkaline groundwater (P &G, 2014).

The acidic nature of bentonite, which is a common property to ZSM-5 or other zeolite catalysts, can easily be tuned by applying appropriate modification to Bentonite or by treating it with a suitable acid reagent, such as sulphuric acid. The above-mentioned properties project an insight that bentonite clay, and very possibly other clay types, can be potentially applied for ethanol transformation to hydrocarbons.

This afore-mentioned is proven and was reported by Widjaya et al. (2012:65-70) of bentonite catalytic application for the transformation of bioethanol into gasoline. The Catalyst loaded with chromium, demonstrated a comparable results as the commercial H-ZSM5 catalyst with regard to catalytic performance and product distribution.

Nonetheless, the HZSM-5 had shown a better catalytic test results than the Cr/bentonite. This was in regard to higher surface area and the fact that this HZSM-5 was a commercial product made with special treatment (Widjaya et al., 2012).

These properties project an insight that bentonite clays and very possibly other clay types can be potentially applied for ethanol transformation into gasoline-range hydrocarbons.

The main advantage of bentonite is that it is very cheap, cheaper than HZSM-5 (both synthetic and commercial) and other zeolite catalysts. In addition, bentonite is widely available in nature and, regarded as a clay mineral; it can possibly be modified and converted into ZSM-5 or any other zeolites catalysts (Chatawong et al., 2003 & Mezni et al., 2011).

2.2.2.2 Kaolin clay

Kaolinite is a naturally occurring clay mineral with the chemical composition $Al_2Si_2O_5(OH)_4$. Kaolinite is 1:1 clay type as it consists of one tetrahedral sheet and one octahedral sheet.

However, a rock or a clay soil that is rich in kaolinite is broadly and commercially referred as kaolin or China clay (Mindat, 2014). Among approximately thirty existing different clay species, kaolin is the purest form in the world (Grim et al., 2012).

Kaolin is a white powdered material, primary clay having the usually chemical formula of $Al_2O_3.2SiO_2.2H_2O$ (Choudhary et al., 2012:775). This can be described as a group of stacked hydrous aluminium silicates composed of approximately 46.54 % silica, 39.5 % alumina, 13.96 % water and minor naturally occurring traces of impurities (Burgess Business Company, 2012). According to Choudhary et al. (2012), the impurities associated with the raw kaolin are majorly iron and titanium, followed by mineralogical impurities such as quartz, mica, tourmaline, anatase, rutile, pyrite, siderite, feldspar; and these usually affect its industrial utilization. Illustrative to the above, Jacob et al. (2004), Chatawong et al. (2003:4) and Choudhary et al. (2012:777) have reported on the XRF analysis of raw kaolin from different sources, such as South Africa, Thailand and China. These are respectively shown in Table 2.2.

Table 2.2: Chemical composition of kaolin clay from various deposits

Mineralogy	**% (w/w)**		
	Beaconsfield Kaolinite clay (South Africa)	Thai Kaolin (Ban Pu Mine in Thailand)	China R.O.M Kaolin (China)
SiO_2	64.56	46.70	63.58
Al_2O_3	23.73	37.33	25.83
Fe_2O_3	0.74	0.75	0.96
TiO_2	0.75	< 0.01	Traces
Na_2O	0.19	< 0.10	In traces
K_2O	2.38	0.93	In traces
CaO	0.03	< 0.10	In traces
MgO	0.36	< 0.10	In traces
MnO	0.01	0.04	-
P_2O_5	0.03	-	-
H_2O	0.32	-	-
Loss on Ignition	6.89	13.68	9.63

ROM kaolin: Run-of-mines kaolin clay

NB: South African Kaoilinitic clay in the Beaconfeld (North of Grahamstown) was obtained 10 m below a 40 m borehole. In addition, It has been found that almost all raw or mined kaolin clay contain impurities which are also classified as the mineralogical content of crude clays. Hence the mineralogical composition of the R.O.M kaolin clay and the Grahamstown kaolin clay deposit from Ecca shale parent rock (Heckroodt, 1991:357), are shown in Table 2.3.

Table 2.3: Mineralogical composition of kaolin clay

Constituents	R.O.M kaolin clay		Grahamstown Ecca shale-derived kaolin clay	
	Weight	% content (w/w)	Weight	% content (w/w)
Kaolinite	252	25	-	20 to 35
Quartz	690.03	69	-	55 to 70
Mica	50.3	5	-	10
Tourmaline	7.76	1	-	-

According to Eman (2013:360), kaolin is the most important clay used in the manufacture of catalysts. Other application of kaolin includes ceramic, textile, paint industry, rubber and mostly paper industry (Choudhary et al., 2012:775). In the recent years, a relatively little catalytic application of kaolin (clays) has been prominent with regard to the conversion of bioethanol. Kaolin clay is a potential source of alumina and synthetic zeolite, and the latter is predominant for the conversion of alcohol to hydrocarbons (Eman, 2013:356 & Milliken, 1950:314). Like other clay types, kaolin occurs as a sedimentary clay. Purification or beneficiation may therefore be prerequisite to grade the crude kaolin for refinement so as to make it appropriate for catalytic application.

2.2.2.3 Talc clay

Talc, like sepiolite, is also 2:1 clay which is commonly defined as a hydrated magnesium sheet silicate with the chemical formula $Mg_3Si_4O_{10}(OH)_2$. In other words, it is a complex magnesium silicate hydrate, with approximately 31.87% MgO, 63.38% SiO_2 and 4.75 % water.

2.2.2.4 Sepiolite clay

Sepiolite is a clay mineral that falls under the 2:1 clay group and is likely present in either fibrous, fine-particulate and solid forms. It is a complex magnesium silicate with the typical general formula of $Mg_4Si_6O_{15}(OH)_2{\cdot}6H_2O$ (Corma et al., 1987).

Sepiolite has high porosity and low specific gravity (beneficiation) which make the clay suitable for catalytic application such as water purification, and predictably for ethanol conversion to hydrocarbons. Sepiolite clay, like several solid catalysts, has also been found to be active catalyst for ethanol conversion (Heckroodt, 1991 & Gruver, 1995: 359-363).

Sepiolite is an active catalyst for the conversion of ethanol and has been found to be active for the conversion of ethanol to ethylene and ethyl ether - at low temperature and pressure of 280 ^oC and 1 atm respectively (Cormal et al., 1987). The resultant product as observed, are similar or comparable to the ones obtained when converting ethanol over zeolite ZSM-5. This as well is an indication that acidic sepiolite can be referenced if using other clay types for ethanol conversion; and these altogether can even be as promising or competitive if the reaction were to be investigated at various conditions (mainly temperature).

Further on, the chemical composition of the sepiolite clay, which had shown similarity to that of kaolin with regards to major chemical content (Aluminium and silica), is presented in Table 2.4.

Table 2.4: Chemical composition of natural sepiolite clay from Vallecas, Spain (Corma et al., 1987:424)

Mineralogy	SiO_2	Al_2O_3	MgO	Fe_2O_3	TiO_2	Na_2O	K_2O	CaO	MnO	Weight loss on calcination (Ignition) at 1000 ^oC
Natural sepiolite clay from Vallecas (Spain), **% (w/w)**	60.31	1.88	25.48	0.48	0.22	0.12	0.26	0.27	-	10.88

2.2.3 Clay modification

Clay minerals possess catalytic propertiessuch as surface acidity and basicity, ion exchange capacity, adsorption and swelling properties (Zhou, 2011:85) . However, not all clays in their natural states may possess the desired catalytic properties or values required for bioethanol conversion. Nevertheless, the above mentioned properties merely provide possibilities, alternatives or approaches for designing and transforming them into catalysts.

Several approaches can therefore be pursued to modify natural clays or clay-based catalysts to various values and the choice to each approach will later dictate on product distribution or selectivity to hydrocarbons-range product in ethanol conversion. For example, certain clays employed in their natural state for the conversion of ethanol may produce light oxygenates or light olefins (Corma et al., 1987). However, designing and investigating possible modification methods, will certainly result to modified value of clays, these which in turn could preferably lead to the formation of complex or higher hydrocarbon molecules and which could make clay-based catalysts quiet competitive if not substitute to zeolites.

Appropriate clay modification approaches in this work includes clay modification by acid treatment, clay beneficiation and promotion by Nickel, Iron and Cobalt element.

2.2.3.1 Clay modification by acid activation

The adsorptive and catalytic properties of clay minerals make them suitable in catalytic processes. These properties mainly depend on the structure and composition of a particular clay mineral. For example, the extent and nature of the external surface of clays govern the behaviour of their catalytic properties. The latter can therefore be modified by suitable methods, of which modification by acid is the most common for clays prior to their use in various applications. In relation to this work, clays modified with acid particularly smectite-type clays, are the first catalysts widely used in petroleum catalytic cracking (Eman, 2013:361& 363). Modifications that are interlinked and related to clay activation with acid are such as thermal and alkaline modifications (Eman 2013: 359 & Igbokwe et al., 2011:3).

Generally, most clay minerals are acidic in nature and exhibit ion exchange ability (Igbokwe et al., 2011). Accordingly when used as catalysts, they have been shown to contain both Lewis and Bronsted acid sites, with Lewis sites mainly associated with edge sites and the Bronsted sites mainly associated with the interlamellar region (Eman, 2013:361). The above however can be obtained or altered prior and depending on the type of activation (Igbokwe et al., 2011:5).

Acidity of a clay sample is mainly a function of surface charge and can be altered due to ion exchange property of clays. In other words, the acidic property of clays, similarly to zeolite, is tunable or can be enhanced as a result of their ion exchange property. Several researchers (Chaudhury et al. 2012 & Inaba et al., 2005:137) have reported that strong bronsted acid sites and more than one proton per unit cell of H-ZSM-5 zeolite are important for catalytic activity in the conversion of ethanol. This can serve in reference to attain appropriate bronstead and lewis acidity of clay-based catalysts towards the conversion of bioethanol

The surface charge of most natural clays can therefore serve as the direct indication (or explain why these are acidic in nature) of their natural acidity, as stated earlier above. The surface charge however, varies for various clay species depending on their corresponding classification as indicated in Table 2.5 below.

Table 2.5: Common natural clay species with corresponding surface charge

Clay classification or group	Clay Species	Charge per formula unit = X
Pyrophylite Talc	Talc	X ≈ 0
Kaolinte Serpentine	Kaolinite or kaolin	X ≈ 0
Smectite	Montmorrilonite or bentonite	X ≈ 0.2 – 0.6
Vermiculite	Dioctahedral vermiculite	X ≈ 0.6 – 0.9
Mica	Illite, muscovite	X ≈ 1
Palygorskite Sepiolite	Sepiolite	X variable
Chlorite	Nimite	X variable

In Table 2.5, low (Bentonite) to neutral acidity (Talc, Kaolinite) is displayed for the various natural clays selected in this work. As a result to the above therefore, alteration of surface acidity by acid activation is necessary and is believed to be the suitable approach for acidity enhacement of clay species in this work so as to meet the potential acidic or catalytic value required for effective conversion of bioethanol.

The variation to the charge of natural sepiolite compliments the report by Corma et al. (1987:423) stating that “natural sepiolite commonly have low to no surface acidity”, and this as a result of its constituent uni-structural main element, being only silicon in the tetrahedral sheet with very little substitution by aluminum ion (Al^{3+}). Consequently, the non-acidic natural sepiolite clay displays a very low catalytic activity on the conversion of ethanol to ethyl ethylene and ethyl ether (Corma et al., 1987: 423), at 280 °C and 1 atm. In addition, the variation in surface charge or acidity of sepiolite clay indicated in Table 2.5, correspond to the fact that sepiolite clay exhibits a very low to almost no ion exchange capacity of 0.07 meq/g (Gruver et al., 1995:359).

Smectite group of clays, on the other hand, at least exhibit natural charge, as in accordance to this, Zhou et al. (2011:85) refered to smectite as cationic clay minerals.

Although natural clays may be acidic, this property can be enhanced by modification with acid or acidic metal solutions. As a result, Corma et al. (1987:423) report that acid activated clay comparable to natural clay, remarkably influences the conversion of bioethanol. In his finding, Corma et al. discovered that generating an acidic medium from a non-acidic natural sepiolite, enhanced the catalytic activity of a dehydration process.

The outcome to clay modification by acid treatment include changes to surface area, porosity and the type and concentration of the ions in the exchange sites (Eman, 2013:363). During acid modifications, Structural cation of aluminium and magnesium (Al^{3+} and Mg^{2+} cations) are removed from the octahedral sites in the clay layers by the action of the acid and are relocated in the interlayer space where they act as acid centres. This in turn, promotes catalytic activity by increasing the number of Bronstead and pontential Lewis acid sites. In addition, clay modification may result to dissolving out of Al, Mg and Fe in the octahedral layers of the clay (Chantawong et al., 2012) , leaving out silica sheet which are able to accomadate larger molecules for catalysis.

Clay activation with acid is a suitable approach for the exchange of the low dense charged hydrogen ion in compensation to the poor cation exchange ability of most clays, unlike zeolites. This method is promising because of the active ingredient of catalysis, the H^+ proton, which can be exchanged and transferred during the conversion of bioethanol. Acidic clay catalysts are widely used for reactions involving organic chemicals, such as esterification which in common to this work, requires protonation chemistry (Heckroodt, 1991).

Acidic activation, generation or promotion of a clay sample can be achieved by various methods. Activation by acid, is however , widely used for reactions involving organic chemicals (Igbokwe et al., 2012) because of the effective charge induced by hydrogen ion required in such processes. As a matter of fact, acidic nature of clays, as similar to ion-exchange capacity, is due as the result of electrostatic surface charge on the surface of the particles (Heckroodt, 1991:345).

Surface charge of clays is one of the surface properties essential for catalysis. This refers to either positive or negatve ions generated on surface of clay particles. Surface charge is brought about by various mechanisms (Heckroodt, 1991:345). However by acid activation, this is generated or altered by ionization of surface groups of the layers, by specific absoption of ions or polyions on the surface of clay particle or by the substituton of clay structural Al^{3+} or Si^{4+} (substitution of Al or Si^+ in clay structural sheet – by leaching) with H^+ (Heckroodt, 1991:345). Clay activation with acid therefore, enhaces or gives rise to bronstead or lewis acidity (on the surface) of the clay minerals and is the most common approach for the generation of lewis acid sites on clay layers. This derives from the fact that most clay species have low ion exchange capacity (Mezni et al., 2011;), and hence are favourbale for the generation of lewis acidity when treated with acid. Limit to ion exchange capacity limits the substitution of clay structural element or ion with an external active element for exchange . As a result, the surface layers of clay particles are rather ionised by acidic proton and thereon generating multiple lewis acidic sites (Heckroodt, 1991)

In contrast (only applies to thermal treatment of clays at temperature of around 100 ºC, while rising the temperature to around 200-300 ºC, generate browsted acidic sites) to acid treatment, alkaline activation and thermal treatment or calcination (generate only bronsted acidic sites on the surface of clay layers (Eman, 2013 & Refaat, 2010:209). The browsted acidity by thermal treatment (at 100^0C) however, are formed as a result of dissociation (removing) of the interstitial or adsorbed water between the clay structure (Eman, 2013:361). Consequently, thermal activation as comparable to an appropriate standard of acid activation, enhaces the surface area of clay particles and hence the catalytic activity of clays (Igbokwe et al., 2011).

Moreover, the acidity of a sample is related to the speficic surface area exposed. This is made reference to the amount of either lewis or basic sites per unit mass of the catalyst, as these increase or decrease as the specific surface area respectively increases or decreases (Lee et al., 2008). Surface area in tun, in relation to earlier discussed crystal size zeolite, is dependent on the size of the particle. The more dispersed or smaller catalyst particles are, the more exposed surface area a catalyst sample contains (Rownaghi et al., 2012). The specific surface area (of particle) therefore, as reported by Refaat (2010:203), influences the catalytic activity of a catalyst . Hence surface area of clays, is related to their acidity and can be further used as a mean to account for acidity change or enahcement of the various clay types used in this work (Viswanadham et al., 2012).

Activation of clays is commonly carried out by treating the clay in an concentrated or aqueous acidic medium under mixing and heating operation. Activation of clay therefore with an acid, does not only give rise to acidity of clay minerals, but it does also enhances the surface area of clay particles to a relatively high degree, due to the appropriate thermal subjection when activating. More over, the H^+ ion exchanged or adsorbed on the surface of clay particles prior to acid activation , is an active ingredient for catalysis (Yahiaoui et al., 2003)). This element is most widely used in catalysis application. The resulting clay surface charge prior to ionisation of H^+, is active centre for the entire ethanol conversion path; with basic sites as active centre to ethanol dehydration and lewis sites to addition polymerization of light hydrocarbons (Hydrogen transfer required to form long chain hydrovarbons (Temuujin et al., 2004).

Acid-modified clays are solid heterogenous catalysts, owing to their advantage of easy separation and removal from the reaction product (Eman 2013:362). The type of reagents used in activation, the strength/molarity of the reagents, the temperature of the activation and the activation duration are all believed to have effects on the effectiveness of the clay catalysts. Subsequent modification can also be carried out on acid-treated clay.

(i) Acidic medium for clay activation

Modification of clay by acid activation is carried out by treating the clay with concentrated acid minerals such as sulphuric acid, phosphoric, hydrochloric acids and nitric acid (Eman, 2013:363).

Sulphuric acid however, is the most commonly used acid mineral for clay activation and it is used by the most common acid catalysis (Lee et al., 2009: 64). In addition, sulphuric acid is produced in greater amounts than any other chemical besides water (Pushpaletha et al., 2005), meaning that it is the most abundant produced acid minerals and may therefore have greater availability than any other acid minerals. However, mainly dilute concentrations of sulphuric acid has been reported in the treatment or activation of clays since highly concentrated acid are detrimental to clay structure. Other acid minerals such as hydrocholoric acid, similar to nitric acid, is as strong acid. This when used for clay activation in comparison to sulphuric acid of the same strength and amount, tend to have a stronger deteriorating effect on the structure of the crystalline materials. Hence the preparation of various acid concentrations is very convenient when using sulphuric acid because this is soluble in water at all concentrations and therefore can compensate for clay structure at required and appropriate concentrations.

Sulphurc acid is well known dehydrating agent and has the capacity to remove water of crystallisation from hydrated organic compound (Meeks, 1979), hydrated metal compound as well as porous, water swelling and hydrophobic crystalline materials such as clays.

Sulphuric acid is a relatively strong dehydrating and oxidizing agent as this property is effectively required for ethanol dehydration, a stage process of bioethanol conversion.

Acid activation of clays has been carried out by several reaserchers for various applications, other than the one to be applied for, in this work. The activation conditions in this approach and the actual values reported are shown in Table 2.6.

Table 2.6: Clay acid activation parameters (Mills et al.,1949; Onal et al., 2002 & Pushpaletha et al., 2005)

Activation parameters				
Clay type	**Acid type and concentration**	**Clay : acid ratio (w/v)**	**Activation temperature and time**	**Source**
Bentonite	5-20 % H_2SO_4	0.2 – 0.8	93 ^{o}C for 16 hours	Mills et al., 1950: 1170
Calcium bentonite	98 % H_2SO_4	**0.05** (i.e. 20 g / 400 ml)	97 ^{o}C	Onal et al. (2002:410)
Bentonite	0.35, 0.70, 1.0, 1.5, 2.0, 3.5, 7.0 and 10 N	0.46 (i.e. 25 % w/w)	105 - 115 ^{o}C for 45 min	Pushpaletha et al. (2005)
Bentonite, kaolin and Talc		0.66 - 0.61 0.9 0.9	98 ^{o}C for 6 -18 - 22 hours	This work

2.2.3.2 Clay beneficiation

Clays are aluminosilicate materials and hence the main chemical constituents which account for clays’ unique characteristics is alumina and silica. However in the very nature of clays, these constituents are always found in combination with other soil or mineral (chemical) species owing to the fact that the primary source of clay is the earth crust and their recovery is achieved mainly through mining. Accordingly, sedimentary clays are seldom beneficiated to any significant extent. In most cases, the remaining components or chemicals that make up the rest of crude clays are undesirable as they do not only restrict the use of clays but also degrade their value, which in turn lowers the economic feasibility of clay production.

Beneficiation of clay minerals is therefore important and is required for most natural sedimentary clays. This makes the catalytic application of clays amenable to chemical processess, including to existing and broader discovery of their use in industry (Heckroodt, 1991:351).

If the term “ore beneficiation” is applied to sedimentary (or crude) clay, clay beneficiation would then mean separating the clay mineral from any unwanted or other materials that make up the rest of the crude (clay) ore. In the context of this work however, clay beneficiation refers to purification and mainly concentration of clay minerals with regards to their major element constituents. The unwanted materials that make the rest of crude clays refers to the significant impure mineralogical contents such as quartz, micaceous minerals, grits, anatase, pyrite, feldspar, siderite etc.(Heckroodt, 1991). The major element constituents of most clays refered above, is alumina and silica. The latter are active and prominent elements which consititue hetrogenous catalyst for various application (Lee et al., 2009:66) and mainly required for catalytic application or modification of clays to valuable catalysts in this work (Gruver et al., 1995).

(i) Benefication methods

The separation of a mineral and gangue in an ore can be achieved through various techniques. Most separation techniques are based on differences in one or more of the properties of the gangue and the mineral to be beneficiated. These differences are commonly in density, magnetic susceptibility, colour, surface chemistry and particle size or shape (Heckroodt, 1991:351).

Beneficiation (Purification and concentration**)** of clay can be accomplished by adopting two different basic routes: The dry and the wet process. The dry process is relatively simpler and less expensive. In this process, clay, commonly kaolin, is crushed, dried and pulverized prior to it being subjected to air floatation to remove the relatively fine materials by air current (Choudhary et al., 2012:777 & Heckroodt 1991:351). However, one of the significant challenges with this process is that the air tends to float even larger particles, thereby decreasing the quantity of the obtained product since coarse particles are the intended products. This in turn degrades the economic feasibility of the process. Moreover, separation by dry process is principally based on difference in size of (clay) particles which result by either crushing or pulverising operation. This raises another shortcoming of the dry process which results to final product with much impurity, as the operation breaks down the quartz content in clay into fine to very fine particles that are captured and retained in the clay product. Therefore dry process is not suitable to produce high graded clay product.

On the other hand, clay beneficiation by wet process is more expensive and yet produces a relatively high purity product as compared to the dry process (Heckroodt, 1991). The relative high cost for wet beneficiation can be accounted due to the complexity of the route. However, obtaining a high graded product is the drive or motive to the adoption of wet beneficiation route in this work. In addition, separation by this route can be carried out by making use of readily available equipment.

Separation by wet beneficiation process, owing to the difference in properties of particles in a clay sample, can be carried out through several separation techniques. Common techniques include magnetic separation, mechanical treatment, differential sedimentation and chemical treatment, floatation, etc. (Heckroodt, 1991:351). Two or multiple of the above techniques, can be adopted in subsequence in order to obtain clay of higher purity, which often cannot be attained by one singurlary.

For a superior recovery of clay minerals (Higher purity), Chapman et al. (1980) in his invention applied two separation techniques of magnetic separation and selective flocculation, presuming that beneficiation cannot be achieved effectively with either process singularly. High intensity magnetic separation of clays is an effective beneficiation method to remove a significant portion of coarser impurities, while selective flocculation of clays does remove finer impurities. Magnetic separation however, is energy extensive for such high intensity (Field strength of over 20 $kg/A.s^2$) require high capital and operating cost and removes mainly magnetic and paragnetic fine particles. This implies that there will be a significant amount of very finer impurities, especially if these are larger portion and non-magnetic.

A feasible beneficiation is generally obtained only if there is a significant difference in size and shape of the various minerals (Particles) present in clay. For this reason, appropriate approaches are applied in this work, whereby screening is rather substitute to magnetic separation, as reported by Chapmen et al. (1980) for the removal of coarser particle. Adopting his multiple approach, the screening could be followed by a refining technique for the removal of finer impurities. Both the above are physical separation techniques, are relatively simple and inexpensive than other separation techniques mentioned earlier (Heckroodt, 1991).

As a matter of fact, Heckroodt (1991:350) and Chauldry et al. (2012:778) also gives the complex image of wet beneficiation by presenting that this process can produce superior quality or a highly beneficiated clay only if the beneficiation is achieved through at least two separation techniques.

Beneficiation through screening technique generally involves the separation of fine particles from coarse particle that constitute a clay sample. This is adopted as the first stage to fractionation or refining in this work, which like magnetic separation, does not remove a significant portion of the finer impurities (Chapmen et al., 1980). In kaolin clay, the above impurities are reported to have very similar density as the actual kaolinite mineral (Heckroodt 1991:351) and hence separation in this case is not practical if it is based on density difference. According to Heckroodt (1991:351), clay (as generally kaolin) produced by screening has been found to still contain an appreciable amount of finer impurities (Quartz, mica, other impuritites, etc.).

Therefore additionally, common fractionating or *refining techniques* that can be used to remove finer impurities from clay include centrifugation, hydrocyclone and sedimentation by gravity (Heckroodt, 1991:351). The latter is the most economical, easy to understand and operate as it requires only a refining tank which can allow for settling of clay suspension in water (Choudray et al., 2012). Like screening, separation by sedimentation is feasible due to the difference in density of particles, this which in turn is as a result of the difference in size and shape of particle present in clay (Heckroodt, 1991) . Clay minerals are relatively denser than the very fine particle making up the impurities and hence are likely to settle by gravity when subjected to water suspension for sedimentation. The very fine impurities have a greater tendency to suspend and float in water when immersed for sedimentation and can therefore be easily removed. The gravity sedimentation technique, is therefore an additional fractionation technique of wet beneficiation, adopted mainly for the removal of significant amount of finer impurities. This may also to a noticeable extent separate the coarser particle remaining from screening (if any), from the actual clay minerals.

Heckroodt (1991:351) in his report included the step of disintegration of clay prior to fractionation / refining and dewatering. Accordingly, clay crystals are often very small and are generally aggregated and agglomerated into mono-mineralic units (Heckroodt (1991:344). The latter can therefore be disintegrated by gentle agitation, which however may not be as effective because certain units are extremely difficult to separate into their individual crystallites. As a result, an appreciable amount of finer impurities will still be retained within the clay irrespective of subsequent separation. However for this to be resolved, the approach of use of chemical deffloculants deduced from Chapman et al. (1980) and as a means of improved clay beneficiation (with regards to mineralogical finer impurities), can be adopted before and during settling of clay suspension.The most commonly known chemical deflocculants includes sodium hydroxide and sodium carbonate.

Eventually, selective flocculation can serve as a mean for rapid settling and effective formation or concentration of clay sediment. Alternatively, concentration of clay in respect to alumina and silica co can be achieved through sedimentation followed by particle-size distribution by screening technique. Zhang et al.(2010:67-68) in his work, reports on the mass concentration of 20 different elements in dust particles (Al, As, Br, Ca, Cl, Cr, Cu, Fe, K, Mg, Mn, Ni, P, Pb, S, Se, Si, Ti, V, and Zn). This was accomplished in different size stages with the aim to characterize the chemical composition in each cut . According to his result, the peak concentrations of each element falls in different size stages. Zn, Cl and Cu were mostly enriched in fine particles, Pb was enriched in intermediate sized particles, but most mineral elements, S and part of Cu were enriched in coarse particles. Similarly in this work, the above approach however by means of screening for particle size distribution, could be applied either before or after sedimentation of clay. This similar to the screening technique described earlier, could serve as the enriching technique for clay purification (with regards to mineralogical impurities), as well as the approach to concentrate clay minerals with regards to Silica and Alumina content. In other words, size distribution in this regards can serve as a mean to assess and concentrate clay for major element contents.

Dewatering of the slurry usually take place in two stages, namely thickening and drying. Centrifuges are mostly used for the initial thickening of the slurries. Drying can be achieved by filtration followed subsequents drying equipments. The latter in this regards appropriately refers to spray drier, followed by tray drier for final drying.

Clay beneficiation is prerequisite for many uses of clays, such as in the ceramic and paper industry. In this work, the effect of clay benefication is studied on their catalytic application and conversion of bioethanol. Hence, laboratory procedures to achieve the above includes screening (Separation based on particle size difference and serves for concentration of the major element contents in clay) and gravity sedimentation – serving for purification.

In illustration that wet beneficiation approach is promising and may similarly apply to this work, the finding reported by Choudhary et al. (2012:777&780) exhibits the recovery of superior quality of clay through the wet beneficiation approach - shown in Table 2.7 below.

Table 2.7: The effect of wet beneficiation of clay (R.O.M Kaolin) on mineralogical impurity

Impurity mineralogical content	Before beneficiation (%, w/w)	After beneficiation (%, w/w)
Clay	25	98
Mica	5	0.5
Quartz	69	0.5
Other impurities	1	-

(ii) Colour and brightness as determining factor for kaolin clay beneficiation

The effectiveness of clay beneficiation can be accounted by assessing change in certain properties of clays, of which variation in colour and brightness can be assessed for clay such as kaolin (Heckroodt, 1991:351). Natural kaolin may vary considerably in their color properties and this is irrespective of them being mined in the same locality, as well as differenct sites in the same mine. As mentioned earlier in literature, clays in their natural states consist of various contaminants, of which certain are discouloring and hence affect the brighteness of clay minerals. The contaminants include iron and titanium, impurity clay minerals such as smectite and illite-smectite mixed-layered clay mineral, and also organic and inorganic carbon content in the clay mineral (Heckroodt, 1991:352). Yellow brown shade appearance of a kaolin clay sample (or mineral) is largely contributed by the presence of Titanium and iron in the crystal structure, including the presence of impurity clay minerals. The carbonaceous matter mentioned above, contribute to gray tint colour (Yuan et al., 1997). Brighterness therefore, of nearly or comparably white in colour, should reflect the quality of a beneficiated (graded or refined) kaolin.

Differential sedimentation, including other beneficiation techiniques such as mechanical treatments, magnetic separation and flotation, can be used to improve the brightness of the kaolin. Fractionation by screening however may only be effective in improving the rheological property of kaolin clay (Heckroodt, 1991:352).

2.2.4 Synthesis of zeolites from clay materials

Zeolites can be synthesised from variety of raw materials, basically from any inorganic materials that chiefly consist of aluminum and silicate (In high proportion). Generally, the synthesis of zeolite is achieved by hydrothermal synthesis and this method thus far, has proven to be the most efficient way to produce microporous materials of such as zeolites (Weitkamp, 2000). Zeolite synthesis by this method requires alumina and silica sources to prepare a freshly aluminosilicate gel (Mezni et al., 2011). For this, the most common or conventional sources are chemicals which when mixed, form aluminosillicate gels. For example solution of sodium silicate and sodium aluminate. Other sources may be refered as non-convential which are such as natural glasses, synthetic glasses, fly ash and clay minerals (Chatawong et al., 2003).

Zeolite synthesis requires conventional chemical sources of silica and alumina and the latter in most cases can only be obtained commercially and are expensive (Mezni et al., 2011). Clay materials possess similar basic components (or minerals) as zeolites, however in clays these may be found in low and various proportion and this can be altered to meet the desired proportion required to synthesize a high siliceous zeolite . The use of clay materials therefore in this work, serves as susbstitute to the expensive sources of alumina and silica and hence reduces cost to zeolite synthesis in this work. Clays are abundant in nature

(Widyaya et al., 2012), have cheaper availability and therefore can serve as starting raw materials for the synthesis of zeolites (Mezni et al., 2011 & Chatawong et al., 2012).

Hence in this work, clay materials are not only investigated for their catalytic potential in the conversion of bioethanol, rather the target owing to their basic catalytic properties, is also to transform them into zeolites. Such findings have been reported mainly for the transformation of kaolin to ZSM-5 zeolite (Wang et al., 2007 ; Khatamian et al., 2009, etc.).

Various methods have been recently investigated for the synthesis of zeolite from alumina-silicate sources. These include alkaline fusion prior to hydrothermal treatment and the conventional hydrothermal alkaline activation.

Most natural clay materials contain a proportional amount of mineralogical impurities such as quartz, feld spar and gypsum (Heckroodt, 1991) and these impurities are not prefered when synthesizing zeolite from clays. In this regard, fusion with sodium hydroxide prior to hydrothermal reaction is an appropriate method to dissolve the impurities as this method proven by Mezni et al. (2011:211) in his work, led to the absence of quartz or natural clay in the final zeolite product. The above outcome is unlike zeolite synthesized by the direct method under same conditions. Futhermore, it was also found that the alkaline fused product (product obtained through fusion with Sodium hydroxide) corresponded to amorphous sodium aluminosilicate.

The developed liquid and gel mixture by fusion of sodium hydroxide is a system rich in silicon and aluminium species and is adequate for the synthesis of zeolites. This method is very effective in extracting the silicon and aluminium species from the clay, and this partially results due to the dry reaction the method promotes between the crystalline mineral phases present in clay and the alkaline activator (Mezni et al, 2011).

As a result, reaction at high tempetature between sodium hydroxide and material such as clay, achieves the highest level of zeolitisation. This is in agreement to results reported by several researchers (Molina et al., 2004, Poole et al., 2000; Querol et al., 2000; Rayalu et al., 2000 and Shigemoto et al., 1993).

This is not the case in the hydrothermal process, where all species, amorphous or crystalline, have to be dissolved in the solution in order to produce the species necessary for the formation of zeolites.

Mezni et al. (2011) further reported that the fusion method as compared to direct hydrothermal method, compensate for shorter reaction times and produces catalyst with high crystallinity and surface area. According to his finding, the maximum crystallinity for the synthesis of zeolite X through the fusion method, was attained only after 24 hours reaction, with a corresponding surface area of 216.3 m^2/g. For direct hydrothermal method under same reaction time as above, the surface area was lowered to 61.3 m^2/g.

The obtainment of high crystallinity and surface area through fusion method may similarly result for zeolite ZSM-5 produced from clay. For this, 48 hours instead as given in literature (Silva et al., 2013:85), is the most commonly and optimum reported for microcrystallinity of zeolite product. Longer reaction time (to such as 168 hours) as according to Khatamian et al. (2009:194), is rather optimum for nanocrystallinity of zeolite from clay.

Both zeolite synthesis methods require several procedures to obtain the product. These include thermal activation of clay (e.g. through calcination) at high temperature (usually above 550 ^{0}C) , injection of sodium hydroxide to form an alkaline alumino-silicate gel; hydrothermal reaction at high temperature for the crystaliiiation of the gel for a certain period of time. The washing and drying of the synthesised product, followed by calcination to finally obtained the zeolite catalytst.

Zeolites can be synthesized with different crystal structures, definitive pore sizes, framework Si/Al ratio ratios and adjustable acid centers to have some important catalytic properties (Guo et al., 2011: 340). These however, are definitive in correspondence to appropriate parameters taken during the synthesis procedure. These parameters include silica and alumina source and ratio in the starting material, Synthesis in the presence or absence of organic template, the synthesis condition of ageing, crystallisation time and temperature and application target of the synthesised zeolite.

Kaolin is the most popular clay material used for the manufacturer of valuable petroleum-directive catalysts (Eman, 2013). In the open literature, kaolin has also been observed to be the most common clay used for the synthesis of zeolite. The preference to kaolin in comparison to other clays includes the fact that it is the purest clay minerals (Grim et al., 2012) and has been reported to contribute to high thermal stability of zeolite (Emam, 2013:361)

The relevance of other clay types is also due in the synthesis of zeolites, except the fact that these have been more directed to synthesis of other zeolites than the ZSM-5 zeolite. For example, Mezni et al. (2002) and De la Villa et al. (2002) have reported on the use of illite and bentonite clay for the synthesis of zeolite X and Y. A relatively few work has been reported on the synthesis of zeolite from other clays (non-kaolin clays). This however may be effective in the conversion of ethanol (Hoang et al., 2010) - Though not as compared to ZSM-5 zeolite catalyst in this regard.

Kaolin as a clay specie, may serve as either alumina or silicate source (Silva et al., 2013: 85) or simply as alumina source (Khatamian et al., 2009). Silica and alumina are usually the major element components in most clays , as shown in Table 3 and Table 5. In both clays and zeolite, silica usually appears in higher proportion than alumina. In most natural clays, SiO_2 / Al_2O_3 ratio ranges between 1 to 3 (Wang et al. 2007:1453). This may be obtained in a slightly higher than the above ratio, depending on the clay type and source. For example, the natural Tunisian illite as described by Mezni et al. (2011: 216), was found to have SiO_2 /Al_2O_3 ratio of 3.43. Those (SiO_2 /Al_2O_3 ratios) of the three different kaolin clays from literature as ealier reported Table 3, were 2.72, 1.25 and 2.46 respectively.

Zeolite catalysts on the other hand in most literature, is observed to be accounted for Si / Al ratio as compared to SiO_2 /Al_2O_3 (Madeira et al., 2011, Viswanadham et al., 2012 & Kathamian et al., 2009). Weitkamp (2000) reported that the minimum SiO_2 /Al_2O_3 ratio required for the synthesis of ZSM-5 is five and this ratio as in terms of Si / Al, can be adjusted to a desired value. For example, several researchers (Madeira et al., 2012) have investigated on the Si/Al ratio ratio of zeolite ranging between 16 and 500. According to his finding, the ratio between 30-40 in zeolite, particularly ZSM-5, has so far been found most effective in the transformation of ethanol to hydrocarbons (Viswanadham et al., 2012).

The higher proportion of silica than alumina in clays, is regardless of the number of layers or structure that a particular clay possesses. For example, sepiolite clay is classified under the 2:1 clay group, yet displays a (very) higher proportion of silica content than alumina (~ 32.08) .

Zeolite are high siliceous materials and oftenly may require high SiO_2 / Al_2O_3 mole ratio in the starting clay material so as to correspond to the high ratio of that in the synthesised zeolite. For example, for a SiO_2 / Al_2O_3 mole ratio of 23.2 in the starting mixture, A SiO_2 / Al_2O_3 ratio of 24.9 was observed in the synthesized ZSM-5 (Mravec et al., 1985:338).

Only low silicious zeolite are more likely to be synthesised from clay materials containing low SiO_2/ Al_2O_3.This can be deducted from the work of Mezni et al. (2011: 216) where faujasite zeolite could be synthesised from illite of a SiO_2/ Al_2O_3 ratio above 1.5.

If or since most clay often contain silica and alumina minerals in low proportion than the one required in zeolite (ZSM-5 in particularly) for the conversion of ethanol, Schwarz et al. (1995:488) suggest for the methodologies employed for changing the SiO_2 / Al_2O_3 ratio in the gel phase In order to achieve exceptionally high SiO_2 / Al_2O_3 ratios ". This can be attained by introducing organic additives , complex agents for the aluminium supplement and mainly adding sources of silica supplement such as sodium silicate , silicic acid or H_2SiF_6. This above approach can be considered in this work for the zeolite synthesis from clay.

Organic templates are used for forming the crystal structure of zeolite (ZSM-5) according to the original procedure of Mobil Oil Co (Mvarec et al. 1985). Tetraprophylammonium compounds such as TPAOH and TPABr are the modern common templates used in the synthesis of zeolite (Khatamian et al., 2008:188). According to Mvarec et al. (1985) , Ethylamine however, has proven to be one of the convenient substitutes for the expensive and hardly available tetrapropylammonium compounds.

The size and crystallinity of the produced ZSM-5 is influenced by the kaolin content, crystallisation temperature and time, as well as the clay content incurred during the catalyst synthesis (Khatamiam et al., 2009) . For this reason, several researchers oftenly set a range of operating conditions and investigate the optimum in respect to the standard degree of size and-crystallinity of a zeolite catalyst for a particular application. The temperature interval for most zeolite synthesis is 120 ^oC and 195 ^oC (Mravec et al.,1985) , as 150 ^oC-180 ^oC has been observed through many actual existing work (Silva et al., 2012; Wang et al., 2007; etc.) to be the best for the preparation of zeolite under given reaction conditions.

Several researchers (Silva et al., 2013; Khatamian et el., 2009) have reported on the reaction temperature and corresponding reaction time of 170–180 ^oC and 48 hours respectively. These seeemigly are the most common conditions and optimum for hydrothermal synthesis of microsize crystalline ZSM-5 zeolite from clay. A higher reaction time however, such as to 164 hours and mainiting the same reaction tempaerure as above, was reported as optimum to obtain a nanocrystalline ZSM-5 zeolite (Khatamian et al., 2007:194). In addition, it has been observed that shorter reaction times such as 24 hours and reaction temperatures such as 110-120 ^oC , are mostly applicable for the synthesis of low silicious zeolite (Mezni et al., 2011).

2.2.5 The properties of zeolite catalysts for ethanol conversion

As mentioned earlier, clay materials possess similar basic components as zeolites and may be utilised as raw materials for the synthesis of zeolite catalysts. Several researchers have proven this (Mezni et., 2011; Silva et al., 2013:85, etc.). ZSM-5 zeolite in particular, is the most predominant catalysts used for the conversion of ethanol to hydrocarbons fuel

(Madeira et al., 2012; Widjaya et al., 2012; Inaba et al., 2006; etc.). hence the properties and corresponding application of zeolite in ethanol conversion is discussed below.

2.2.5.1 Source, structure and application of zeolites

Zeolite catalysts have been used for industrial Fluid Catalytic Cracking for over forty years (*P & G, 2014)*. These have also been identified as active catalysts for the conversion of alcohol to hydrocarbons. Several researchers (Guo et al., 2011:340) have refered to zeolites generally as hydrous crystalline microporous alumina-silicate minerals and their representative general formula is $Na_X[(AlO_2)_X (SiO_2)_y]$ x zH_2O.

Zeolites occur naturally and preferably are synthesised through various methods to meet the required application standards (Wang et al., 2006; Mezni et al., 2011; etc.). Consequently, zeolites are probably so far the most popular and investigated inorganic solid acid catalyst (Sivasamy et al., 2009: 287 & Guo et al., 2011: 341). According to Lee et al. (2009:69), the versatile catalysis ability of zeolites results from their chemical composition, pore size distribution and ion-exchange abilities.

A typical zeolite material consists of a porous structure which can accommodate a wide variety of cations, such as Na^+, Ca^{2+}, Mg^{2+} and K^+. These cations are rather loosely held and can readily be exchanged for other cations in a contact solution (*P & G, 2014*). The above make zeolites commonly useful as ion exchangers, adsorbents or catalysts in important processes – such as petroleum refining, separation and purification processes, including ethanol conversion to various hydrocarbons (Eman, 2013; Chantawong et al., 2003 & Weitkamp, 2000).

Furthermore, zeolite materials have peculiar shape-selective property which makes them useful for superior control of reactions selectivity and competitive for catalysis in petroleum processes (Chatawong et al., 2003:9 & Lancashire, 2007- 2013). Properties of zeolites which make them useful and prominent catalysts in the conversion of ethanol is further discussed below my making reference to ZSM-5 zeolite catalyst.

ZSM-5 is representative of high-siliceous zeolites (a zeolite mineral) and belongs to the pentasil family of zeolites. It has a MFI structural type and excels in shape selectivity of reagents set for the reaction. As a matter of fact, ZSM-5 zeolite is popularly refered as a molecular sieve because of its structure (First et al., 2011, Petani, n.d, etc.). The ZSM-5 has a three dimensional and regular distributed porous structure which contains alkali or alkali earth cations (Guo et al.2011:340 & Widjaya et al., 2012) and has a high and tuneable acidic property.

The mentioned are the main attributes which have made the application of ZSM-5 successful for catalysis in several important industrial processes, including the transformation of alcohols to olefins and higher value hydrocarbons (Mravec et al.,1985, Gounaris et al., 2011 & , Widjaya et al., 2012:66). As a matter of fact, Viswanadham et al. (2011) reported that ZSM-5 catalyst possesses a special high selectivity to gasoline-range hydrocarbons when used for the conversion of ethanol.

Zeolite application for alcohol dehydration includes the production of light to heavy olefins, mono-functional oxygenates such as aldehydes (e.g. propenal or acrolein), ketones, carboxylic acid and other forms of alcohols. Zeolites can further be used to extend the conversion of the mono-functional oxygenates into gasoline-range hydrocarbons (Hoang et al., 2010).

2.2.5.2 Classification of zeolite catalysts for ethanol conversion

Zeolite A, Zeolite X and ZSM-5 are the most commonly reported zeolites to have been synthesized from clay as respectively reported by Chatawong et al. (2003) ; Mezni et al., (2011) and Wang et al., (2007). According to Lee et al. (2009:69), Zeolite X is generally accepted as one of the most basic zeolites and has a more appropriate application in esterification or water purification process than in the conversion of ethanol. Zeolites and zeolite-based catalysts for the latter purpose, exist in large numbers and have proven active for the conversion of ethanol to hydrocarbons (Inaba et al., 2005 & Hoang et al., 2010). The various types includes HY zeolite, USY Zeolite, Modernite (or the H-mordenite), the H-Beta, the HZSM-22, HBEA, HFAU and the ZSM-5 zeolites (Inaba et al., 2005 & Hoang et al., 2010). The above classification is based on their catalytic supports and morphologies.

Selection of a particular zeolite catalyst for ethanol conversion often depends on the overall performance of this catalyst in respect to activity, selectivity and stability (Inaba et al., 2006).

The use of ZSM-5 zeolite catalyst for ethanol conversion possesses numerous advantages when compared to other zeolites types and these have been reported in many literature. The ZSM-5 is representative of high-siliceous zeolites which exhibits exceptional catalytic properties and high temperature stability resulting from their structure (Guo at al., 2011:

341). In recent years, this catalyst has demonstrated its potential in the conversion of biomass resources to hydrocarbons chemicals (Rownaghi et al., 2011). As a matter of fact, the ZSM-5 is one of the most studied and so far one of the best catalysts for the conversion of ethanol into light olefins and/or higher hydrocarbons (Madeira et al., 2010). In the regard of the latter, the ZSM-5 is the only zeolites which exhibits a special greater selectivity and high activity to high value hydrocarbons molecules, particular gasoline-range and BTX aromatics molecules (Inaba et al.,2005:140). Hoang et al. (2010) reported that the HZSM-5, in exclusion to HY zeolite, is the only catalyst to form aromatics from glycerol conversion. High concentration of aromatic compounds within the gasoline-range hydrocarbons is favourable for the derivation and application of gasoline as a fuel (Viswanadham, 2011). Inaba et al. (2010) further reported that the use of other zeolites types for the conversion of alcohol have shown no aromatics formation , but rather exclusive formation of ethylene and oxygenates.

The catalysis of the clay-derived ZSM-5 on bioethanol conversion in this work, aim at obtaining higher value hydrocarbons, such as gasoline range hydrocarbons. Due the shape selectivity of ZMS-5 zeolite, the further reaction path of bioethanol conversion should result to oligomerisation, isomerization, aromatization and alkalylation of the intermediate products from the former bioethanol dehydration (Viswanadham et al., 2012; Mravec et al., 1985: 335; etc.). According to Mravec et al. (1985:335), the use of ZSM-5 zeolite ever since its early development in the early seventies, has attracted global attention owing to its diverse applications in petrochemicals, and mainly production of gasoline from ethanol or methanol (Rownaghi et al., 2011).

The use of naturally benign catalysts such as clays and zeolites for chemical reactions is an important aspect of the green chemistry crusade. Their obvious benefits generally include low cost, ease of separation, reduced waste generations and environmental friendliness (Petani et al., 2013).

Textual properties and crystal phase composition are the most important data for characterization of a powdered catalyst. These are also tools that can be used to compare the similarity between a commercial and a synthesized catalyst. The case to this work refers to clay-based synthetic zeolite and the commercial zeolite ZSM-5 catalyst.

Catalyst surface area and porosity as the identifying textual properties, followed by the typical XRD pattern of ZSM-5 crystals are presented in the following Table 2.8 and Figure 2.1 (Rowaghi et al., 2011:39; Viswanadham et al.,2012:300 and Widjaya et al., 2012:67).

Table 2.8: The range of surface area and total pore volume to identify for ZSM-5 crystals

ZSM-5	**BET Surface area** (m^2 / g)	**Total pore Volume (Cm^3/ g)**
Nano-ZSM-5	379-461	0.34 – 0.3855
Micro-crystalline or Conventional ZSM-5	301.7 – 330 – 338 - 346	0.1536 – 0.1720 – 0.1763 – 0.18

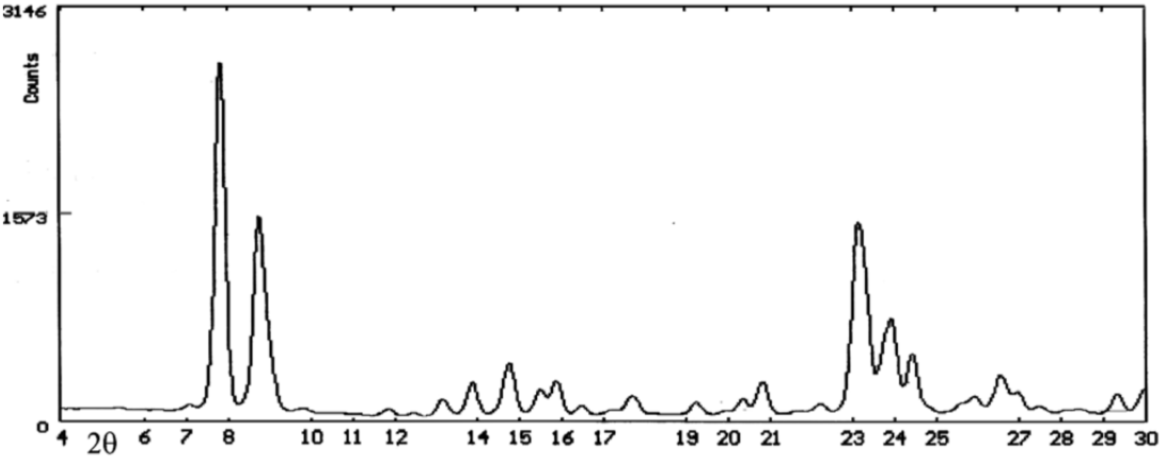


Figure 2.1: The typical powder XRD pattern of ZSM-5 (Khatamian et al., 2008:188)

The XRD pattern of a crystalline (micro or nano) powder catalyst specifically identifies the crystal type of the catalyst and can be regarded as the DNA patterns which uniquely distinguish this particular catalyst sample from any other sample.

2.2.5.3 Zeolite modification for ethanol conversion

Catalytic conversion of ethanol to hydrocarbons products has been an area of interest for several reseachers and contribute largely to the development of petrochemicals production. However the nature, distribution and selectivity of hydrocarbon molecules obtained from the above reaction processes, are influenced by several factors. Chemical and physical properties of the applied catalyst are the most important factors and these have been continually investigated to assess for the catalyst performance. Following, are the reaction operating conditions such as the feed space velocity, temperature and pressure (Rownaghi et al., 2011).

Physical properties of the catalyst includes catalyst crystal size and porosity (Pore size and channel structure) while chemical properties, of catalyst in this work, can be viewed in terms acidity of the catalyst, Si/Al ratio ratio, or any chemical alteration or modification on the catalyst, such as metal incorporation.

A correlation exists between the above properties, the catalytic performance and product distribution or selectivity. A correlation also exists between some of these properties, such as acidity level and Si/Al ratio ratio of the zeolites, catalyst size and chemical incorporation.

However in ethanol conversion to fuel product, the main importance of varying any of the catalyst property is to optimise the yield and a specific selectivity of molecules upon product distribution.

The catalyst properties on ethanol conversion process strongly influence the product distribution. This is discussed below by making reference to various literatures. Preferably, zeolites are the most common catalyst in this regard, while an insight on clay-based materials has also been brought about for catalytic assessment.

(i) Silicon to aluminium ratio of zeolites catalyst (Si/Al ratio)

Si/Al ratio of zeolites catalyst is another textual property that plays a vital role in determining the nature of the product. According to Madeira et al. (2012), the framework Si/Al ratio is related to the acidity of a zeolite catalyst. Viswanadham et al. (2010:301) mentioned this “related” rather as, “Framework Si/Al ratio governs the acidity of a zeolite”. This can be elucidated through the commonly ZSM-5 catalyst.

The ZSM-5 is one of the most promising zeolites catalysts for ethanol conversion and has been reported to have a high Si/Al ratio ratio and high acidic. These are among the properties which make it advantageous in ethanol conversion (Widjaya et al., 2012:65).

However, the acidity of ZSM-5 is tuneable and such situation usually calls when Al^{3+} substitutes for Si^{4+}, this makes the catalyst to be unstable with regards to a required positive charge. To this, adding hydrogen cation is a common approach to keep the catalyst neutrally charged (Lancashire, 1995 - 2013). It is therefore clear that the acidity of a zeolite catalyst is proportional to the Al content. Acidic sites provide active sites for ethanol conversion into higher hydrocarbons. Optimizing the acidity of the catalyst is therefore among the important factors to improve the catalyst stability against coking (Viswanadham et al., 2010: 298).

Furthermore, Si/Al ratio of zeolite can be regarded as a parameter since it can be varied, and this parameter in turn also has impact on the nature of the product from ethanol conversion (Madeira et al., 2012). An investigation was reported by Madeira et al. (2012) on 5 samples of HZSM-5 having 16 to 500 Si/Al ratio ratio, and it was noticed that the one with Si/Al ratio of 40 proved to possess the optimum balance between the acid sites and the amount of radicals and hence, was the most stable and selective catalyst.

(ii) The crystal size and acidity of a zeolite catalyst

The crystal size of the ZSM-5 catalyst is another property of the catalyst which influences product distribution and selectivity. According to various literatures, the crystal size of the catalyst significantly affects the catalyst life time and fuel distribution in the product. This was proven by Viswanadham et al. (2010) whereby a microcrystal zeolite sample was reduced to nanocrystal size of the same acidity and this decrease led to higher yield of gasoline. The nanocrystal size particles had acquired mesopores, and based on this size, they showed long-term catalytic stability (Rownaghi et al., 2011). Nonetheless, mesoporous and small crystalline sample enhances the resistance to coke poising, shortens the diffusion paths of the catalyst; and due to the enhanced and the exposure of the inner surface area of the catalyst, they favour the formation of higher hydrocarbon products (Viswanadham et al., 2010).

In contrast to Si/Al ratio ratio, it was reported that the acidic nature of the sample is not influenced by the decrease in crystal size of the catalyst. However, variation in acidity also has an effect on the yield. In most literature, the basic chemistry of the dehydration of alcohol (ethanol or methanol) yield light olefins as the main product. What can explain the selectivity of this reaction product especially if the reaction is proceeding over a zeolites catalyst?

In this case, the product selectivity is determined based on either the kind of zeolite support used or the acidity level of the zeolite.

If particularly, for instance the zeolite HZSM-5 is used for the whole ethanol conversion process, the acidic level of the catalyst will play a role towards the selectivity of either the olefins or formation of higher hydrocarbons from these olefins (intermediates) in the subsequent reaction path.

According to Viswanadham et al. (2010:303), a strong acidic zeolite is effective for the conversion of ethanol to light olefins and its subsequent transformation to gasoline-range hydrocarbons. Therefore, a strong acidic zeolite is necessary for the oligomerization of olefins to higher hydrocarbons. This produces higher yield of higher hydrocarbons (preferably in the gasoline-range) as compared to a low acidic catalyst of similar size. A low acidic zeolite catalyst therefore, is selectively favourable when considering yielding light olefins (ethylene and propylene) along with low yield of gasoline-range hydrocarbons.

If both properties are favourably varied, that is a reduced crystal size (mesoporous catalyst) and a high acidity of the sample is provided or employed simultaneously, tthe possibility of synergetic effect in catalyst activity could be observed.

The pore structure of zeolites is another property which would crucially impacts on product distribution upon ethanol conversion. The ZSM-5 has two types of pores, both formed by 10-membered medium oxygen rings (Petani et al., 2013). However, variation of this rings to 8-membered ring small-pores has influence on product distribution and this has proven variation on product yield from aromatics-rich hydrocarbons to mainly light olefins product (Hoang et al., 2010:5.77).

Clay modification in this work, is made in reference to modification to zeolite catalyst as above. However for clay sample, physical property of particle size or size range will be kept constant. Acidity of various clay samples may differ since these are obtained from difference sources and therefore are likely to have difference Si/Al ratio. Porosity (Pore size and channel structure) of clays is generic for most clay types and this is the reason why all clays are represented in one general structure as indicated in Figure 2.2.

(iii) Clay and zeolite structure

As mentioned earlier, clays consist of assemblies of tetrahedral layers of silicate units and octahedral layers of aluminate units (Igbokwe et al., 2011). Silicate units, consist of silicon-oxygen tetrahedral groups which are linked by sharing three of every four oxygen atoms so as to form sheets of indefinite extent (silicates sheet).
Tetrahedral sheets on the other hand, consist of O_2 and OH^- which are linked by sharing every four oxygen atoms so as to form sheets of indefinite extent, known as the aluminate sheet (Emam, 2013). Depending on the clay type, Tetrahedral sheet is usually linked through oxygen atoms to one octahedral sheet.

Zeolites on the other hands, are constructed of tetrahedral AlO_4^{-5} and SiO_4^{-4} molecules bound by oxygen atoms, with cation tightly held in the porous structure (Petani et al., 2013).

The general (sheets) structure of clay and general zeolites structure are shown in Figure 2.2.

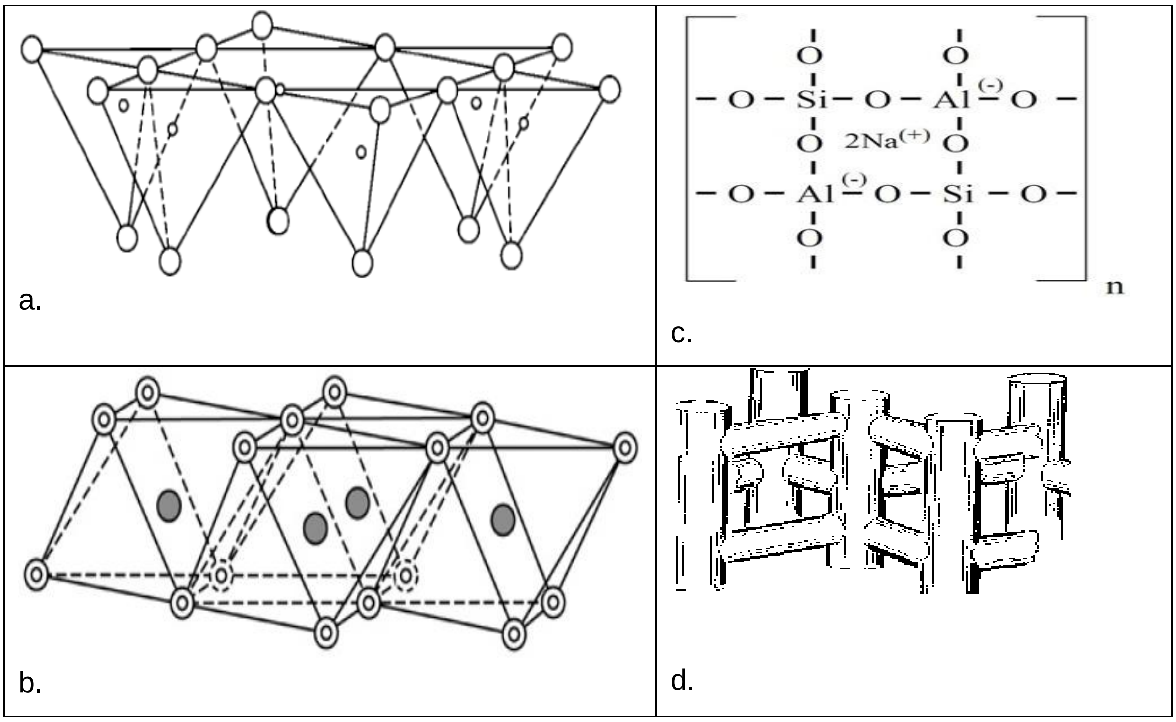


Figure 2.2: General structure of clay and zeolites

a.Tetrahedral and **b.** Octahedral sheet

c. Basic structure of a zeolite with Na^+ ion tightly held in the porous structure (Chemical engineering tools and information, 2011 & Marcus et al., 1990).

d. Microporous structure of zeolite (Lancashire, 2013)

(iv) Clay and zeolite surface area and acidity

Clay materials have low surface area in comparison to zeolite. This further on explain the reason why they also have low acidty than zeolites, because the number of exposed acid sites decreases with decreasing specific surface area (Refaat, 2010:208).

Table 2.9: Comparison of catalytic properties of clays and zeolite for the conversion of ethanol (Eman, 2013; Mezni et al., 2011)

Catalyst	**Chemical composition and formula**	**Geometry** (types) **of the Structure** (Framework)	**Chemical Properties**				
			Surface area Specific BET (m^2 / g**)**	**Acidity**	**SiO_2/Al_2O_3 And Si/Al for Zeolite**	**CEC (**meq/g**)**	**Thermostability**
Bentonite	Hydrous magnesium-calcium-sodium aluminum silicate	Two silica tetrahedral sheets (chains) with a central octahedral sheet structure (2:1 layer mineral)	Relatively very high than other clays, 79.4 m^2/gr (Widjaya et al., 2012:67)	-	-	Generally ranges between 0.80-1.1 meq/g (Eman, 2013:363;Yahiao et al., 2003:550)	-
Kaolin	Silica, alumina, iron (oxide) and titanium (oxide), quartz, mica, water etc.. : $Al_2Si_2O_5(OH)_4$	One tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina Octahedral (1:1 layer mineral)	Low (Relatively). 96. 1 m^2 / g for Natural illite containing 26 % Kaolinite (Mezni et al., 2011:216 & 211).	-	± 2 (Watawong et al.,2003)	Low base exchange capacity (Eman, 2013:360). CEC ≈ 1.243×10^{-4} meq/g (Watawong et al., 2003).	Low. Improves when in a matrix with zeolite (Eman, 2013:361)
Natural illite	-	-	96.1 m^2 / g containing 26 % of kaolinite (Mezni et al.,2011:216 &211)	-	3343 (Mezni et al., 2011)	0.186 meq/g	-
Talc	Hydrated magnesium silicate: $Mg_3Si_4O_{10}(OH)_2$.	(2:1 layer mineral)	-	-		-	-

Catalyst	**Chemical composition and formula**	**Geometry** (types) **of the Structure** (Framework)	**Chemical Properties**			
			Surface area Specific BET (m^2 / g**)**	**Acidity**	**SiO_2 / Al_2O_3 And Si/Al ratio for Zeolite**	**CEC (**meq/g**) and Thermostability (T)**
Sepiolite	Magnesium silicate: $Mg_4Si_6O_{15}(OH)_2·6H_2O$	Double silica tetrahedral chains linked together by octahedral O_2 and OH^- groups containing Mg ions in a chainlike inverted.structure.	-	From very low surface acidity to no acidity	± 2	0.07 meq/g (Very low to almost no CEC) – (Gruver et al., 1995:359). (T) Poor.
Zeolites, ZSM-5	Hydrated aluminosilicate, containing alkali or alkaline earth cations: $Na_nAl_nSi_{96n}O_{192}·16H_2O$ $(0<n<27)$	Three dimensional porous structure (Framework).	High, 301.7-346 range (Micro particle size) and 379-461 (Nanosize particle).	Varies, however usually high.	Si/Al ratio ≈ variable, however minimum is 5 and between 30-40 for appropriate conversion of ethanol (Viswanadham et al., 2012).	CEC (–) (T) – High. Generally 1000 ºC for zeolites (Guo et al., 2011:341)
Zeolite X	-	-	-	-	-	3.42 meq/g at Si/Al ratio of 2 (Mezni et al., 2011).

2.2.6 Promotion of clay-based and zeolite catalysts by metal elements

Promotion of clay-based catalyst entails a physical or chemical phenomenon to enhace the catalyst activity in adding an active element to the catalyst. Catalysts promotion is very quite applicable to any catalytic system and is an important aspect to assess for optimisizing the performance of the catalyst.

Promotion of clay-based catalysts is mainly targeted for activity enhacement which ties up to changes in certain catalytic properties of clays, mainly surface properties. Depending on the method of promotion however, promotion may not (Hypothesis) only enhance the catalytic activity, it may simultaneously impact on catalyst stability and selectivity (Machado et al., 2006).

Like acid activation of a clay sample , certain promotion techniques are accounted for surface charge generated on surface of clay particles.

The breakage of bonds at the edges of clay layers is alternative to the surface charge generation on clay particles (Heckroodt, 1991). This can be caused by the interaction or pillarisation of a metal element in the clay structure prior to promotion approach.

Ionization of the surface layers of clay by the active metal element (other than hydrogen ion); and specific adsorption of active ion or polyions of the metal element on the surface of clay particles.

Moreover, surface charge through promotion can be generated or altered by mechanisms which in general bring out the unbalanced charge of structural elements in clay (either Al^{3+} or Si^{4+} or Magnesium in some cases) as a result to substitution of a high dense charged ion of an element (Heckroodt, 1991:345). For example, Corma *et al.(*1984) in his work reported that when the trivalent cation of aluminium ions,substitute for Magnesium ion in the octahedral sheet of sepiolite clay, as in montmorillonite (Morita *et al.,* 1972; De Boer *et al.,* 1967), a medium and strong acidity is generated on the surface of the clay minerals. As a result, the (sepiolite) clay becomes an active catalyst for the conversion of ethanol, with a reaction pathway and kinetics characteristic of a strong acid.

Modification of zeolite catalysts by addition of active metal elements, as anticipated for clay-based catalyst, is a reliable promotion with regards to the conversion of ethanol (Calsavara et al., 2007; Inaba et al., 2005; Machado et al., 2005). The structure, the composition of the clay and the extent to which they interact with a metal support may influence the catalytic activity.

Therefore, unlike activity enhacement of clay catalysts by acid or other active elements, the promotion of clay-based catalysts in this work is only channeled to the incorporation of only active metal elements, such as iron (Fe), Copper (Cu), Cromium (Cr), Cobalt (Co), Lead (Pd), silver (Ag), Gold (Au) and Magnesium (Inaba et al., 2005:136).

From the above, Gold followed by silver, Iron, Nickel, Cobalt , Chromium and then Cupper metal, were reported to be the order of increasing catalytic activity when impregnated over the H-ZSM-5 zeolite catalyst at similar reaction conditions (i.e. temperature 400 ^{0}C). Magnesium in contrast, and hence representative for Alkali earth metals, was reported to suppress the conversion of ethanol , making the promotion of clay in this work to mostly apply or rely on transition metals for a more effective conversion of bioethanol. The selection for transition metals for the promotion of clay-based catalyst in this work , will consider the activity, the availability and the cost to obtain the metals.

Iron is a common and well-known active catalyst and catalyst support in several applications. In petroleum synthesis, iron catalyst is historical known for its potential catalytic application for hydrocarbons production from syngas by the Fisher-Tropsch-Process (Machado et al., 2006:193). Machado et al. (2006:193) reports on the use of iron for the modification of ZSM-5 by different methods which in turn had led to several applications of the latter (Machado et al., 2006:193). Such applications include benzene oxidation to phenol, ethane aromatization and the related and concerned conversion of ethanol to hydrocarbons (Macado et al., 2005:2064). The HZSM-5 modified with iron (iron-inpregnated into H-ZSM-5) shows a relatively higher conversion of ethanol to hydrocarbons as compare to other metal elements (except silver), leading to formation of higher olefins (C_3^+) in the gasoline range. (Inaba et al., 2005:138). Unlike Silver, Iron is an abundant element and can easily be obtained, is cheap and is a non-toxic metal (Machado et al., 2005).

Metal promotion of Chromium in bentonite clay enhances the catalytic activity of the clay catalyst in the conversion of ethanol (Widjaya et al., 2010:65). This is as a result to increased surface area, acidic sites and porosity on the promoted clay sample compared to natural clay in the non-promoted state. The increase in the specific surface area is caused by the Cr-pillar interaction in bentonite. As a matter of fact, the increased acidity of the clay sample exhibits higher acidity than acid activated bentonite clay and than the H-ZSM-5 catalyst (Widjaya et al. 2010:67) . Morever, bentonite clay supported over chromium shows high resistant to a lot of moisture content, which usually comes in ethanol feed and contribute / lead to faster deactivation of catalyst (Widjaya et al.,2012)

Zinc may be the additional metal for promotion in this work owing to the fact that no work, except the commonly above metals, has been reported on Zinc promotion to zeolite.

Metal containing iron are particular attractive and iron containing zeolites have specifically been applied as heterogeneous catalysts in petrochemical production. However, majority of zeolites used in the field of petrochemical engineering are employed for ethanol conversion to hydrocarbons products (Madeira et al., 2010; Inaba et al., 2006).

2.2.6.1 Methods of catalyst promotion by metal element (s)

There are various methods of metal incorporation into solid catalysts. The most commonly which have led to broad applications of zeolite as partuclarly in the conversion of ethanol, include direct synthesis (Machado et al., 2006), ion exchange and the impregnation method (Machado et al., 2005).

Direct synthesis is more of physical phenomemon whereby the metal species is directly placed into the framework of the precatalyst (Kim et al., 2013:268). This method conveniently applies in adding the active metal element during the synthetic course of the precatalyst, as it would be during the synthesis of zeolite, adding the active metal to the silica gel prior to hydrothermal reaction. This method may not be convenient for clay catalysts since most clays in their natural state often contain metal elements and there may rather be need for modiciation, other than preparation.

Impregnation is one of the main methods used to prepare supported catalysts. It is a aqueous method in which the solution of the precatalyst is contacted with a solid support for as long as the volume of solution either equals or is less than the pore volume of the support (James, 1994:495). The resulting material is then activated under conditions that will convert the precatalyst to a more active state (Shwarz et al., 1994). This promotion method is oftenly applicable to metal salt and the catalyst support is usually in the pellets form. A support is also refered as the surface on which the precatalyst is spread to increase the surface area and more often these two may or may not interact, leading to enhanced catalytic performance. Moreover, catalyst supports in petrohydrocarbons-based reaction hinders the formation and deposition of coke, to exposing more surface area and making the catalyst to have a higher specific activity (per gram) on a support (Eman, 2013). Metal supports over clay-based catalysts are refered to in this work.

In this work, promototion by ion exchange method entails the exchange of ions between an electrolyte solution and a complex. This method lines up or agrees to the ion exchange ability of clays, as well as zeolites. In fact, clays are cation exchangers as they contain either Mg^+ or Al^+ or Si^{4+} which can be substituted or exchanged with external ion in the electrolyte solution.

Promotion by ion exchange is relatively simple and is the most common approach for metal incorporation into zeolite catalysts (Machado et al. 2005). As a matter of fact, one of the major advantages of employing zeolites in petrochemical production is due their outstanding ion exchange capacity (Kin et al., 2013:267). Accordingly, promotion of zeolite by ion exchange method compensate for high charged ions in exchange of sodium ions in zeolite, commonly such as iron and oxide of other transition metal elements or group VIII metals.

For example, incorporation of iron metal into zeolite by ion exchange only require low content of this metal to exhibit better result in the conversion of bioethanol. This method exgibited the best result, yet with the lowest iron content than the other methods of impregnation or direct synthesis (Machado et al., 2005: 2069 and Calsavara et al., 2008:1635).

In addition, Leet at al. (2009:) reported that the kinds and quantities of ion-exchanged cations and Si/Al ratio control the acid-base properties of zeolites. Ion exchange with alkali metal ions and the impregnation of basic components on the inner surface of the zeolite pores are the two general approaches for control of the basicity of zeolite. The former approach produces relatively weak basic sites and the latter strong basic sites (Lee., 2009). As a matter of fact, several researchers (Refaat, 2010:2008) have reported that alkali and alkali earth metals or their oxides are basic materials and therefore their incorporation or presence into solid catalysts such as zeolite, generally promotes the basicity of such catalysts (Lee at al., 2009:69).

Impregnation also modifies the acidity due to varying dispersion and interaction with the clay surface and contributes to conversion and selectivity.

For clay catalyst however, (such) metal promotion (of high dense) by ion exchange may not be an effective method because clays generally, comparable to zeolites , as reported by several reporters and as shown in Table 2.9, have lower ion exchange capacity (Gruver et al., 1995:359; Watawong et al., 2003 & Eman, 2013:363). In contrast to clays, zeolite with lower ratio of SiO_2 / Al_2O_3 favours ion exchange processes and have high Cation Exchange Capacity, so it is vice-versa (Schwarz et al., 1994:488).

Emam (2013:364) in his work revealed that impregnation method is complimentary to both the recipient catalyst and incipient metal element. He made reference to nickel supplying hydrogenation function to support the cracking function caused by recipient acid or acid-modified clays. Impregnation method therefore is alternative to iron exchange and for clay catalysts in reference to zeolites (Inaba et al., 2005), this can be favourably considered using Iron, Nickel and Chromium support onto clay. A comparable promotion using iron and other transition metals could therefore be carried out in this work to investigate the effect each has on the conversion of bioethanol.

2.2.7 Catalyst activity, stability and selectivity

The suitability of a catalyst in reaction processes mainly depends on the activity, selectivity and stability of the catalyst (Hagen, 2006). These may be regarded as the basic factors to assess for the catalytic performance of a catalyst and are therefore dependent on the nature and properties of a catalyst. The modern industries' prefered order/sequence of the above factors in favour of optimisation is activity, stability and then selectivity (Activity > Stability > Selectivity).

Catalyst selectivity involves obtaining different products from a given or similar starting compound by using different catalyst system . This allows many reaserchers on making choice or design appropriate catalysts for the product of interest. For example, the use of ZSM-5 zeolite among other zeolites or active catalysts on ethanol conversion, is popular due that fact that the ZSM-5 is highly selective to gasoline-range hydrocarbons (Rownhagi et al, 2011). Selectivity in this case is therefore driven or dependent on the property of the catalyst, such as shape selectivity and microporosity of the ZSM-5 in the above (Guo et al., 2011). Product distribution from a reaction is a function of selectivity and the latter can also be dependent on the operating conditions under which the catalyst is subjected to in the reaction. For example, Inaba et al. (2005:137) from his work reported that zeolite catalysts at reaction temperature of far below 400 ^{o}C, was exclusively selective to diethyl ether. With increase in temperature to 400 ^{0}C, the selectivity shifted to ethylene while at reaction temperature above 400 °C, the catalytic system became dominantly selective to higher hydrocarbons molecules, of course with the decreasing selectivity of ethylene and diethyl ether. Selectivity therefore, is dependent on the catalytic properties, the type of catalyst, as well as the catalytic operating conditions.

Catalyst activity is a measure of the reaction rate in the presence of the catalyst.
This as well, is generally dependent on the catalytic properties and may as well be dependent on the operating conditions. Modifying clays with acid or promotion of either clay or zeolite catalyst have so far been observed as the most common approaches for activity enhacement with regard to ethanol conversion. For example, Corma et al. (1987:423) reported that a non-acidic natural sepiolite clay was found to have a very low catalytic activity. However, upon promoting the clay with aluminium ion, the sample became acidic and its catalytic activity on ethanol dehydration, was enhanced.

Catalyst activity is a function of time and in actual practise, a catalyst undergoes chemical changes thereof. These changes subject to decrease in activity of the catalyst, which is refered as catalyst deactivation (Wilczura-Wachnik, 2006:3). Similarly , catalyst stability in a continuous process such as in this work, is a direct correlation to catalyst lifetime. Catalytic activity can also be an indirect indication of selectivity in cases where the selectivity of a certain molecule in the reaction product depends on the overall activity of the process. As a mater of fact , both stability and selectivity are measured as a function of time (Wilczura-Wachnik, 2006:4) .

The best and alterantive approach to account for activity and stability of clay or zeolite in this work, is by identifying factors that lead to deactivation of these given catalysts. Hence, the activity and stability of a catalyst can be favoured by suppressing the effects from these factors. However, many researchres have identified some of these factors which hinders the activity and stability of zeolite and clay catalysts in ethanol conversion processes. These includes the purity of ethanol feed (Widjaya et al., 2012), coke or metal deposition and poisoning on the catalyst during the conversion of ethanol (Eman, 2013:356), decrease in activity or selectivity as a function of time, as well as reaction temperature (Inaba et al., 2005).

Catalyst stability are aspects attached to catalyst lifetime in the reactor. These can be viewed in terms of chemical, thermal and mechanical stability of a catalyst.The total catalyst lifetime is of crucial importance for the economics of a technological process.

Clay materials oftently have lower thermal stability than zeolite. In contrast, Eman (2013) reported that kaolin clay in a matrix with zeolite lead to high thermal stability , reduces coke yield and improves attrition resistance. Gruver et al. (1995:359) also reported on the increase in thermal stability of sepiolite clay by alumination and suggested that this could further improve if sepiolite clay is subjected to an alkaline treatment with $KAlO_2$.

Information regarding the activity, selectivity and activation or deactivation of the individual catalyst is highly desirable for optimizing the performance of a catalytic system (Hagen, 2006).

2.2.7.1 Thermal modification and stability of clays

Clays are porous crystalline material and in their very nature, they contain a minimal amount of water between their structural sheets. It has been reported however that the amount of water between these sheets hugely influences the acidity of clay minerals (Musyika et et al., 2003:548), while also considering that most clays generally have acidic nature which can be accounted for by both the Lewis and Bronstead acid sites they contain.

Thermal subjection on a clay mineral, refered as “thermal treatment”, has been observed and reported as a mean of obtaining clay catalysts with different acidities (Eman, 2013:362). This approach can be adopted for the development of valuable clay-based catalyst.

A 100 ^oC thermal subjection on a typical clay such as montmorrilonite (bentonite), can correspond to the drying operation at 105 ^oC whereby water is removed from the inner structure, altering the acidity of the clay sample to a markedly increase in Bronstead acidity at this temperature.

An increased temperature to between 200 - 300 ^oC on clay, has been reported to subject clay to partial dehydroxilation and this simultaneously lead to collapse or deterioration of the interlayer structure of the clay (Eman, 2013:362), resulting to decrease in Bronstead acidity and increase in Lewis acidity of clay (Yahiaoui et al., 2003:549). A temperature of 400 ^oC and above however, result to complete dehydroxylation and structural deterioration , forming a completely amorphous solid and increasingly generating and retaining Lewis acidity. This temperature range is equivalent to the most commonly calcination temperature range for catalyst prior to certain catalytic reactions (Emam, 2013). Prior to clay activity test, the only heat subjection to account for could therefore be that which is required to raise the temperature of the catalyst bed to be equal to that of the furnace. If high enough, then this could also be regarded as calcination temperature.

Various reporters (Silva et al., 2013:85; Chantawong et al., 2003) have reported on thermal subjection on clay in the temperature range of between 700 ºC and 900 ºC, serving for pretreatment and thermal activation of clay (typically kaolin) by calcination to form a metaphase state of the clay specie – For example Kaolin to form metakaolin.

Calcination of clay has thereby been reported for zeolite synthesis from clay in this manner and also so as to activate the commonly precursor in clays, alumina and silica and lewis acidity required for futher transformation or polymerization of ethanol during the conversion.

Zeolite have relatively higher thermal stability, 1000 ºC being reported by Guo et al. (2011:341). Zeolite therefore, are much more convenient for calcination or thermal treatment prior to a catalytic reaction test with the advantage that such thermal subjection enhances their catalytic activity in the conversion of ethanol (Widjaya et al., 2012).

2.2.7.2 Catalyst protonation and activation

The amount and distribution of acid sites of a catalyst are responsible for both conversion and product distribution. Hence, the protonation degree, as observed for most zeolite or zeolite-based catalysts, has effects on catalyst performance. To this end, Arcoya et al. (1990) reported that the stability of a zeolite catalysts are related to the protonation degree of the samples. Catalyst protonation, therefore, is required to generate the protonic form of zeolite. Most commonly, protonation is required for zeolite catalysts for their application in the conversion of ethanol.

Various substances can be used to protonate a ZSM-5 (zeolite) catalyst, among which ammonium chloride and ammonium nitrate are commonly used (Van Den Berg, 1981:11). Any other protonic (H^+) containing substance can also serve for this purpose, and preferably bi-compound containing ammonium ions. Thereby, Ammonium chloride is the most common susbstance for this purpose. This will be mixed with zeolite and reacted at high temperature under atmoshperic conditions, to obtain the H-form of zeolite. Moreno-Piraján et al. (2010) achieved a suitable ZSM-5 protonation outcome at the temperature of 550 ºC and 12 hours heating time. Hence, more or less the same conditions are adopted in this work.

Hence, catalyst protonation in most ethanol or methanol conversion processes over zeolite-based catalysts is usually followed by catalyst activation with a certain inert gas prior to the immediate subsequent catalytic test . Nitrogen gas is the most common used for this purpose. If the ethanol fed to the reactor is at gaseous phase, nitrogen would serve as the

carrier gas or gas medium to ethnaol towards the catalyst. Liquid ethanol feed however, will rather be contacted as most commonly in situ (By means of a pumping device) on the homogenous catalyst for certain period of time. Hoang et al. (2010) reported one hour contact. Further on, the catalyst activation should be carried out at the same operating conditions (mainly temperature and pressure) as the actual subsequent catalytic test.
Helium gas is also known for the above purpose, Hoang et al. (2012:5.79) stated that it leads to an improved catalytic stability as compared to Nitrogen gas.

In overall, the purpose of activating (also referred as pre treating) a catalyst (with nitrogen) is to desorb any potential pollutants before its catalytic use (Hoang et al., 2010). Generally, this treatment is applicable to zeolite-based catalysts and can also be test for clay-based catalysts in this work.

2.3 Catalytic conversion of ethanol to hydrocarbon fuels over clay-based catalysts

Catalytic conversion of synthetic fuels to hydrocarbons is famous and has been on popular pursue by many researchers. Ethanol is among the most popular and potential fuel studied for the above purpose and focus has been directed towards its application (Inaba et al., 2006). Other synthetic fuels include methanol, glycerol and most importantly those that simultaneously are derivative of biomass sources. Ethanol again earns this advantage to be obtained from biomass , its has environmental and economic benefit.

2.3.1 Ethanol conversion over clay-based catalysts

Clays or modified clay catalysts are used in petroleum cracking processes, as well as in processes such as isomerisation, alkylation, hydrogenation, hydrocracking, including other petroleum refining processes. One of their most prominent application is in petroleum cracking process, where they serve as core-catalysts or catalyst aid (Eman, 2013:360).

Cracking of petroleum is a common term which entails breaking down complex (mixture of) hydrocarbons into smaller hydrocarbon molecules. Example of application of catalytic cracking using clay-based catalysts was reported by Manos et al. (2001), whereby polyethylene was converted to various and relatively non-complex hydrocarbons. Further on to the above, clays were compared to zeolites for their catalytic cracking application (Manos et al., 2001:2220-4). The example above serves to indicate the promising application of clay-based catalysts in the conversion of ethanol, in reference to predominant zeolite catalysts for the purpose.

Further on it was deduced from Manos et al. (2001:2224) that clays can effectively be made active for cracking process provided the acidity of the catalyst is strengthen to enable high ocurrence of hydrogen transfer reactions . This goes in agreement with Eman (2013: 360), indicating that clay-based catalysts are applicable for hydrogenation reaction in petroleum cracking, and could similarly be applied in other fuel production reactions where hydrogenation is or may be required.

Clay-based catalysts can as well be used for processes that are reversal to cracking of hydrocarbons. For example, Figure 2.3 depicts a proposed mechanism for catalytic hydrocracking of a complex aromatic hydrocarbon at the given conditions, resulting to saturated and lighter hydrocarbon products.

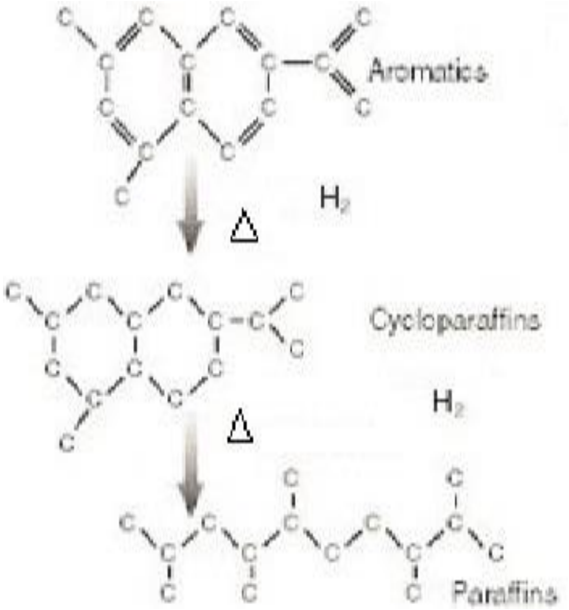


Figure 2.3: Hydrocracking reaction mechanism (Eman, 2013).

Assume the above reaction is reversed and ethanol is used as the starting material to be transformed to the heavy complex aromatic hydrocarbons. The reverse reaction will then be referred to as cyclization and aromatization; can be attained by the core ability of zeolite catalysts in ethanol conversion (Viswanadham, 301-302). In the same manner, this reverse operation can as well be promising for a clay-based catalyst in the transformation of ethanol.

In many literature, olefins (more particularly ethylene) is observed as the most common hydrocarbon product obtained through the transformation of petroleum or biomass-based feedstock over clay-based catalysts (Manos et al., 2001:2224; Gruver, 1995: 361; Corma et al., 1987:425). Ethylene similarly, is main product to ethanol catalytic dehydration (≥180 ^{o}C) and monomer to polyethylene. The above serves for evidence that clay-based catalysts, in agreement to Eman et al.(2013:360), can be used for ethylation, isomerisation or polymerization reactions.

Clay-based catalysts (Clay or modified-clay catalysts) are therefore suitable catalysts for the conversion of bioethanol to various hydrocarbons, with the advantage that they have additional wide applications (catalysts or catalyst supports) huge importance in petroleum processes – Particular the ones discused above, including many others (Like Alkylation processes, reforming etc.).

The catalytic potential of clay-based catalysts in aromatics cracking processes (such as depicted in Figure 2.3), serves as indication for their effectiveness in the transformation of ethanol. Likewise, the potential of clay-based catalysts for processes such as isomerisation in petroleum production, makes this capacity promising in the conversion of ethanol.

The chemical reaction of bioethanol (starting material) over clay or clay-based catalyst in the presence of heat, is illustrated in Figure 2.4.

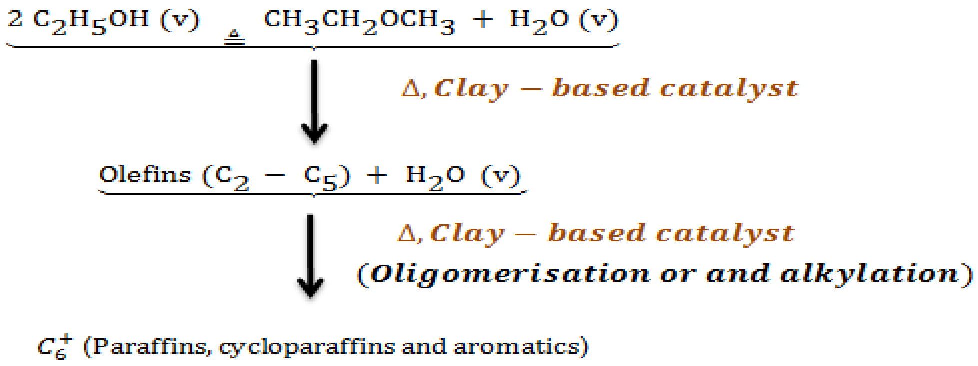


Figure 2.4: Chemical illustrative of bioethanol conversion over clay-based catalyst (Viswanadham et al., 2012; Gruver 1995; Cormal et al., 1987).

Ethylene as observed in literature (Gruver, 1995: 361; Corma et al., 1987:425; etc.) is a very commonly produced hydrocarbon from the ethanol conversion reactions over several clay-based catalysts. Ethylene as the main olefin product, is as famous in petroleum cracking reactions (Rahimi et al., 2011:1-3). Nonetheless, ethylene has been observed in various studies to be the intermediate product from ethanol multi-step conversion or dispropotionation to hydrocarbons (Viswanadham et al., 2012:301 & Inaba et al., 2005:138 & 141).

It is also deduced from Corma et al.(1987:426) and Dandy et al.(1982) that butadiene in propotional amount with ethylene, are the anticipated product from the conversion of ethanol over natural clays or modified clay catalysts. Similarly, acetaldehyde in proportional amount with ethylene or diethyl ether as product, is also reported by Gruver (1995: 361) and Corma et al. (1987:425) from the above-mentioned reaction.

Sepiolite and modified sepiolite clay in particular, is the clay-based catalyst over which the above products were obtained. Sepiolite is therefore made referenced to other clay-based catalysts due the fact that typically sepilotie clay has comparable properties (such as basic constituents) as those of other clay types (Corma et al., 1987:424).

Additional hydrocarbons such as ketone could also be observed by reacting ethanol over sepiolite-based catalyst, as this could similarly apply in using certain other clay catalysts. Depending on the reaction conditions, the possible occurrence of Prins reaction may further lead to the production of butadiene from the above (Gruver et al., 1995).

Higher selectivity to diethyl ether, along with ethylene and water identified in product have been however generally identified for low reaction temperature (200 – 280 ºC) when reacting ethanol over either clay, zeolite-based or several other solid catalysts (Corma et al; 1987:423; Inaba et al., 2005:141; etc.). Branched-chain paraffins were are also the identified product from a clay based catalyst, this being bentonite promoted with Cr (Widjaya et al., 2012: 69).

The detail of the most common anticipated products from the conversion of ethanol over clay-based catalysts, is further summarised in Table 2.10.

2.3.2 Conversion of ethanol over non-clay catalysts

The common conversion of ethanol to hydrocarbons is by catalytic dehydration, of which homogenous acidic catalysts were predominant known for this puporse (Such as sulphuric and phosphoric acid). Reacting ethanol in the above reaction to a temperature of about 140 ^{0}C would lead to production of diethyl ether. This similar reaction at 180 ºC, whould result to high yield of ethylene and water vapour shown below (Chematur Engineering Group, 2012).

$$C_2H_5OH_{\,(l)} \xrightarrow{\Delta,\ acid\ catalyst\ -\ e.g\ H_2SO_4} C_2H_{4\,(l)} + H_2O_{\,(v)}$$

The above reaction can be furthered to produce heavier and higher value hydrocarbons, provided that a suitable catalytic system (Catalyst and operating conditions) is employed. Heterogeneous catalysts, unlike the homogenous as employed in the above conventional dehydration of alcohol, have been introduced because of their wider availability, relative ease application, regeneration and separation from the reaction mixture. This further entails that hetrogenous catalysts are recyclable (reusable) and have better compliance to green chemistry when used for biofuel production. As a result, the use of heterogenous catalysts for the conversion of bioethanol is , by overall, more cost-effective.

Zeolite catalysts are high acidic materials and this is one of the important property that enhances their catalytic performance in the conversion of ethanol (Sivasamy et al., 2009). This property is among those in common to clay materials for the above similar purpose.

Widjaya et al (2012:66) and Hoang et al. (2010:5.77) reported that the conversion of ethanol over zeolite catalyst, occurs in three main steps. The first step (Step 1) includes alcohol dehydration to light alkyl ether at low temperature (e.g methyl-ethyl ether and lilltle proportion ketone and acetone oxygenates); the second step (Step 2) is subsequent to further dehydration of the latter products to light olefins by the increase in temperature and in the third step (step 3), the letter olefins are oligomerised and aromatised (through hydrogen transfer) to relatively heavier hydrocarbons, such as gasoline-range hydrocarbons.

Several reporters (Viswanadham et al., 2012: 301; Rownaghi et al., 2011 & Inaba et al., 2006:141) illustrate the above reaction path as follows:

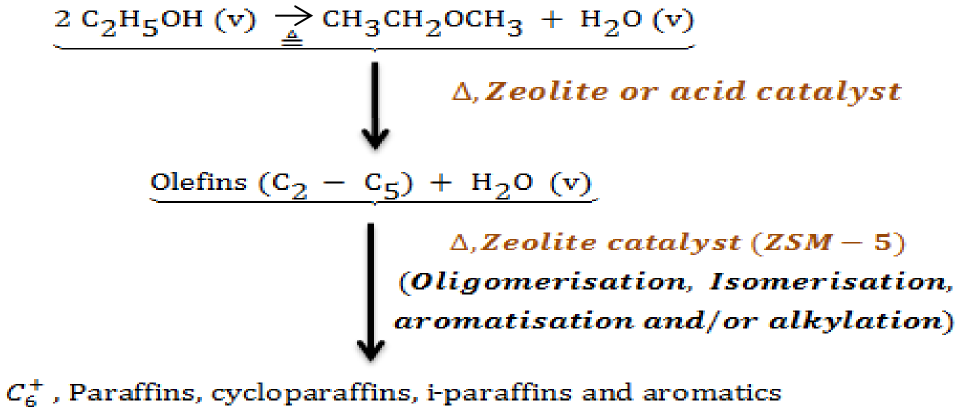


Figure 2.5: Chemical illustrative of ethanol conversion over zeolite catalyst (Rownaghi et al., 2011; Hoang et al., 2010)

Most reactions of ethanol conversion over zeolite catalytic system subjected to low temperature range (Often classified as below 400 °C), are exclusively selective to alkyl ether (or any other oxygenates) – reference step 1 above. These have as well been observed to result to low conversion of ethanol (Gruver 1995: 361). In contrast to the above, selectivity of diethyl ether decreases with relative increase in reaction temperature (In reference to step

2 mentioned earlier). This simultaneously is reported to have favoured the formation of olefins and resulted to high conversion of ethanol (Inaba et al., 2005:137).

The product obtained in completion of the above reaction consists of light petroleum gases and a liquid mixture of gasoline-range hydrocarbons. Gasoline-range hydrocarbons of carbon range between C_6 - C_{10} (Prefered range) consists mainly of heavy olefins (denoted as C_3^+ or C_6^+) , higher paraffins and various aromatics compounds (Hoang et al., 2010:5.77). Olefins in general are popularly known for their applications as chemicals and fuels derivatives; such as ethylene the principal building block or raw material in the manufacturing various form of polymers (ICIS, 2007) .

Gasoline is commonly known and reported as the final mixture of paraffins and aromatics (Peteni et al., 2013 & Lancashire, 2013). According to Viswanadham et al. (2012:303-4) , the composition required for a gasoline mixture for fuel applications include high concentration of xylene and toluene, with a low concentration of benzene, paraffins (such as isodecane) and other hydrocarbons. The above selectivity can be attained through investigation of appropriate catalyst properties and reaction conditions

Table 2.11 summarises the anticipated products to obtain (reflective to literature) when reacting ethanol over zeolites and clay-based catalysts (As reference to this work).

Table 2.10: Product distribution of ethanol conversion from different researchers (Widjaya et al., 2012; Inaba et al., 2005; Corma et al.,1987)

Feedstock	Catalyst	Operating condition	Product detected		Source
			Major	Minor / Small amount	
Ethanol	Solid catalysts (Zeolite or clay-based catalyst)	Low reaction temperatures (200 – 280 ^{0}C)	Diethyl ether,	Ethylene and water	Inaba et al., 2005:136
Ethanol	Cr/ Bentonite		Butanol; (iso)hexanol	Undecane; Dodecane.	Widjaya et al., 2012:69
Ethanol	Al^{3+} exchanged sepiolite (Sep-Al)	Relatively low reaction temperatures	Diethyl ether.	Ethylene	Corma et al. (1987:425)
		≥ 400 ^{0}C reaction temperatures	Diethyl ether, water, ethylene	Acetaldehyde (Very small amount)	
Ethanol	Natural sepiolite	300 ^{0}C	Butadiene	Ethylene (small amount)	Corma et al. (1987:426); Dandy & Nadiye-Tabbiruka (1982)
Ethanol	Aluminated sepiolite	280 and 50 torr	Lower yield - Diethyl ether & Ethylene	Acetaldehyde, Butadiene.	Gruver (1995: 361)
Ethanol	Silver exchanged aluminated sepiolite (Sep-KAlO$_2$)- Ag	280 and 50 torr	Acetaldehyde	Diethyl ether, Butadiene	Gruver (1995:361)
Ethanol	HZSM-5 (29)	400 ^{0}C	BTX; olefins (C^{3+});	Paraffins; ethylene and diethyl ether.	Inaba et al., 2005: 136 & 138
	Iron-modified ZSM-5		**Organic phase/fraction –** BTX; **gaseous product –** Ethylene, propene, propane and C$_4$ and C$_5$ of both olefins and paraffins		Hoang et al., 2010
Glycerol	HZSM-22	300-400 ^{0}C	**Aqueous phase** - Oxygenates (Propenal, acetol, acetalhyde and heavy oxygenates) and water		Hoang et al., 2010
Glycerol	HY or HZSM-5		**Aromatics** phase - Alkyl-aromatics		Hoang et al., 2010

2.3.3 The effect of operating conditions on ethanol conversion

Operating conditions are process parameters which also influence product distribution and selectivity of ethanol conversion reaction. Investigation of these parameters is as important so as to assess their synergetic effect with the catalyst. Many literature (Inaba et al., 2006; Viswanadham et al., 2012) have reported on the effect of several operating conditions in the conversion of ethanol over zeolite, as well as clay or clay-based catalysts. The operating conditions referred to are catalyst concentration, reactor type, pressure; and primarily operating temperature and reaction time in reference to this work. Investigation of the operating conditions can also contribute towards the obtainment of optimum catalytic system.

From the initial application of ZSM-5 during the energy crisis, the optimum and first operating conditions for ethanol transformation to hydrocarbons was 371 ^oC, 1 hour reaction time and under atmospheric pressure (Chang et al., 2011).

However with development in reaserch, on the ZSM-5, any temperature range below 400 ^oC such as the commonly range of between 340 - 371 ^oC, can be regarded relatively low temperature and starting from 400 ^oC upwards, can be relatively regarded as high temperature range for the conversion of ethanol to hydrocarbons (Inabal et al, 2005 & hoang et al., 2010).

Accordingly, ethanol conversion over ZSM-5 at temperature range below 400 ^oC, are highly selective and lead to exclusive formation of low-range hydrocarbons such as oxygenates light aldehydes and ether , and light olefins (Inaba et al, 2005). Surprisingly, such low hydrocarbon formation at this low temperature range, does not only apply to the ZSM-5 but also to other zeolites types, including clay catalysts (Gruver et al.,1995).

Conversion over clays requires low temperature range, because clays generally have low thermal stability than zeolite. Several work on the conversion of ethanol over clay or clay-supported catalysts are reported under a temperature range of between 250- 280 ^oC (Gruver et al., 1995 , Corma et al., 1987).

Such low temperature could be due to the restriction in thermal stability of clays or perhaps by the fact that at this temperature, clay catalysts primarily lead to the formation of lighter hydrocarbon molecules (Inaba et al., 2005:137). The latter includes oxygenates hydrocarbons such as aldehyde, ketones and light olefins such as ethylene and propylene.

Most reactions however, where ethanol is transformed to heavier hydrocarbons such as gasoline-range, are primarily carried out at higher temperature over zeolite or zeolite-based catalysts such as ZSM-5 (Viswanadham et al., 2012 & Inaba et al., 2006) . The minimum temperature range to account for gasoline-range hydrocarbons from methanol was 371 ^oC (Lancashire, 1995-2013).

However at high reaction temperature of ethanol over ZSM-5, starting from 400 ^oC, the formation of high hydrocarbons, particular aromatics was favoured; with only low to no selectivity of light hydrocarbons (Inaba et al., 2005:137).

It may therefore be stated that the application of high temperature range (Starting from 400 ^oC) speeds up the overall conversion path of ethanol to higher hydrocarbons – a more direct and shorter conversion path.

The reaction temperature discussed as above was based on the fact and assumptions that time on stream, acidity of the catalyst as depending on the catalyst type, and the operating pressure were kept constant for both low and high temperature ethanol conversion process.

According to Inaba et al. (2012), a high temperature catalytic system (>400 ^oC) was found to lead to increased activity of zeolite catalyst during ethanol conversion. This in turn reduces the operating reaction time to attain a particular conversion. Furthermore, the variation of temperature within the high temperature range (> 400 ^oC), also influences on product distribution. This can be deducted from a work reported by Viswanadham et al. (2011:301); in which the operating temperature of ethanol conversion over ZSM-5 was initially set up for 450 ^oC. It was then observed that varying this temperature to 500 ^oC, had led to a slight evaporation of the aqueous hydrocarbons mixture, and hence to increased gas contents in the product.

The optimum values of other conditions, such as WSHV, operating pressure, are often set during the preliminary experimental trials.

2.4 Clay occurrence and economy in South Africa

The republic of South Africa is well endowed with a number of clay minerals. The occurence of different clay minerals vary from place to place with some of the places being so rich in deposit of certain clay minerals. Clay minerals occur in significant deposits within geographical region of the republic of South Africa. The grpup under which clay are classified are Kaolinite, Chlorite, Hydromica, illite, Muscovite, Palygorskite, Pyrophilite, Smectite and Vemiculite.

kaolinite, among the above, are the most abundant natural occurring clay in Africa, followed by illite and smectite (Ekosse, 2010 2010:214 & 218). South Africa peculiarly, has the largest amount of kaolin deposits in the Southern Africa , with the Grahamstown deposits associated with good-quality kaolin (Jacob, 2004). Kaolin is refered as the clay specie rich in kaolinite mineral.

The most application of kaolin is found in paper and ceramic industry, followed by its application as adsorbents (Ekosse, 2010:222). According to Eman (2013:360), "kaolin is the most important clay used in the manufacture of catalysts". The abundance of kaolinite owes to its great use , value and discovery. The abundant availability of kaolin clay in a country such as South Africa, reveals its importance in contributing towards the country's economy. Unlike kaolinite, other clay types occur in relatively small quanities and thus their exploitation for catalyst development, may not be as economical feasible. According to mineralogical studies (Council for Geoscience, 2014), most exploitable mineral deposits of clays in South Africa and their detailed exploration are found in the Western Cape. The clay minerals refered to comprise bentonite, kaolin, sepiolite clay, including other several minerals. The resource fields of the minerals mentioned above are shown in the following map in Figure 2.6.

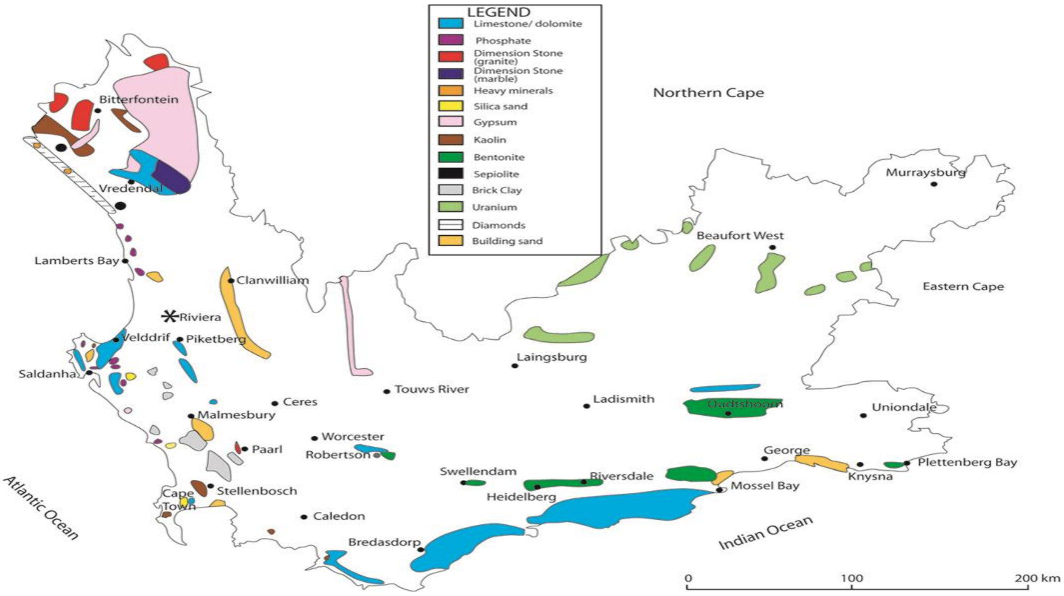


Figure 2.6: Mineral Resource Fields in the Western Cape province (Council for Geoscience, 2014)

3. Methodology

3.1 Catalysts preparation

Clay-based catalysts were developed from a number of natural clays which served as the starting materials. The preparation of these catalysts was carried out by modifying the clay materials using various methods. The various processes used in the clay modification include beneficiation, acid modification, production of zeolite catalyst from clay by hydrothermal synthesis and promotion of clay-based catalyst(s).

Figure 3.1 illustrates the procedures for the preparation and characterization of clay-based catalysts.

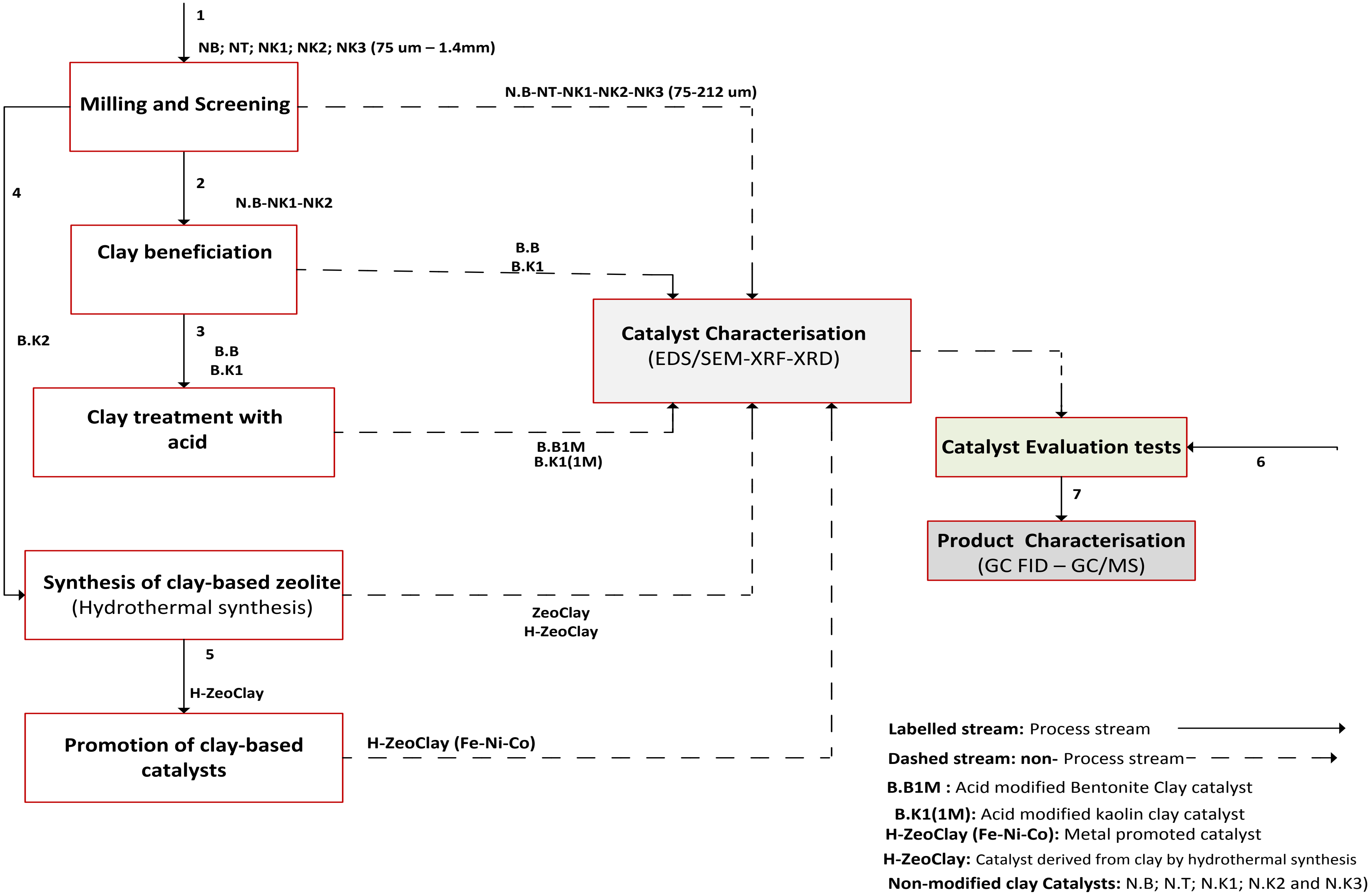


Figure 3.1: Diagram illustrating the synthesis of clay-based catalysts through various (modification) approaches

Natural clay materials required for the development of catalysts were obtained from various deposits in Africa. Bentonite clay (N.B) from Cape Bentonite Mines in South Africa (Cape Town); Natural non-modified Talc clay (N.T) was obtained as the gangue residue to a nickel ore from Tati Nickel Mine (in Botswana); and three natural kaolin clays (N.K_1; N.K_2 and N.K_3) were obtained from various sources in Nigeria. The clays used are listed in Table 3.1.

Table 3.1: Lists of the used clays, their distinctive sources and code

Clay specie	**Source**	**Code (**Non-modified**)**
Talc	Botswana, Tati Nickel Mining (TNMC)	N.T
Bentonite	Cape Bentonite Mines (SA)	N.B
Kaolin (Source 1)	Kankara, Nigeria	N.K_1
Kaolin (Source 2)	Kankara, Nigeria	N.K_2
Kaolin (Source 3)	Alkaleri, Nigeria	N.K_3

Chemical reagents required to carry out the various modifications on natural clays were commercially obtained; these include high purity *ethanol* (≥ 96 %) from *Scienceworld*; salts of transition metals were purchased from *Kimix*, which include Iron (Fe), Copper (Cu) and Nickel (Ni) in the nitrate hydrated form. Commercial zeolite catalyst was obtained from *Zeolyst International* and used as a yardstick for measuring the performance of the synthesized clay based catalysts in bioethanol conversion.

In addition to the above, necessary reagents and equipment required for the various stages of the experiment, are further listed in Table 3.2.

Table 3.2: Reagents and equipment required for the experiment

Materials	Equipments	
Clays (Raw non-modified clays): Bentonite, talc and kaolin	**Major**	**Minor**
Sulphuric acid (≥ 98 %)	Stainless tubular fixed bed reactor	Set of laboratory micro-sieves (53 ≤ 1.4 mm)
Zeolite catalyst (Commercial)	Peristaltic pump	Magnetic stirrer
NaOH pellets	Temperature control shaker	Rod Mill Machine
Sodium silicate or silicic acid	Teflon-lined Stainless Steel Autoclaves (75 mL)	Separatory funnel
$Al(NO_3)_3•9H_2O$	Muffle furnace	Vacuum filter apparatus
TPABr or TPAOH	Oven	pH meter
$Fe\ (NO_3)_2 \cdot 6H_2O$		
$Ni\ (NO_3)_2 \cdot 6\ H_2O$		
$Co\ (NO_3)_2 \cdot 6\ H_2O$		
Ethanol (96 % pure, v/v)		

3.1.1 Milling and screening of clays in natural mined state

Clay materials as initially obtained in their non-modified states were individually crushed and ground in a rod mill. These were then screened through a 1.4 mm sieve for grit removal and further screening was carried out through a set of laboratory sieves (75-600µm). The obtained fractions were sent for analyses, among which the 75-212 µm fraction was isolated for beneficiation in further experiments.

3.1.2 Clay beneficiation

Beneficiation was carried out in two (adoptives) separation techniques (So as to concentrate the clay sample with Si and Al content and to effectively minimise the impurity content in the sample). Screening was followed by gravity sedimentation.

In the first technique, the 75-212 µm fraction of N.B and N.K$_1$ (Non-modified clay samples) was thoroughly screened in a controlled sieve shaker through a set of laboratory sieves for 30 minutes (53-75-150-180-212 µm set of sieves). In the second technique, the clay fraction obtained below 53 µm sieve was then mixed with water in a separatory funnel. The obtained suspension mixture was then gently agitated and let to settle for 48 hours. After settling, the clay sediment (at the bottom of the funnel) was collected in a beaker and dried in the oven at 105 ^{0}C. The resultant sample, B.B and B.K$_1$ (Beneficiated clay catalyst) was then sent for analysis.

Table 3.3: Beneficiation conditions by gravity sedimentation techniques

Clay samples (Below 53 µm after Screening)	**Settling conditions**		**Resultant beneficiated samples**
	Clay to water ratio (w/w %)	Settling period (hours)	
	31.6 %	**48**	
N.B (<53 µm)			**B.B**
N.K$_1$ (<53 µm)			**B.K$_1$**

3.1.3 Clay modification with sulphuric acid

Clay modification with sulphuric acid was carried out on B.B and B.K$_1$. These two among the non-modified catalysts, were selected due to their best catalytic activity on bioethanol conversion.

Sulphuric acid solutions of different molarities (1 M; 3 M and 5 M) were prepared from 98 % concentrated sulphuric acid with deionized water. These were then used separately to activate the B.B, B.K$_1$ and B.K$_2$ samples.

A certain quantity of each clay sample was mixed with the prepared sulphuric acid solutions to 35.3 % (w/w). The acid activation was carried out by heating each mixture suspension in a temperature controlled shaker at 98 ºC for 6 hours. The activated samples were filtered, and then the precipitate was washed with deionized water. The resultant samples, B.B$_{1M}$, B.K$_{1(1M)}$ and B.K$_{2(1M)}$, were then dried overnight in the oven at 105 ºC. These were then let for cool before being analysed.

3.1.4 Synthesis of clay-based zeolites

Catalysts from clay was synthesised by fusion of Sodium hydroxide prior to hydrothermal synthesis. For this purpose, a solution of 4M sodium hydroxide was prepared.

An amount of kaolin, N.K$_2$ was then mixed with the prepared NaOH solution, under stirring for 24 hours in temperature controlled shaker at temperature of 100 ºC. The mixture was then let to settle; after which the resultant NaOH fused kaolin cake (sediment) was dried at 105 ºC overnight. The above procedure was repeated using B.B sample, however the synthesis of zeolite from this (bentonite clay) could not continue because the material became hard after drying due to sodium hydroxide fusion.

The resultant NaOH fused kaolin was then calcined for 3 hours at 700 ºC to obtain the metastable phase of kaolin, metakaolin (M.K$_2$). A certain amount of the metakaolin recovered was sent for XRD characterisation.

To prepare the zeolite batch mixture, sodium silicate solution was then added onto metakaolin and this resultant mixture was stirred for 2 hours at room temperature. In the meanwhile solutions of sodium hydroxide and TPABr were prepared separately, and then added to the mixture above , followed by addition of required amount of deionized water.

The three mixtures were then mixed into one beaker and a required amount of deionized water was added. The entire new mixture was then stirred for one hour at room temperature; after which the pH of the mixture was adjusted to 11 by drop wise addition of sulphuric acid. Drops of ethanol was then added to the resultant gel, which in turn was transferred into autoclaves (Three 75 ml autoclaves). The Teflon autoclaves were put into oven for hydrothermal synthesis at 175 ºC for 48 hours.

The resultant sample was cooled to room temperature, filtered and washed with deionised water, and then let for drying at 105 ºC. The recovered solid product was calcined for 5 hours at 600 ºC. The calcined sample, ZeoClay, was further protonated using ammonium chloride as described below. A small amount of the sample was however sent for analyses.

An amount of the ZeoClay was mixed into 1 M ammonium chloride solution (NH_4Cl) and the resultant mixture was further stirred for 6 hours at 100 ºC. The resultant suspension mixture was filtered, washed with deionised water and then the cake was let to dry at 105 ºC overnight. The dried solid sample was then calcined in the muffle furnace for 5 hours at 600 ºC.

The above protonation procedure was similarly repeated on the sample of commercial zeolite catalyst (ZeoCOM). The protonated samples; H-ZeoClay and H-ZeoCOM, were sent for analyses.

3.1.5 Metal promotion of the clay-based catalysts

(i) Impregnation of clay-based catalyst with Fe; Co and Ni

Three samples of H-ZeoClay (H-Zeoclay 1; H-ZeoClay 2 and H-ZeoClay 3) were impregnated with Iron (Fe), Nickel (Ni) and Cobalt (Co) metals respectively. The latter were obtained in the form of nitrate salts.

A solution of each metal nitrate was prepared and impregnated into H-ZeoClay1; H-ZeoClay2 and H-ZeoClay3 support to attain 20 wt.% of pure metal loading. These were let to dry overnight at 105 ºC. Each sample was then calcined 600-700 ºC for 3h30 minutes in a muffle furnace, to give H-ZeoClay(Fe), H-ZeoClay (Ni) and H-ZeoClay(Co).

The latter promoted clay-based catalysts, were then sent for analyses.

3.2 Catalyst characterisation

In this work; EDS and SEM and XRF analyses were done at UCT in CIA laboratory. EDS was carried out to determine the major element analysis of various samples, and SEM the morphology of the catalysts. In addition to the above, XRD analysis was done at Ithemba lab to determine phases present in the samples. The XRD experimental patterns of the prepared clay-based catalysts in this work, were generated and interpreted using the XRD Match Software (Version 1.11h and V3.1).

3.3 Catalytic evaluation

3.3.1 Equipment set-up for catalysts evaluation

Catalyst evaluation tests using prepared catalysts were carried out in a stainless steel-tubular fixed-bed reactor so as to assess catalysts activity on the conversion of bioethanol. Prior to each catalytic reaction, each catalyst was thermally activated in the reactor for one hour at 400 ºC.

In a typical evaluation test, bioethanol was fed continuously and downstream into the reactor using a Peristaltic pump at 2 h^{-1} WHSV. The reactor was fitted with a thermocouple set to measure reaction temperature. The product leaving the reactor was cooled in the condesor; the condensate liquid product was collected accumulatively and the gaseous product was collected using Teddler bags. These were then sent for GC analyses for product identification and quantification.

Process diagram illustrating the section on the reaction tests of the synthesized clay-based catalysts for bioethanol conversion, is shown in Figure 3.2.

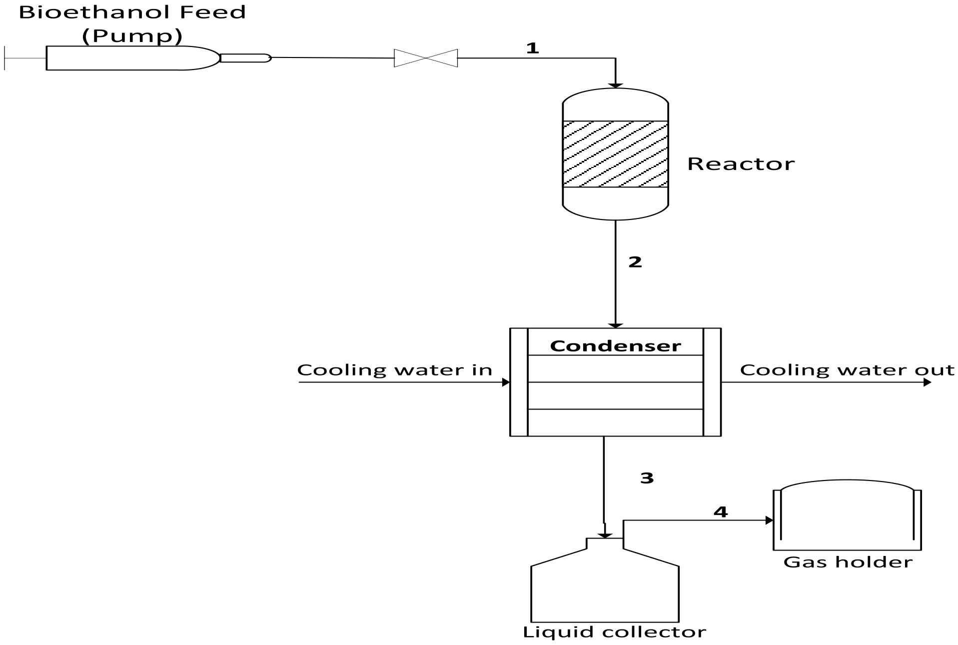


Figure 3.2: Simplified diagram for bioethanol conversion

3.3.2 Catalysts evaluation

Each individual clay-based prepared catalyst was evaluated in the fixed-bed reactor using bioethanol, as described in section 3.3.1.

At first the non-modified clay catalysts ; N.B; N.T; $N.K_1$; $N.K_2$ and ; $N.K_3$ were evaluated at 350 ^{0}C for 6 hours and 2 h^{-1} WHSV. Among these, N.B was selected and further evualated at 4 hours and 2 hours reaction time.

This was followed by evaluation of catalyst B.B, $B.B_{1M}$, H-ZeoClay, H-ZeoCOM, H-ZeoClay(Fe), H-ZeoClay (Ni) and H-ZeoClay (Co) at the same reaction conditions (350 ºC for 6 hours at 2 h^{-1} WHSV). $B.B_{1M}$ among these, was also evaluated for 2 hours reaction time.

The H-ZeoClay selected among these, was further evaluated at 400 ºC (For fixed reaction time of 6 hours and WHSV of 2 h^{-1} as the above)

B.B: Beneficated bentonite catalyst
$B.B_{1M}$: Acid-modified bentonite catalyst
H-ZeoClay: Clay-based Zeolite catalyst sample
H-ZeoCOM: Commercial Zeolite catalyst sample
H-ZeoClay (400 ºC): Clay-based zeolite evaluated at 400 ºC

3.3.3 Product characterisation

Chromatographic analyses, for product identification and quantification (Concentration) of the constituent components in produced samples (both liquid and gaseous) from catalytic reactions, were carried out using a GC-FID equipped with a polar capillary column and GC/MS with a non-polar capillary column (Both were Hp88 model 7890B GC system). This GC facility was obtained at Agrifood Technology Department (CPUT Bellville campus).

The identification of the components through GC/MS was obtained by comparing their Gas Chromatogram with the spectra of the *WILEY 6N* library.

Table 3.4: Catalysts evaluation tests and corresponding operating conditions

Samples (Prepared clay-based catalysts)	**Catalyst evaluation** ($2h^{-1}$ WHSV)	
	Temperature (ºC)	**Time (hours)**
NB; NT; $N.K_1$; $N.K_2$; $N.K_3$	350	6 4 2
B.B; $B.K_1$	350	6
$B.B_{1M}$	350	6 4 2
ZeoClay, H-ZeoClay; H-ZeoCOM	350	6
H-ZeoClay (Fe); H-ZeoClay (Ni); H-ZeoClay (Co)	350	6
H-ZeoClay (400 ºC)	400	6

4. Result and Discussion

4.1 Characterization of the produced clay-based catalysts

The catalytic properties of non-modified, modified clay catalysts, including that of clay-based zeolite catalysts produced in this work, have been studied using EDS, XRF, SEM and XRD techniques. The Si/Al ratio in clay-based catalysts (Si/Al), mineralogical composition and catalyst morphology are among the properties analysed to account for their performance on bioethanol conversion. Catalyst porosity was slightly estimated on basis of SEM images of the prepared samples

4.1.1. Elemental composition and Si/Al ratio of non-modified clays

The EDS results in Table 4.1 show that clay materials have similar basic elemental composition, which however appear in different relative proportions.

Table 4.1: Elemental composition of the various non-modified clay minerals (EDS results)

Major element (EDS analysis)	**Non-modified clay minerals** (%, w/w)				
	(N.T)	N.B	N.K_1	(N.K_2)	(N.K_3)
Si	**18.98**	**13.5**	**23.87**	**32.14**	**13.12**
Al	**11.43**	**12.63**	**18.13**	**8.84**	**13.03**
Fe	10.12	-	-	4.67	-
Ti	-	-		-	0.41
Cu	2.38	-	-	-	-
K	6.14	-	2.97	-	-
Mg	4.32	-	-	2.51	-
C	-	21.1	-	-	20.64
O	46.63	52.78	55.03	51.84	52.81
Si/Al ratio	1.66	**1.07**	1.3166	**3.636**	1.007

The results to XRF analyses of kaolin clay are presented in Table 4.2 and this by compostion corresponds to those of clays given earlier in literature in Table 2.3 and Table 2.5 (pg.15 & 17 respectively*)*.

Table 4.2: Comparison of XRF data of non-modified kaolin in the experiment and that of kaolin in literature

XRF		SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	MgO	Na_2O	CaO	P_2O_5	H_2O^-	LOI	**SiO_2/ Al_2O_3**
N.K_2	% (w/w)	54.04	29.95	0.46	0.35	4.02	0.15	0.28	0.07	0.03	0.47	9.05	1.8
C.R K	% (w/w)	63.58	25.83	0.96	Traces	Traces	Traces	Traces	Traces	-	-	9.63	2.46

N.K_2: Clay used for experiment Literature: C.R.K (China R.O.M Kaolin)

As observed in Table 4.1, the proportion of Si and Al content in the given clay minerals is highest compared to other elements*;* except for oxygen elements that link the clay structure. This similarly applies for XRF data (Detailed in Table 7.7_*Appendix 2*), displaying the highest proportion of Silica (SiO_2) and Alumina (Al_2O_3) contents in clays. This in turn serves as evidence for identities of the materials used as clays or alumino-silicate materials .

The difference in Si/Al ratio obtained through the EDS data of the various clays, corresponds to their distincts structural Si and Al proportion. For Example, N.K_1 contained Si and Al to be 23.87 and 18.13 % respectively, which correspond to Si/Al ratio of 1.3. This for N.K_2 and N.K_3 was found to be 3.6 and 1.01 respectively. This ratio in terms of SiO_2 /Al_2O_3 of the obtained clays given by XRF data (Table 7.7_Appendix 2), was found by average to correspond to that of clays in literarure as shown in Table 4.2 (The average SiO_2 / Al_2O_3 of the obtained clays was 2.49 while that from literature was 2.46).

4.1.1.1 Effect of beneficiation and acid modification on Si/Al ratio (elemental composition)

The non-modifed clay (N.B in particular) was further beneficiated, which as a result led to enrichment of Si content in the resultant sample(B.B) from 13.5 to 19.73 %. The weight content of Alumimium(Al) on the other hand was decreased from 12.63 % to 6.98 % , resulting to increase in the Si/Al ratio of the resultant catalyst (B.B) from 1.7 to 2.93. Hence, clay beneficiation led to increased Si/Al ratio of bentonite catalyst.

Upon further modification of the later resultant catalyst (B.B) with sulphuric acid (resulting to B.B_{1M}), the Si content was decreased by 10.33 % (From 19.73 to 9.4 %) and the Alumimium (Al) was further decrease to 3.42 % content (From 6.98 %). The above discussed are reported in Table 4.3.

Acid modification, unlike clay beneficiation as observed in Figure 4.1, led to decrease in *Si* content of the catalyst (by 6.23 %); while like beneficiation, this led to decrease in Al content. Acid modification as a result, resulted to decrease in Si/Al ratio of the catalyst (2.83 to 2.75) as shown in Table 4.3.

Table 4.3: Effect of beneficiation and acid modification on catalyst composition

(*See* ***Figure 4.6*** *for effect on morphology_ pg****.83)***

		O	**Si**	**Al**	**Fe**	**Cu**	**Mg**	**Na**	**C**	**S**	**Total**	**Si/Al ratio**
N.B	(%)	52.78	13.5	12.63	-	-	-	-	21.1	-	100.0	1.07
B.B	(%)	55.79	19.73	6.98	1.78	-	2.15	-	-	0.24	86.67	2.83
B.B$_{1M}$	(%)	84.13	9.4	3.42	-	-	1.98	-	-	0.32	99.24	2.75

Note that % is w/w

Clay beneficiation followed by acid modification (regarded) as a whole, has resulted to decrease in both Si and Al content of the catalyst. *Si* content was decreased by 4.1 % (13.5 to 9.4 %) and Al content the most by 9.21 % (12.63 to 3.42 %). This as a result favoured the overal increase in Si/Al ratio of the acid modified clay catalyst (B.B$_{1M}$).

4.1.2 Morphology of clay-based catalysts

The structural morphology of the non-modified clay catalysts was observed using Scanning Electron Microscopy (SEM). In Figure 4.1, the micrographs show that the samples range from quadrilateral to hexagonal in shape. The morphology of N.B catalyst was observed to dominantly consist of quadrilateral to pentagonal cuboidal particles. The other clay catalysts, N.T and kaolin catalysts (N.K$_1$; N.K$_2$ and N.K$_3$) on the other hand, were observed to consist rather of particles in hexagonal shape.

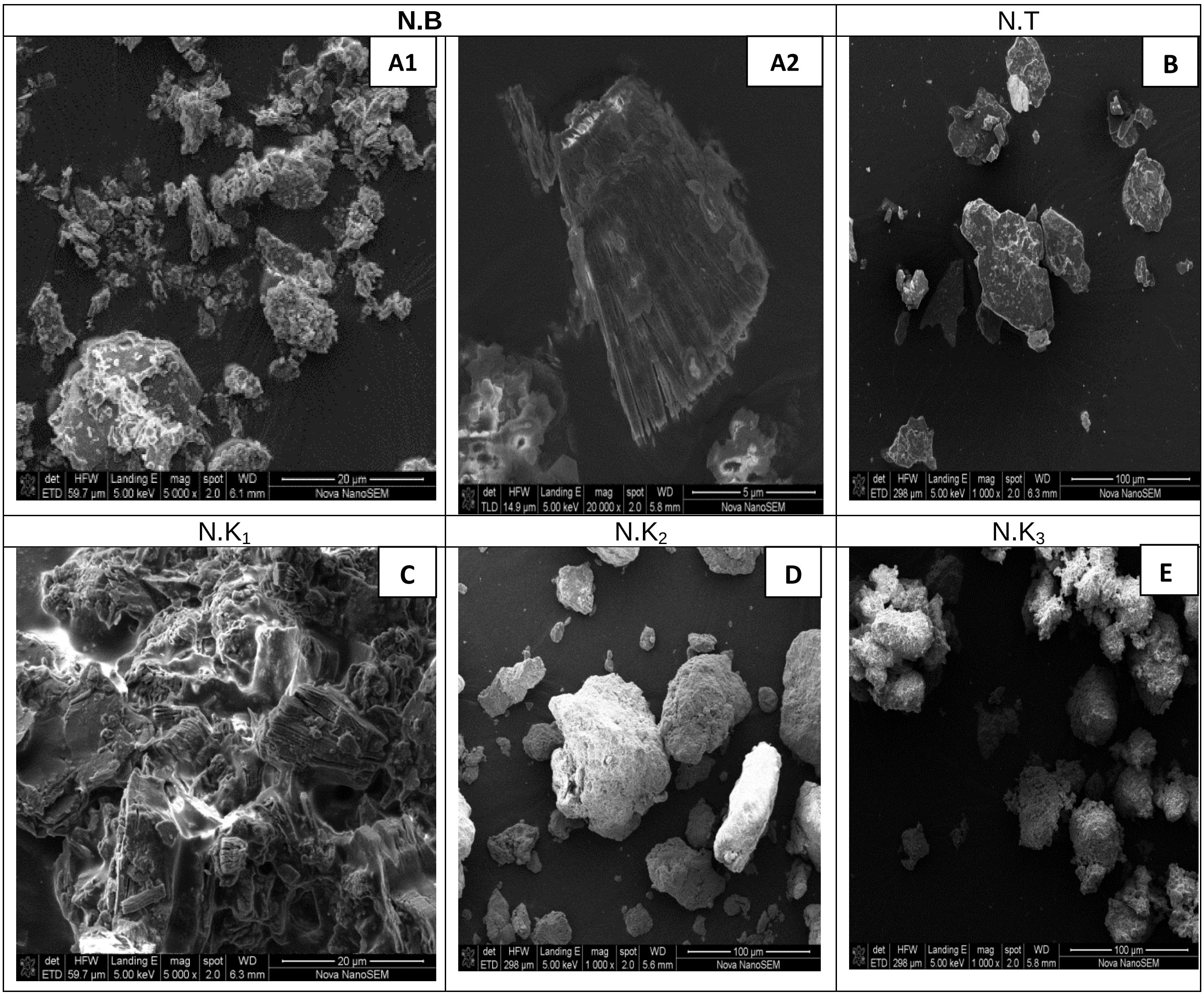


Figure 4.1: SEM image of non-modified clay catalysts

4.1.2.1 Effect of beneficiation and acid modification on clay catalyst morphology

N.B catalyst among the non-modified clay catalyst discussed above, was selected for beneficiation and acid modification. These as a result, led to variation in morphology in the resultant catalyst, B.B and B.B$_{1M}$. The resultant B.B catalyst (beneficiated bentonite clay) was found to contain particles that are dominantly quadrilateral cuboid, which has a similar morphology as N.B catalyst (the non-beneficiated catalyst) in exception to trace proportion of pentagonal cuboidal particles that were present or observed in the N.B catalyst (Catalyst before beneficiation). SEM images accounting for effect of beneficiation on clay catalyst morpholgy are reported in the Figure 4.2.

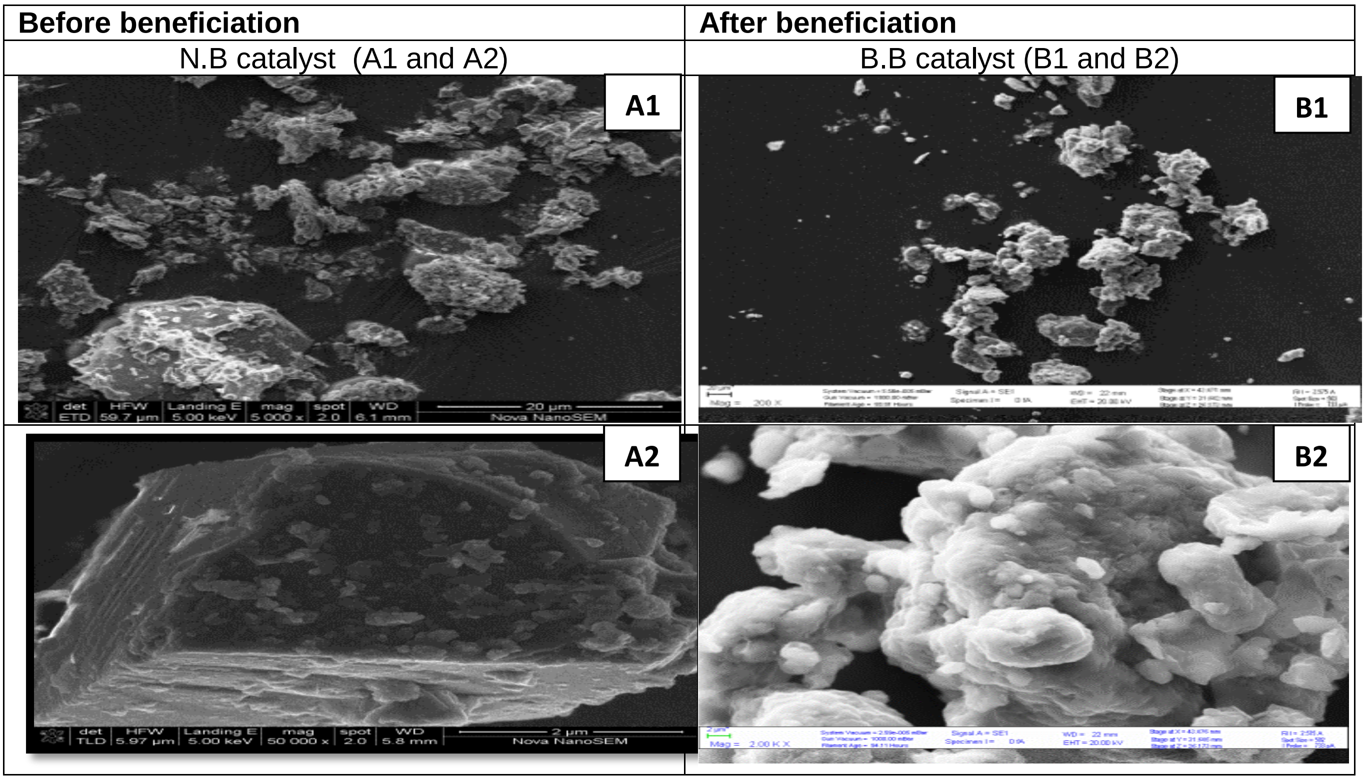


Figure 4.2: SEM image of non-modified (N.B) and benificiated (B.B) catalyst

The particles of the resultant B.K_1 catalyst on the other hand as observed in Figure 4.3, were observed not to have altered but rather maintained the exact same morphology as the N.K_1 catalyst, consisting of rectangular/quadrilateral cuboidal and minorly cuboidal particles. Kaolin (N.K_1) catalyst as the selected , serve for comparision to bentonite (N.B) to account for the effect of beneficiation and acid modification on catalyst morphology.

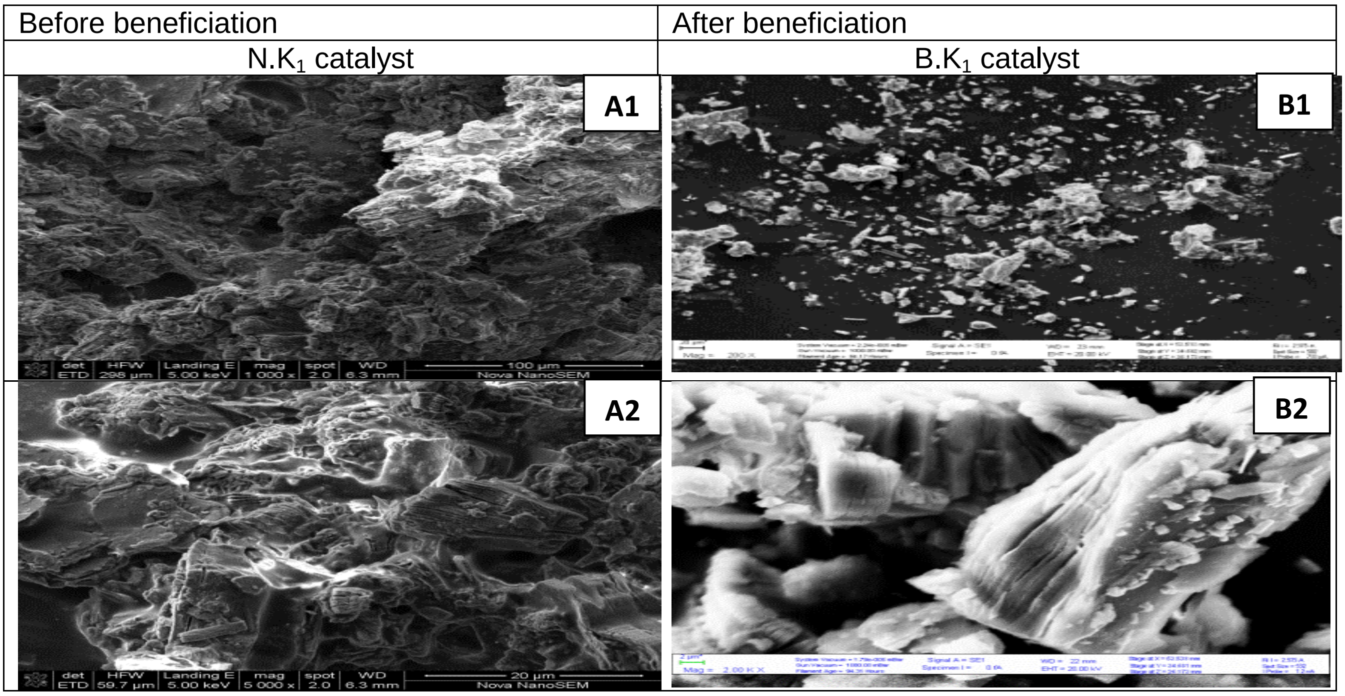


Figure 4.3: SEM image of non-modified (N.K_1) and benificiated (B.K_1) catalyst

From the above overall observation, it was therefore found that clay beneficiation showed no significant effect on the structural morphology of clay catalyst; except on most possibly catalyst particle size (disintegration) and porosity as respectively discussed further below.

Disintegration of N.B catalyst (crystal particles) was observed as a result of beneficiation and acid modification. In other words, the B.B (Beneficiated Bentonite) catalyst was found to consist of more disintegrated and hence at most possibly observed smaller particle size than the N.B catalyst. This similarly applied to B.K_1 compared to N.K_1 as observed in Figure 4.3 above. The former observation was made through Figure 4.2.

Structural porosity of the resultant clay catalyst sample(s) was also altered as a result of beneficiation. It is observed in Figure 4.2 and Figure 4.3 that the particles of initial non-beneficiated catalyst (N.B and N.K_1) mostly appear to overlap one another than those of the beneficiatied catalysts (B.B and N.K_1). In otherwords, this is a possible mean to estimate that beneficiation resulted to a more porous catalyst or an beneficiated catalyst is most possibly estimated to be more porous than the initial non-modified catalyst (N.B and N.K_1). The fact that above variation applies similarly to both bentonite and kaolin catalysts, this is then evdience in support to the above observation or finding. Clay beneficiation as a result, resulted to enhanced structural porosity of the clay catalysts.

Further modification of B.B catalyst with sulphuric acid, resulted to further disintegration of the catalyst with most possibly observed smaller particle size (See Figure 4.4). The B.B catalyst as stated earlier (the catalyst obtained as a result of beneficiation), was observed to dominantly consist of quadrilateral particles. The morphology of B.B catalyst was then varied to pentagonal cuboidal particles as a result of subsequent acid modification.In other words, the morphology of resultant B.B_{1M} catalyst was found to consist dominantly of pentagonal cuboidal particles.

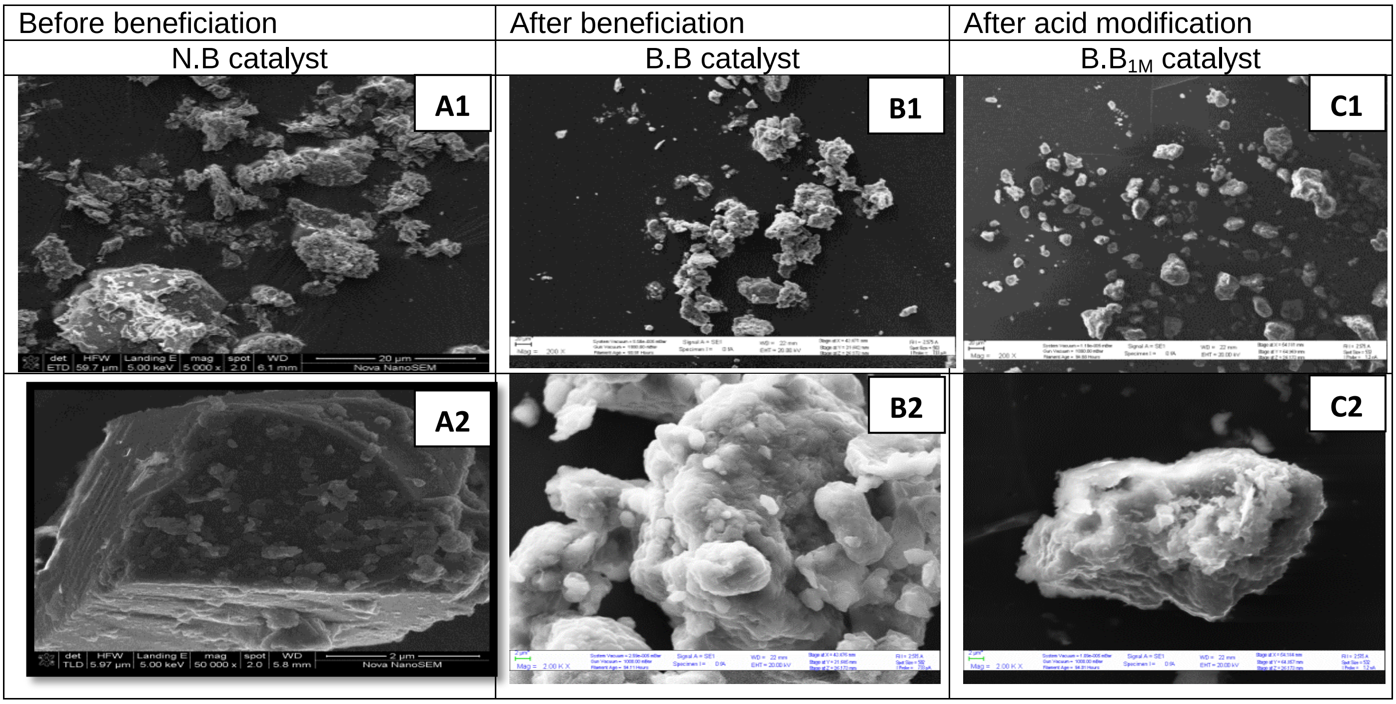


Figure 4.4: SEM image of N.B; B.B and B.B$_{1M}$ catalyst before beneficiation (A1-A2), after beneficiation (B1-B2) and after acid modification (C1-C2)

Particle disintegration of the N.B catalyst if observed as a result of beneficiation followed by acid modification as a whole, is greater than that observed as a result of either of the above modification alone.

The morphology of B.B$_{1M}$ catalyst as mentioned earlier, consisted dominantly of pentagonal cuboidal particles. In other words, clay beneficiation and acid modification (as a whole) resulted to variation in the structural morphology of the catalyst as observed in Figure 4.5.

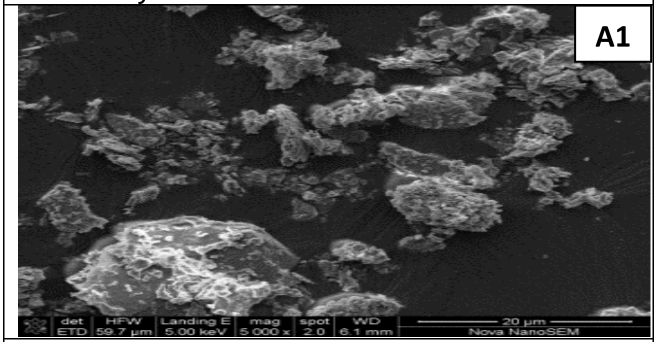
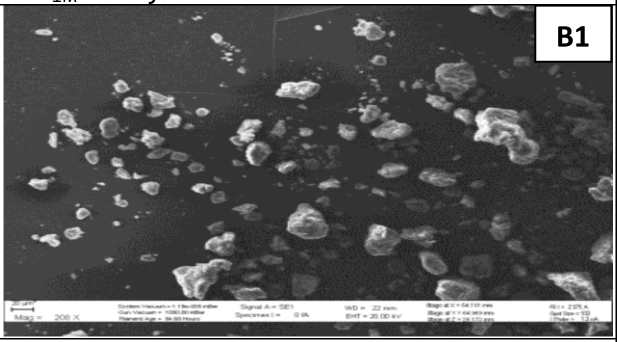
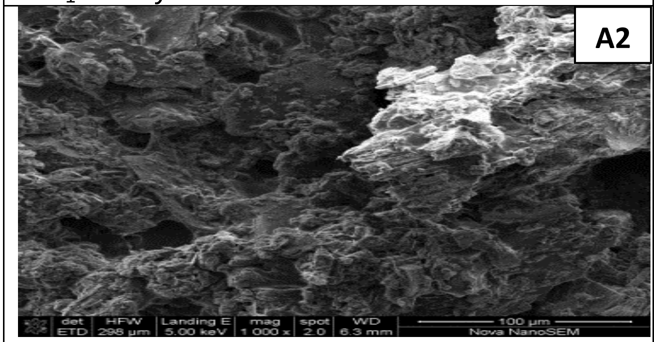
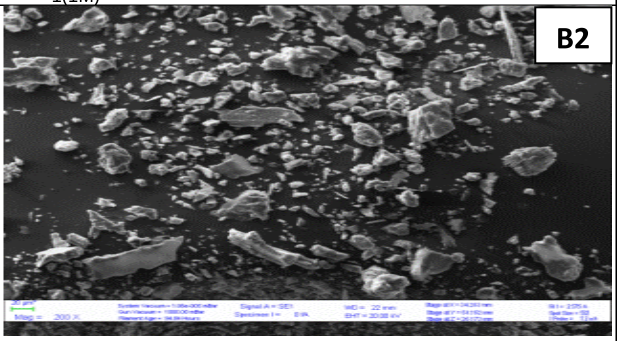
Before modification	After beneficiation and acid modification
N.B catalyst	B.B_{1M} catalyst
 	
B.K_1 catalyst	B.$K_{1(1M)}$
 	

Figure 4.5: SEM image of non-modified and acid-modified catalysts before beneficiation (A1-A2) and after beneficiation and acid modifification (B1-B2) (Overall variation of catalyst morphology).

Hence upon catalyst beneficiation followed acid modification, the N.B catalyst which dominantly consisted of quadrilateral cuboidal particles, was modified to B.B_{1M} catalyst consisting dominantly of pentagonal cuboidal particles.

The above similarly applies to N.K_1 (Kaolin clay) catalyst, for which the structural morphology was varied as a result of beneficiation and acid-mofification (As also observed in Figure 4.5). Initially, the N.K_1 catalyst consisting dominantly of rectangular (quadrilateral) cuboidal morphology, was varied to B.K_{1M} of dominantly pyramidal morphology. This as also observed, led to decrease in catalyst particle size.

4.1.2.2 Morphology and composition of the produced clay-based zeolite

SEM and EDS data are among the tools used to identify the clay-based zeolite with actual zeolite catalysts. SEM results revealed that the morphology of the H-ZeoClay (Clay-based zeolite) catalyst produced in this work consists mostly of cuboidal to rectangulaoidal crystals, including a relatively small proportion of spheroidal crystal units. This was observed through SEM images A1 and A2 in Figure 4.6. The above observed morphology is very comparable to those of zeolites in literature; such as Rownaghi et al. (2011:41) reported on the dominance of cuboidal and small proportion of spheroidal morphology of zeolite catalysts.

Further on, the EDS results revealed that the Si/Al ratio of H-ZeoClay catalyst was found to be 23; whereas this catalyst was produced from N.K_2 (kaolin raw material) of Si/Al ratio of 3.6 (See Table 4.1_pg.76). The precusor mixture however in the preparation of H-ZeoClay, was experimentally measured to have Si/Al ratio ratio of 30.

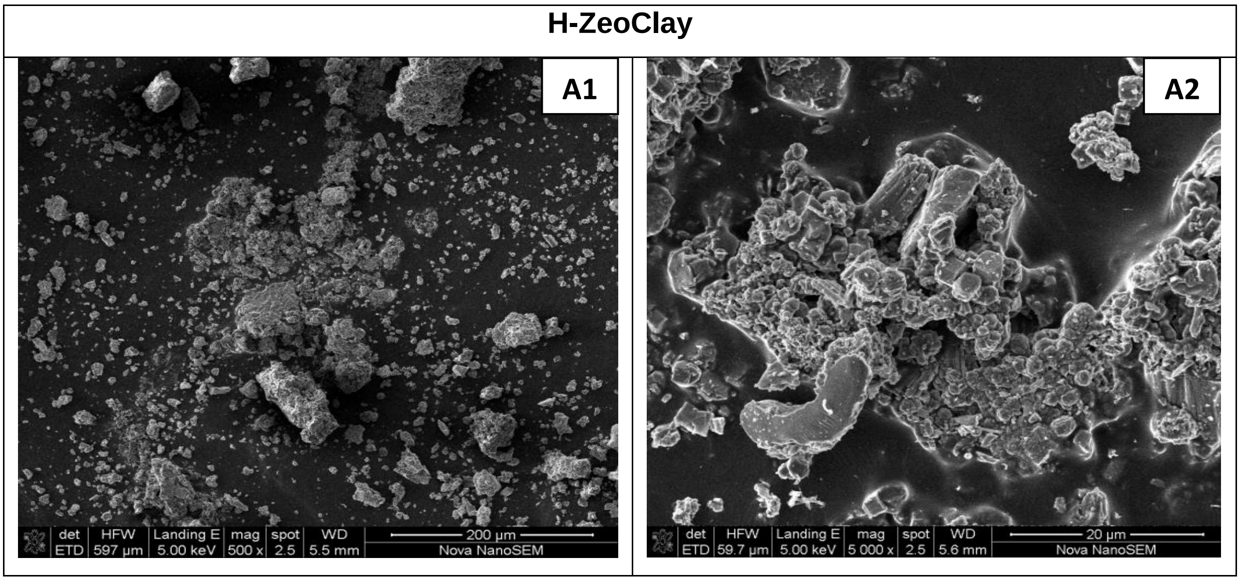


Figure 4.6: SEM image of H-ZeoClay catalyst (A1-A2)

The morphology and Si/Al ratio of the clay-based zeolite (H-Zeoclay) was further compared to that of the actual commercial zeolite as an additonal mean to identity it with zeolites.

4.1.2.2.1 Comparison of H-ZeoClay and H-ZeoCOM catalyst by SEM and EDS results

SEM result revealed that the morphology the H-ZeoClay (clay-based zeolite) ranged mostly from cuboidal to rectangular hexahedron (cuboidal), and also was found to consist of a relatively small proportion of spheroidal crystal units. This is observed through SEM image A2 and A1 in Figure 4.7.

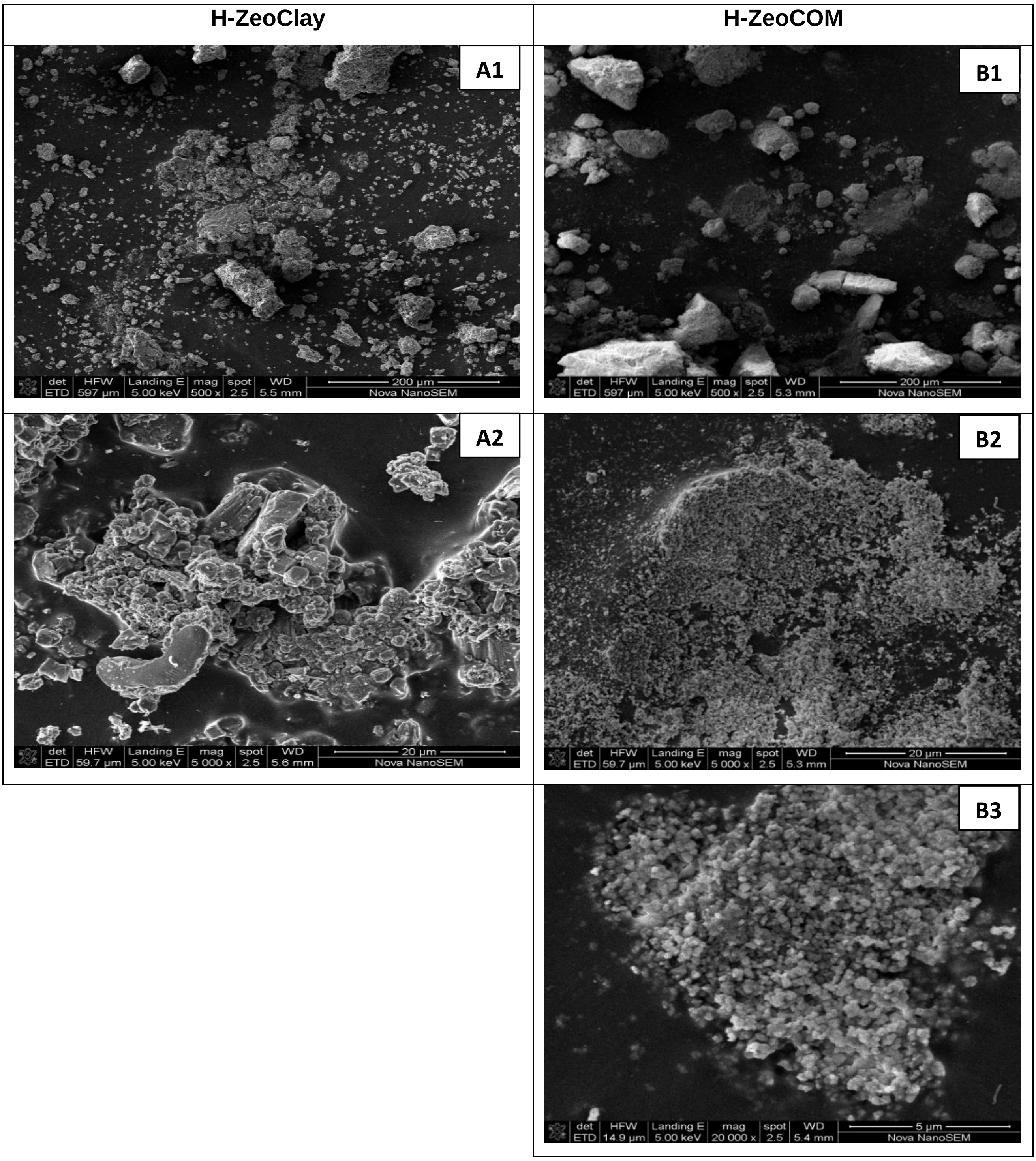


Figure 4.7: Comparison of H-ZeoClay (A1-A3) and H-ZeoCOM (B1-B3) catalyst by SEM image.

The morphology of H-ZeoCOM (Commercial) catalyst on the other hand, was similarly found to consist dominantly of cuboidal particles (as observed through SEM image B3 above), whereas with a little proportion of rectangular to pyramidal particles (As observed through SEM image B1). Nonetheless, the dominance in cuboidal morphology of the catalysts (H-ZeoClay and H-ZeoCOM) was observed with increased magnification of the SEM image.

Various researchers have also reported on the morphology of zeolite catalysts by SEM, such as Rownaghi et al. (2011:41), who through his work found that zeolites (ZSM-5 in particular) generally consist mostly of cuboidal to ellipsoidal crystal units; whereas small proportion of zeolite catalysts consist of spheroidal crystal units.

The comparison of the above catalysts through SEM image A2 and C2 reveals that the particles of the H-ZeoCOM catalyst were more integrated or closely overllaped and hence this catalyst was estimatedly less porous than the H-ZeoClay (Clay-based zeolite).

The H-ZeoCOM (commercial zeolite) as supplied by Zeolyst international, was reported to have a Si/Al ratio of 50. The prepared H-Zeoclay on the other hand, was revealed by EDS result to have a Si/Al ratio of 23.

4.1.2.3 Evaluation of SEM Data of the resultant metal promoted clay-based catalysts

The morphology of the resultant metal promoted clay-based zeolite catalysts was found to consist dominantly of rectangular cuboidal particles. Further on, it was observed through the EDS result in Figure 4.11 that the particles of H-ZeoClay (Ni) catalyst were found to be the most integrated, followed H-ZeoClay (Fe) and H-ZeoClay (Co) catalyst. In otherwords, the more integrated or closely overlapped (tighly close) these particles were observed, the most possibly less porous the catalyst was estimated and vice versa. Catalyst porosity by mere inspection on SEM data, was therefore estimated through closeness and overlaping of the catalyst particles. Hence the H-ZeoClay (Ni), by basis of SEM comparison of the same magnification , was estimated as the most porous catalyst among the metal promoted clay-based zeolite.

As afore mentioned, impregnation of H-ZeoClay by Nickel (Ni) resulted to H-ZeoClay (Ni) with relatively more integrated particles or as the most integrated catalyst. This as a result, exhibited a catalyst sample with larger particle size as compared through SEM image A1-A2 in Figure 4.10; and estimatedly with decreased porosity due to compactness of the sample as observed through SEM image B1 and B2.

Unlike the Nickel (Ni), impregnation of H-ZeoClay with Cobalt (Co) and Iron (Fe), resulted to estimately more porous promoted catalysts (i.e. H-ZeoClay (Co) and H-ZeoClay (Fe)) than the precursor H-ZeoClay catalyst. Meanwhile, the particle size of H-ZeoClay (Fe) and H-ZeoClay (Co) catalyst were at most observed bigger than that of H-ZeoClay (Ni) and the precusor H-ZeoClay catalyst. H-ZeoClay (Co) catalyst among all these and as most possibly and comparably observed through SEM image A3 in Figure 4.8, was (By basis of comparison of SEM image of the same magnification) the clay-based promoted catalyst with relatively largest particle size.

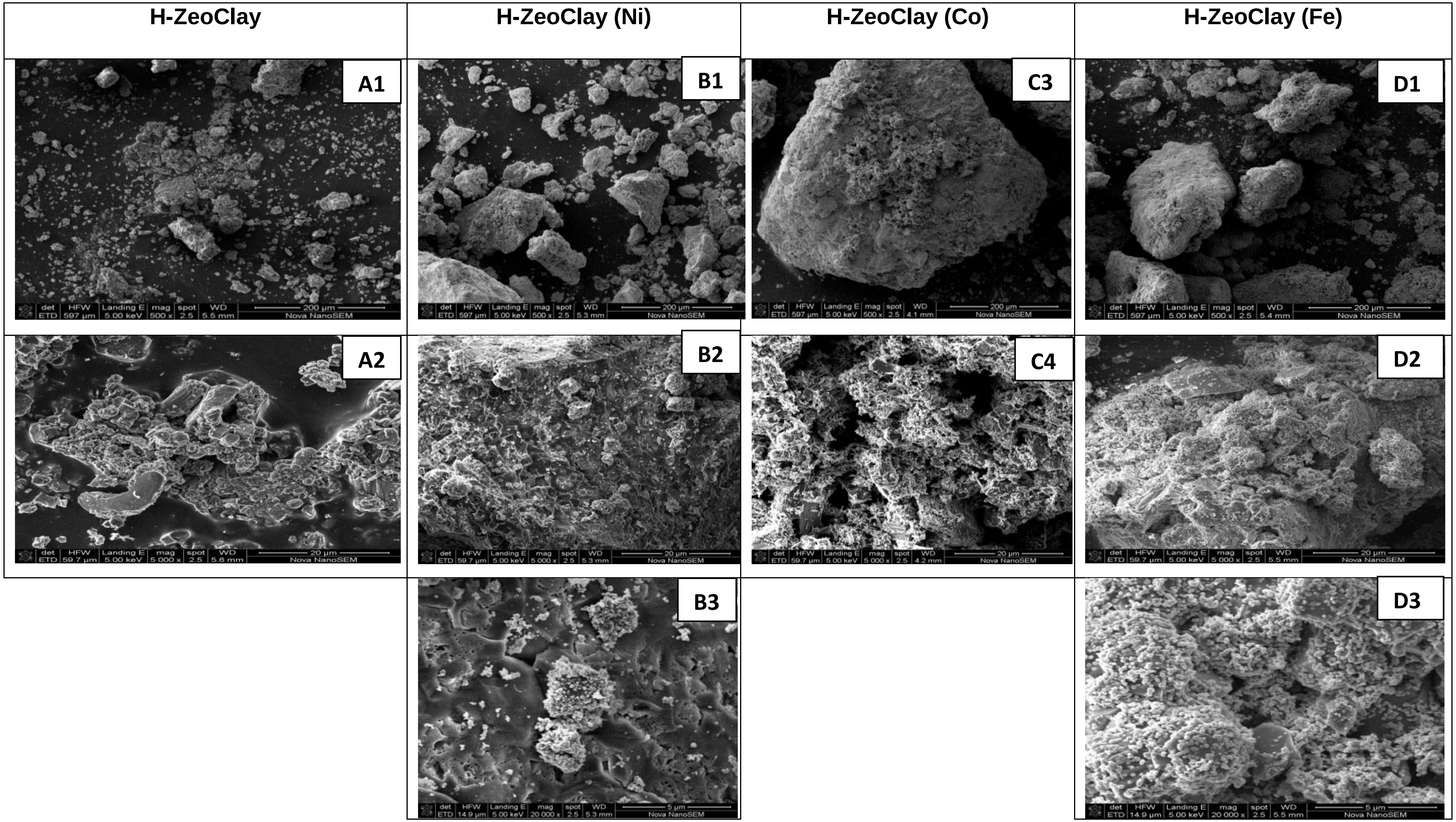


Figure 4.8: Comparison between H-ZeoClay and metal promoted catalysts by SEM image (A1-A2 , B1-B3; C3-C4 and D1-D3 respectively)

Thus far, the trend in metal promotion on H-ZeoClay revealed that the bigger the particle size, the higher the estimate porosity (due to compactness of the sample) observed of the promoted catalyst. The least porosity of H-ZeoClay (Ni) as shown through SEM image B2 and C2 in Figure 4.8 and which serves to prove thereof the resultant highest bioethanol conversion , is an indication of high retention of bioethanol fed over the catalyst during the reaction course. The above similarly applies between of H-ZeoClay (Fe) of H-ZeoClay (Co) on account of their higher activity in the conversion of bioethanol conversion. In other words, H-ZeoClay (Fe) was observed to be most possibly less porous than H-ZeoClay (Co) catalyst.

Ni-promoted catalyst as shown through SEM image B2 was found to consist dominantly of disintegrated rectangular cuboidal particles overlapping other closely integrated particles of the catalyst. In otherwords, this shows greater possibility that H-ZeoClay catalyst sample was highly non-porous (Least porous).

4.1.3 Effect of beneficiation and acid modification on mineralogical composition of clay catalyst

The mineralogical composition of non- modified clays, are among the possible factors to account for their catalytic performance on bioethanol conversion. Clay catalysts were found to contain additional non-clay minerals, which most possibly had effect on catalytic activity.

The XRD data serving as a tool for phase identitication of clay materials, was also used to account for mineralogical composition in the obtained clay materials. Hence The XRD patterns (diffractogram) of the non-modified clays used as starting materials for catalyst development, areshown in Figure 4.9.

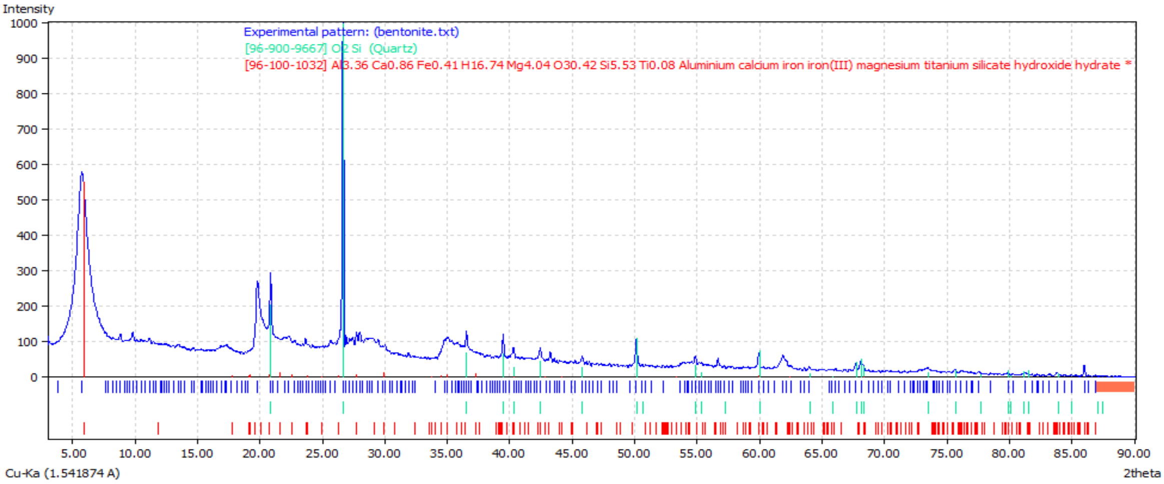


Figure 4. 9 (a) : XRD pattern of N.B catalyst clay catalysts

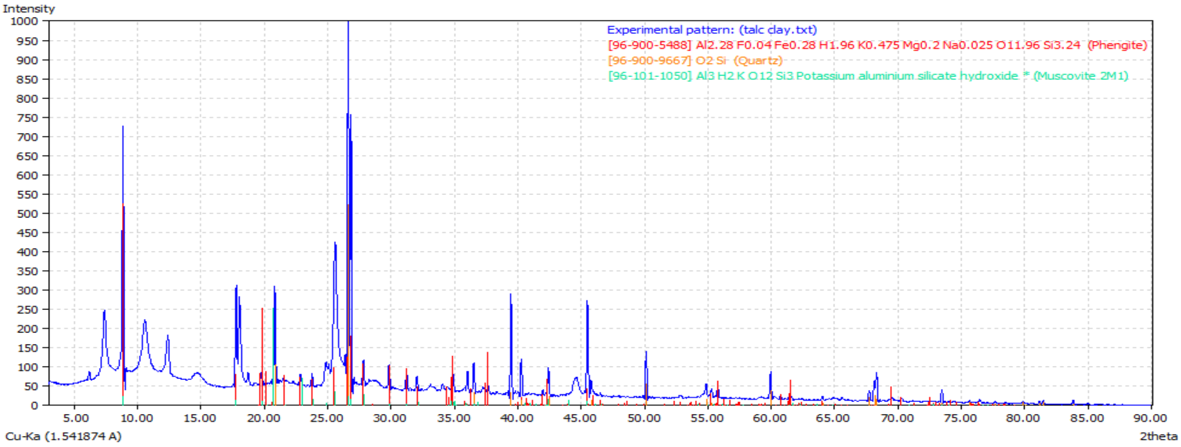


Figure 4.9 (b): XRD pattern of N.T catalyst

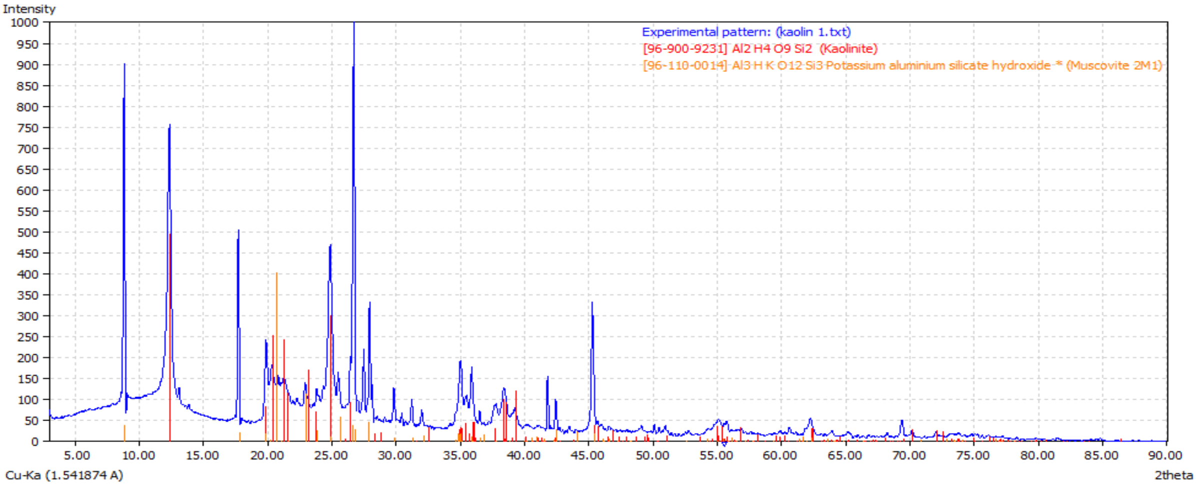


Figure 4.9 (c) : XRD pattern of N.K_1 catalyst.

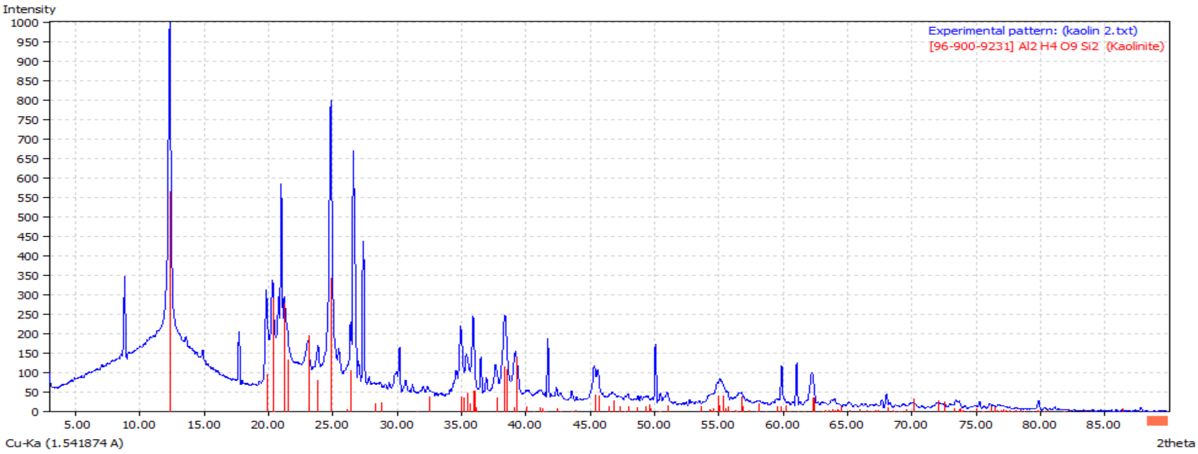


Figure 4.9 (d): XRD pattern of N.K_2 catalyst.

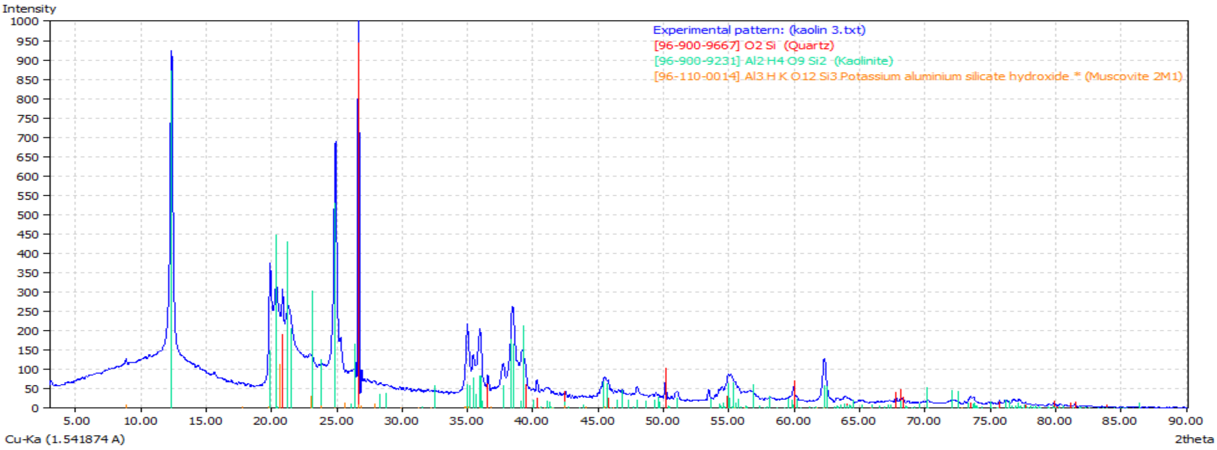


Figure 4.9 (e): XRD pattern of N.K_3 catalyst.

Beneficiation was carried out on the selected clay, bentonite (N.B), and was intended to increase the Si/Al ratio by varying and preferably reducing the amount of mineralogical impurities or non-clay minerals present in the sample.

Beneficiation and most regardingly, acid modification however, were each found not to have effect on phase identification of bentonite material, except leading to variation in proportions of mineralogical compositions of the catalyst. This variation was also accounted through XRD data (Figure 7.26-7.28; Appendix 2), and has been simplified in the form of pie charts presented in Figures 4.10 and Figure 4.11.

The core mineralogical content (phase) identified in bentonite catalyst were Montmorrilonite, silica quartz and an aluminium-silicate based mineral component. Initially as observed in Figure 4.10, N.B (bentonite) catalyst considerably contained 42.6 % of montmollonite mineral phase by mass; 48.8 % silica quartz and 8.6 % alumimium-silicate based mineral content.

In contrast to the expected, beneficiation rather resulted to enrichment of clay catalyst with (the phase of) silica quartz to 89.4 % and reduction in weight percentage phase content of montmorrilonite content to 4.4 %.

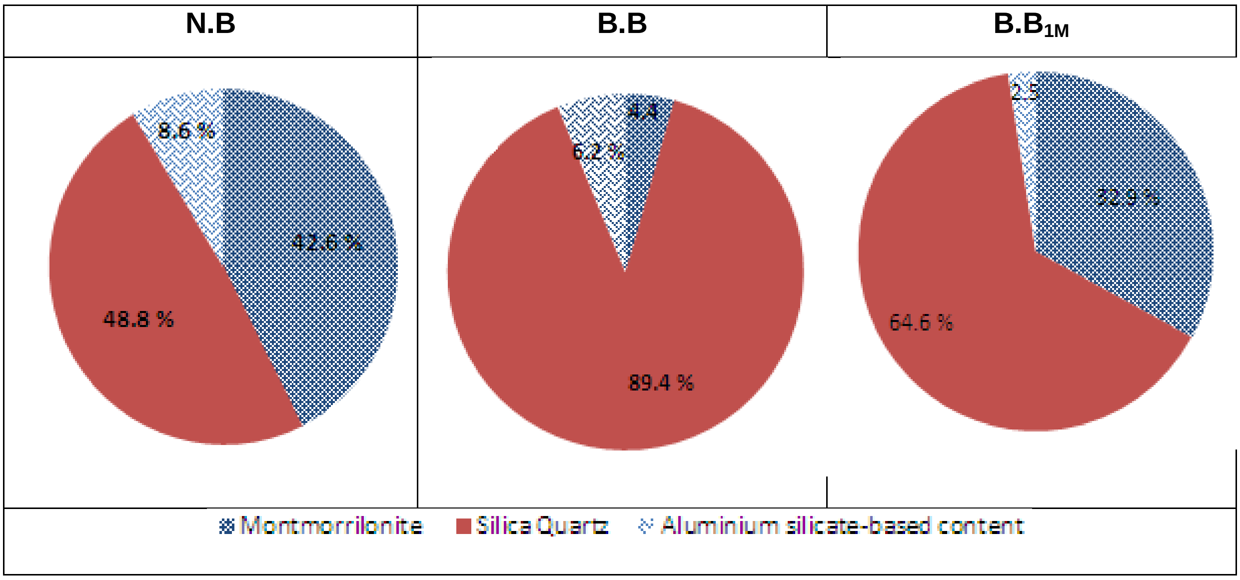


Figure 4.10: Effect of beneficiation and acid modification on mineralogical composition of the developed catalysts (N.B, B.B and B.B_{1M}).

There is a high possibility that the enrichment of the B.B with silica quartz corresponds to the large mass distribution of this sample, which was obtained as the lowest fraction (< 53 µm) from screening prior to subsequent washing and settling technique of beneficiation. In other words, this indicates the fact the silica quartz consists of very tiny particles which in large amount inevitably passed through within the recovered sample to the lowest fraction of sample distribution. Sample distribution and the recovered B.B catalyst during beneficiation is displayed in Table 4.4

Table 4.4: The effect of screening beneficiation on mass and size distribution of clay catalysts

Particle size range	**Mass distribution (g) (N. B)**	**Mass distribution (%)**
300 – 1.7 mm	272.17g	19.7 %
212-300	181.99 g	13.17 %
180-212	18.2 g	1.32 %
150-180	4.86 g	0.35 %
75-150	401.31g	29.05 %
53-75	233.57g	16.91 %
<53 µm	**255.36g**	18.49 %
Total mass fed (g)	**1381.19**	**100 %**
Distribution	75-150 µm >> 300-1.7mm >>**Below-53 µm** >>53-75 >>212-300 >>180-212 >>150-180 µm	

Clay beneficiation on the other hand led to tremenous decrease in the phase content of montmorrilonite (42.6 to 4.4 % = 38.2 % decrease), which through further modification of the catalyst sample (B.B) with acid (As further reported in Figure 4.10) was recoveredly enhanced to 32.9 % (Weight phase content). Silica quartz however with further acid modification of the catalyst (B.B), relatively decreased to 64.6 %.

Unlike variation in montmorrilonite and silica quartz phase compositions, the phase content of alumimum-silicate based mineral in clay sample (which in the initial N.B catalyst was 8.6 % by phase content), consecutively decreased to 6.2 and 2.5 % content as a result of beneficiation followed by acid modification.

4.1.4 Phase identification of the produced clay-based zeolites

The XRD data presentedin Figure 4.11, reports on the pattern of H-ZeoClay (clay-based zeolite) and those of intermediate products (N.K_2 followed by Metakaolin and ZeoClay) obtained along the production of this catalyst. The XRD pattern of the clay-based zeolite was then further compared to that of H-ZeoCOM – Displayed in the upper-most section of Figure 4.11.

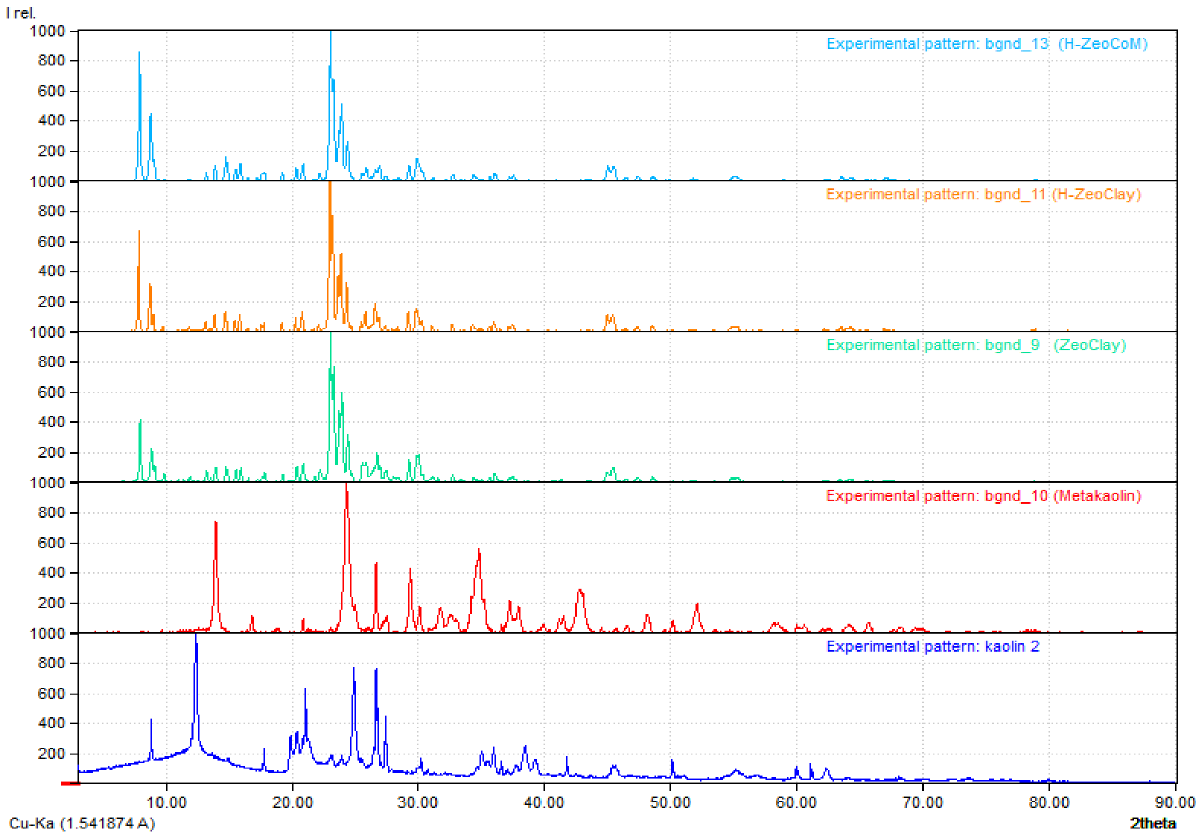


Figure 4.11: XRD patterns for zeolization products starting from Kaolin (N.K$_2$) to Clay-based zeolite (H-ZeoClay)

As observed above, the XRD pattern of the kaolin (N.K$_2$) starting raw material, is much relatively deviated to the first intermediate M.K$_2$ (metakaolin) product with regards to majority of the peaks in its pattern; such as at peak values of 2θ ≈ 10^0; 12; 20; 22; 50; 60^0. Further along the production, the XRD pattern of kaolin (N.K$_2$) did not closely correspond to that of the second intermediate product (ZeoClay) along the procedure.

The XRD pattern of the latter (ZeoClay) also significantly deviates from that of the metakaolin (its precedent intermediate product) and was the first observed to exhibit a triplet at 22-25^0 2θ. This values as reported by Viswanadham et al., 2011 partly represents an initial attempt to Zeolite (ZSM-5) framework. Further on, the relative deviation in the pattern of the ZeoClay from M.K$_2$ makes the graphical comparison of these two as a non- reliable mean to predict for ZeoClay as a direct derivative from M.K$_2$ (Metakaolin) along the production procedure of H-ZeoClay. This deviation also reveals the significant effect of the hydrothermal reaction in the transformation of M.K$_2$ (Metakaolin) to ZeoClay and H-ZeoClay.

Further on along the production procedure, the XRD pattern of the ZeoClay was observed to highly correspond to that of its derivative H-ZeoClay (Fourth pattern upwards). These two mainly match at peak values at 7-10^0; 3-6^0 ; 20-21.5^0; 22-25^0 ; 26-27^0; 29-30.5^0 and 45^0 2θ.

It was also further observed in Figure 4.14 that the XRD pattern of the H-ZeoClay (Clay-based Zeolite) did in turn match the most that of the H-ZeoCOM (commercial zeolite) catalyst with regard to almost all peak values (As very like the above). A doublet at 6-10^0 2θ along with a triplet at 22-25^0 were observed along the (peak) pattern of the clay-based zeolite (H-ZeoClay) and these are the most significant peaks, in agreement to literature (Viswanadham et al., 2011: 299-300), to confirm that the clay-based zeolite catalyst represents the structural framework of ZSM-5 zeolite.

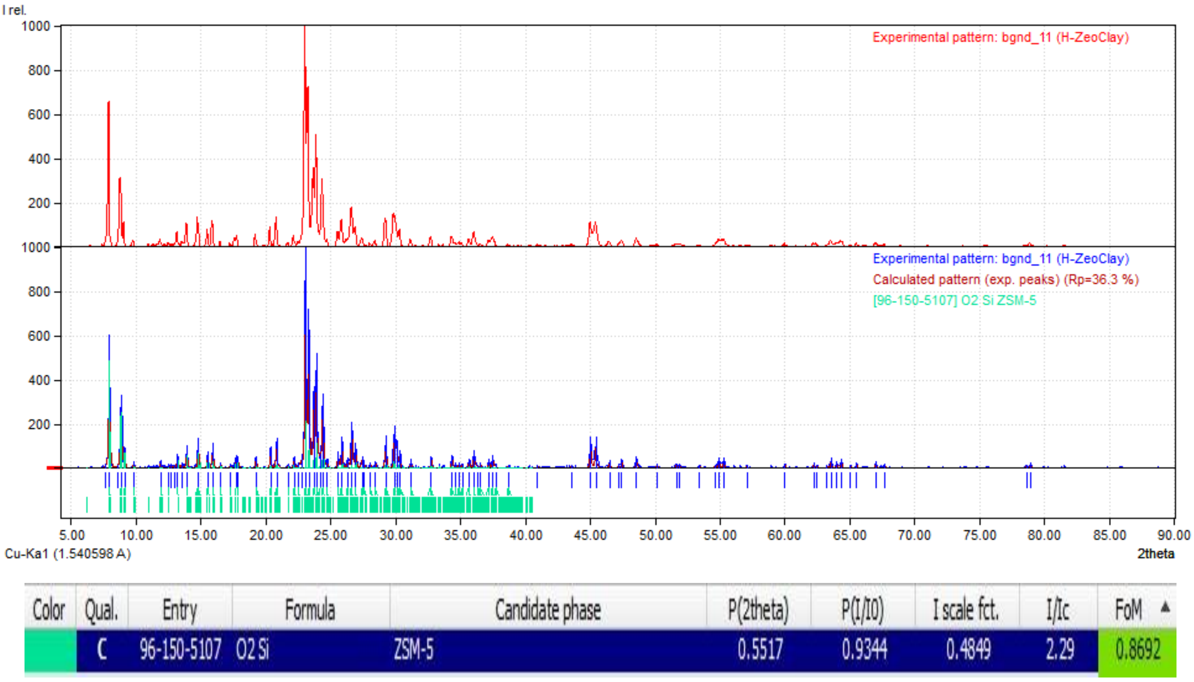
The peak value or pattern at 25^o 2θ was found to be the most common of all the intermdiate products along the production procedure of H-ZeoClay, including the H-Zeoclay itself and H-ZeoCOM. This reference value in the pattern at least serves to prove that the clay-based zeolite (H-ZeoClay) in particular was derived from $N.K_2$ and $M.K_2$ (Kaolin and metakolin) and that this catalyst had a similar structural framework as that of H-ZeoCOM catalyst.

Moreover, a mere inspection and close comparison of the XRD patterns in Figure 4.11, serves as prove for identification of H-ZeoClay as a zeolite catalyst. Additional information of the respective XRD patterns are discussed in section 4.1.4.1 and this serves as additional prove for identification of H-ZeoClay as a Zeolite catalyst.

4.1.4.1 XRD pattern similarities of H-ZeoClay and ZSM-5 zeolite

The XRD data (as shown in Figure 4.12) revealed that H-ZeoClay catalyst, resulted to ZMS-5 phase by 86.92% match, and to the phase of an aluminosilicate-based compound ($Al_3.43Si_{92}.S_7 O_{192}$) by 89.95 %

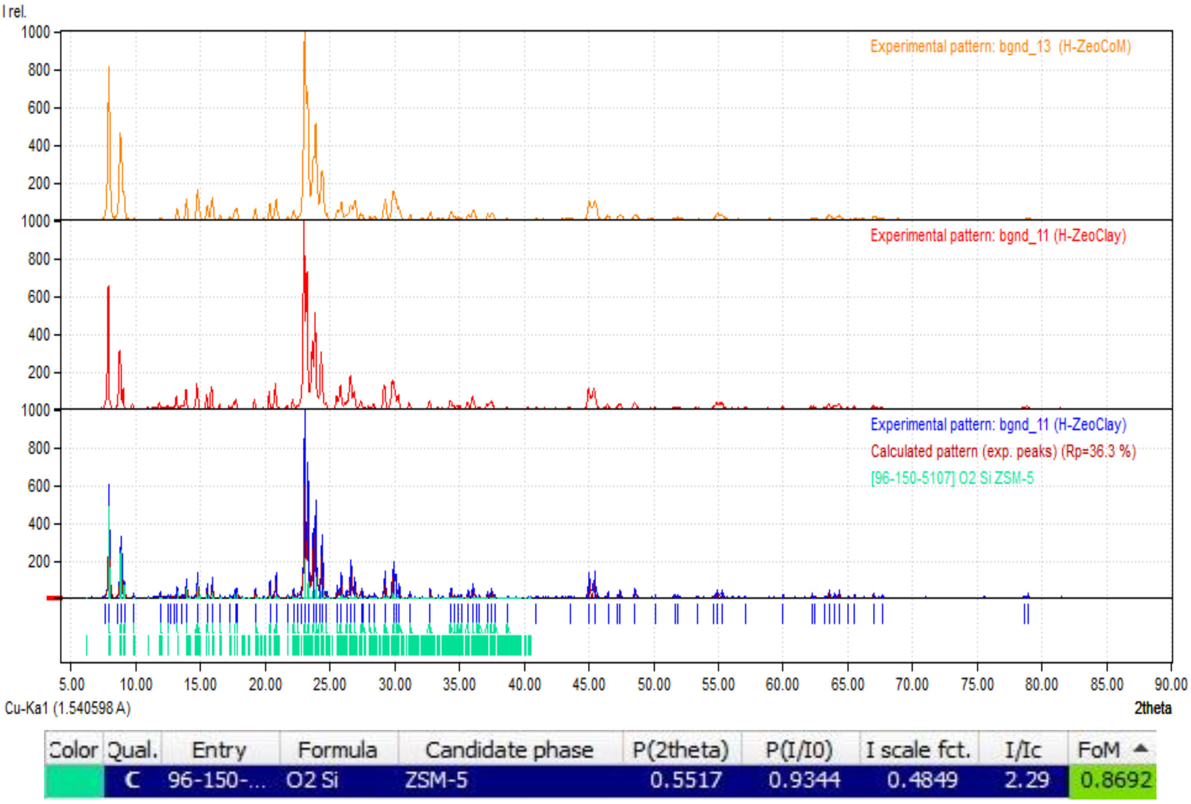
86.92 % Figure of Match is quiet acceptable and outstanding in proving the indentifty of H-ZeoClay (clay-based zeolite) as a zeolite catalyst, precisely the ZSM-5 catalyst.



Color	Qual.	Entry	Formula	Candidate phase	P(2theta)	P(I/I0)	I scale fct.	I/Ic	FoM ▲
🟩	C	96-150-5107	O2 Si	ZSM-5	0.5517	0.9344	0.4849	2.29	0.8692

Figure 4.12: XRD pattern of H-ZeoClay with respective Figure of Match to ZSM-5 catalyst

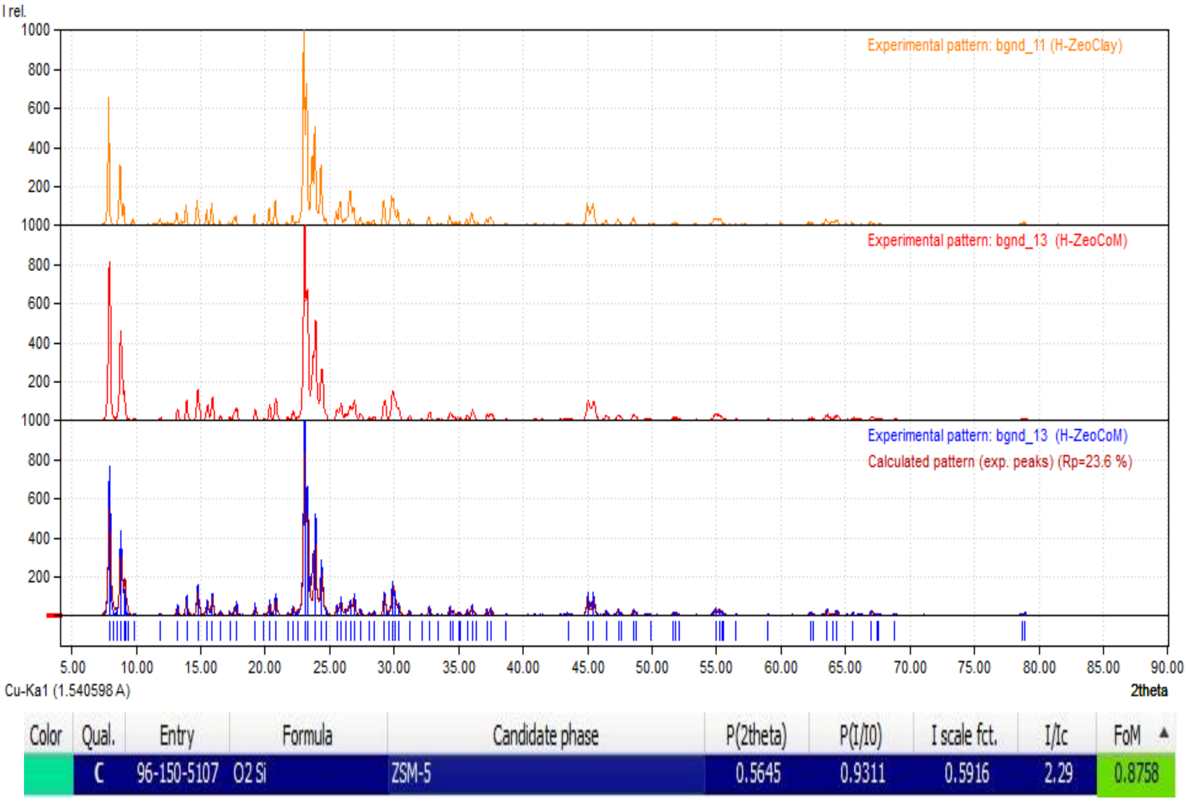
The XRD data of H-ZeoClay was then compared to that of H-ZeoCOM (Commercial zeolite), relative to ZSM-5 catalyst. The pattern of both samples simply by inspection as shown in Figure 4.13-14, was observed to be very closely corresponding.



Color	Qual.	Entry	Formula	Candidate phase	P(2theta)	P(I/I0)	I scale fct.	I/Ic	FoM ▲
🟩	C	96-150-...	O2 Si	ZSM-5	0.5517	0.9344	0.4849	2.29	0.8692

Figure 4.13: Comparison of H-ZeoClay to H-ZeoCOM catalyst by XRD pattern and respective FoM of H-ZeoClay to ZSM-5

The experimental XRD pattern of H-ZeoClay was found to match that of the ZSM-5 catalyst in phase by 86.92% . The H-ZeoCOM used for comparison on the other hand and as shown in Figure 4.14, resulted to ZSM-5 phase by 87.58 % match.



Color	Qual.	Entry	Formula	Candidate phase	P(2theta)	P(I/I0)	I scale fct.	I/Ic	FoM ▲
🟩	C	96-150-5107	O2 Si	ZSM-5	0.5645	0.9311	0.5916	2.29	0.8758

Figure 4.14: Comparison of H-ZeoCOM to H-ZeoClay catalyst by XRD pattern and respective FoM of H-ZeoCOM to ZSM-5.

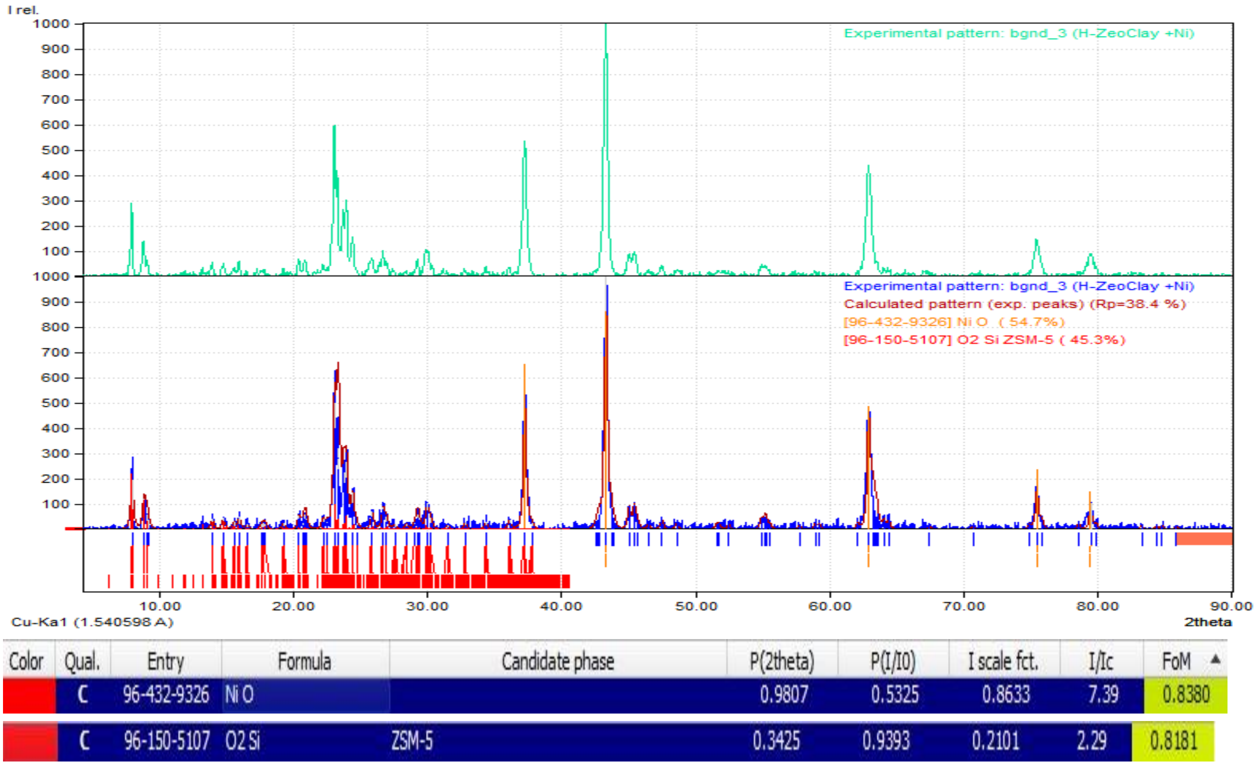
Further on, the XRD patterns of both H-ZeoClay and H-ZeoCOM were found to match the phase of an alumina-silicate compound ($Al_3.\ 43\ Si_{92}.S_7\ O_{192}$) the most by 89.45 % and 89.24 % respectively. The difference therefore in their relative Figure of Match to ZSM-5 catalyst was only 0.66 %, and 0.21 % relative difference to their Figure of Match to the alumina-silicate compound. Hence the H-ZeoCOM in reference to ZSM-5 zeolite, resulted to a very comparable phase identity to that of H-ZeoClay.

Moreover, the XRD patterns of the two catalysts by mere inspection in Figure 4.14-15 correspond the most through matching of various and similar peak values of 2θ. The XRD pattern of the two catalysts (H-ZeoClay and H-ZeoCOM) conform to that of ZSM-5 Zeolite catalyst and represent the structural framework of ZSM-5 zeolite with regard to most peak values. These more precisely, refer to the most identifying peak values of H-ZeoClay as ZSM-5 catalyst at 6-10^0 and at 22-25^0 2θ.

The above findings also serve to prove that the H-ZeoClay (Clay-based zeolite) is the ZSM-5 zeolite catalyst by identity, as similarly applies for H-ZeoCOM (Commercial Zeolite). The H-ZeoClay and H-ZeoCOM are therefore identical by phase.

4.1.5 Effect of metal promotion on phase composition of the clay-based zeolite

The XRD results reported through Figure 4.15 revealed that the pattern of H-ZeoClay (Ni) sample was found to correspond to NiO compound and ZSM-5 catalyst by 83.8 % and 81.8 % respectively. The pattern of H-ZeoClay sample on the hand, was rather revealed to correspond to that of NiO and ZSM-5 by 36.05 % and 86.92 % respectively. Increase in phase composition of NiO therefore serves as indication of successful loading of the metal into the H-ZeoClay catalyst during preparation. Further on as shown in Figure 4.16, the Match Software (Version 3.1) used for interpretation of XRD results also revealed the weight percentage of NiO onto H-ZeoClay (Ni) as 54.7 % (NiO / H-ZeoClay(Ni), w/w %), whereas this was detected only by 1.5 wt.% onto the precursor H-ZeoClay catalyst. The balance weight content to NiO in the H-ZeoClay (Ni) was ZSM-5 by 45.3 % as displayed in Figure 4.15.



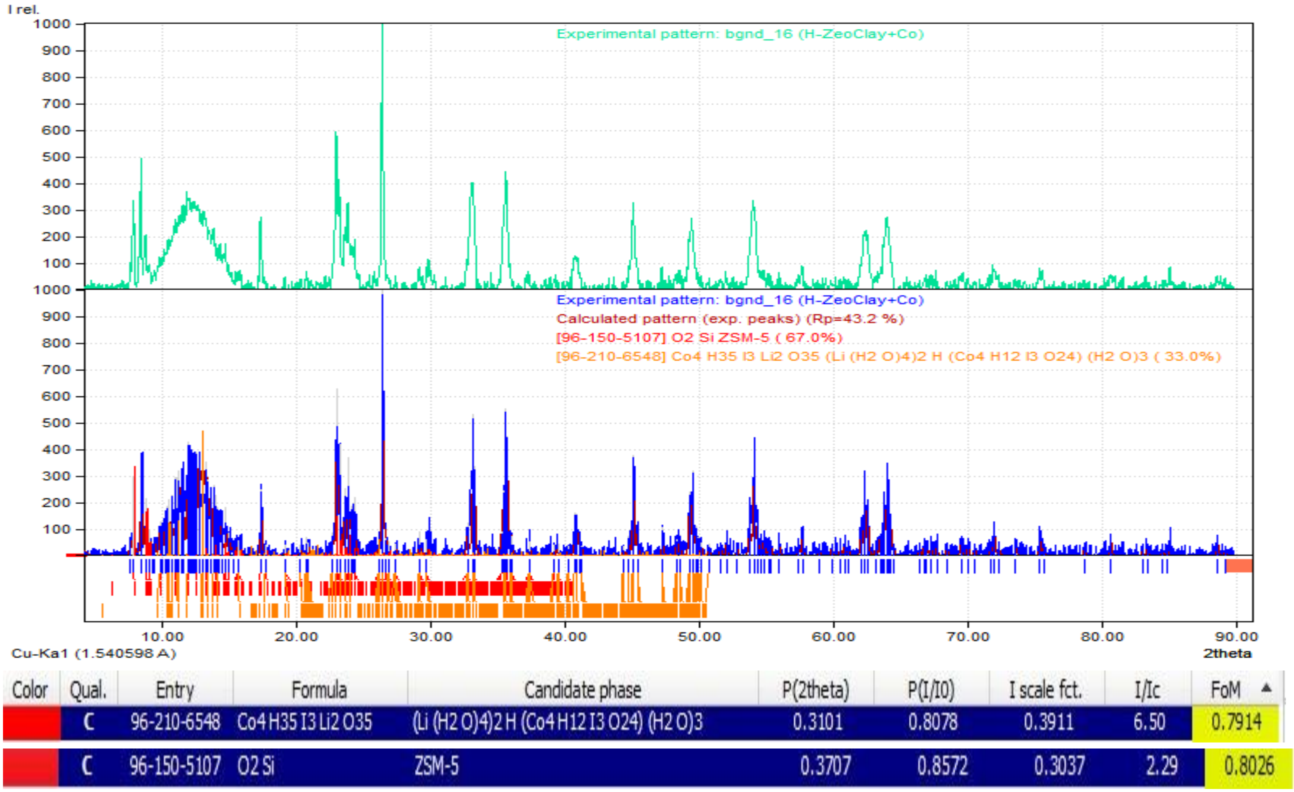
Color	Qual.	Entry	Formula	Candidate phase	P(2theta)	P(I/I0)	I scale fct.	I/Ic	FoM ▲
🟥	C	96-432-9326	Ni O		0.9807	0.5325	0.8633	7.39	0.8380
🟥	C	96-150-5107	O2 Si	ZSM-5	0.3425	0.9393	0.2101	2.29	0.8181

Figure 4.15: XRD pattern of H-ZeoClay (Ni) catalyst

The above discussed and shown are among indications to successful impact of metal promotion on phase composition of H-ZeoClay.

The XRD data of the resultant H-ZeoClay (Co) on the other hand, was found to correspond a Cobalt-based compound (i.e. $Co_4 H_{35} I_3 O_{24}$) *by* 79.14 % and the ZMS-5 catalyst by 80.26 %. The H-ZeoClay the precursor catalyst, was rather respectively 50.2 % and 86.92 % corresponding by phase to the Cobalt-based compound and the ZMS-5 catalyst. Further revealed by XRD results in Figure 4.16, the weight percentage of the the Cobalt-based compound on to H-ZeoClay (Co) was 33 % (w/w) whereas this was detected as 5.4 wt.% in the precursor H-ZeoClay catalyst. The balance in weight percentage was the phase content of ZSM-5 catalyst. The above finding also serves as proof to successful metal impregnation during the preparation of H-ZeoClay (Co) from H-ZeoClay catalyst.

The XRD pattern of H-ZeoClay (Co) catalyst is shown in Figure 4.16. This is also further shown together with that of H-ZeoClay (Ni) and hence these in comparison to the XRD pattern of their precursor H-ZeoClay catalysts in Figure 4.17.



Color	Qual.	Entry	Formula	Candidate phase	P(2theta)	P(I/I0)	I scale fct.	I/Ic	FoM ▲
🟥	C	96-210-6548	Co4 H35 I3 Li2 O35	(Li (H2 O)4)2 H (Co4 H12 I3 O24) (H2 O)3	0.3101	0.8078	0.3911	6.50	0.7914
🟥	C	96-150-5107	O2 Si	ZSM-5	0.3707	0.8572	0.3037	2.29	0.8026

Figure 4.16: XRD pattern of H-ZeoClay (Co) catalyst

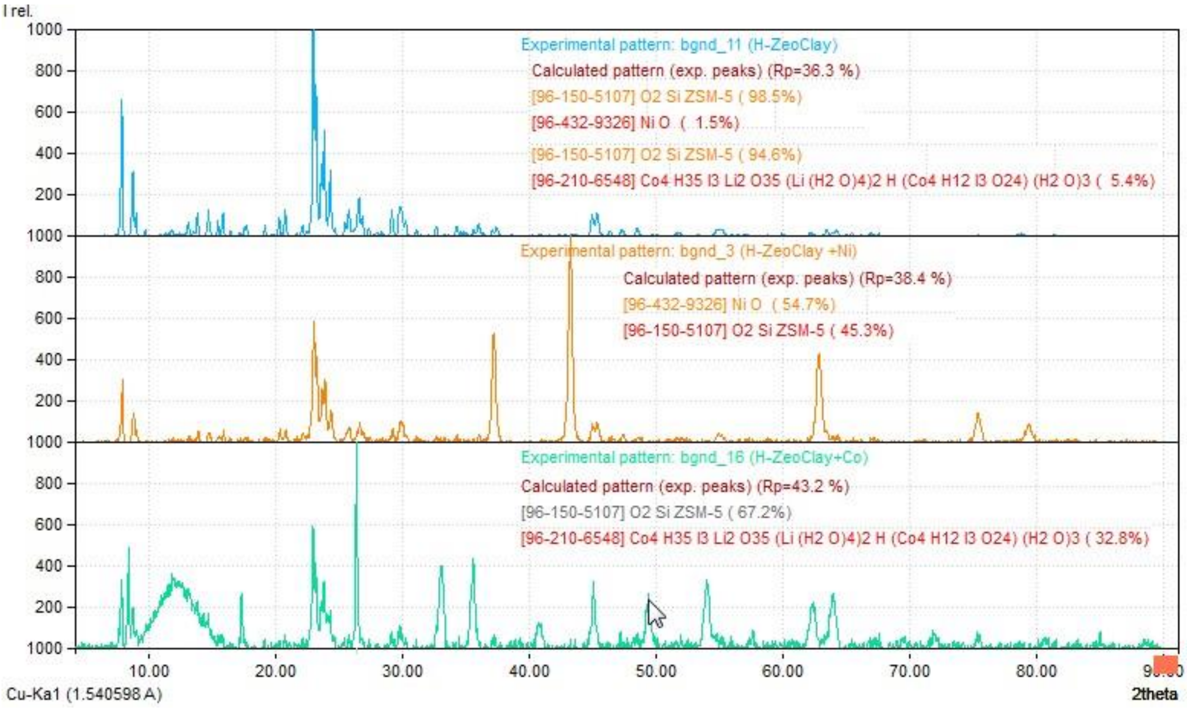


Figure 4. 17: Comparison of the XRD pattern of H-ZeoClay to that of H-ZeoClay (Co) and of H-ZeoClay (Ni) catalyst.

4.1.5.1 Effect of promotion on metal loading onto the catalyst (H-ZeoClay)

The XRD patterns as observed in Figure 4.17, revealed the weight content of Nickel onto H-ZeoClay (Ni) to be 54.7 %; while that of Cobalt onto H-ZeoClay (Co) was found to be 33 % (w/w).

The impregnation of H-ZeoClay by Nickel (Ni) and Cobalt (Co) therefore proved to be successful due to increased relative loading of metal element observed in the promoted catalyst. It is observed that the resultant loading of the metal elements onto the promoted catalysts was however higher than the 25 % (w/w) measured in the experiment. For this reason it is therefore recommended to repeat the experiment to eliminate the error. Alternatively the experiment could be repeated by impregnating the H-ZeoClay sample with metal loading of less than 25 % (w/w), so that the resultant amount in the promoted catalysts correspond to metal loading range of 20-25 %.

Table 4.5 compares the weight percentage loading of metal elements into H-ZeoClay, prior and after the Incipient Wetness Impregnation (IWI). This further reports and compares the pattern of H-ZeoClay catalyst and that of the promoted catalysts to the respective transition metalss. In otherwords, the effect of metal impregnation on relative phase and metal content of H-ZeoClay.Content and loading of each metal element onto the H-ZeoClay catalyst, as well as the phase match of this catalyst to metal elements, before and after promotion.

Table 4.5: Effect of metal promotion on metal loading and corresponding phase of H-ZeoClay.

Effect of promotion	Wt.% loading of metal onto catalyst (XRD result)		**FoM**	
	NiO	Co4	NiO	Co4
Before Promotion (XRD Result)	1.5	5.4	36.05	50.2
On Promotion (Actual experimental)	25	25	-	-
After Promotion (XRD Result)	54.7	33	83.8	79.14

NB: FoM – is the Figure of Match of the experimental sample to the theoretical one (Given through XRD data).

4.2 Activity of clay-based catalysts on bioethanol conversion

4.2.1 Activity of non-modified clays on bioethanol conversion

All the obtained clay catalysts (in their non-modified natural state) were found active in the conversion bioethanol. Among these, N.B (bentonite clay) as shown in Figure 4.18, was the most active in the conversion of bioethanol with 84.95 % conversion (Under Fixed reaction conditions).

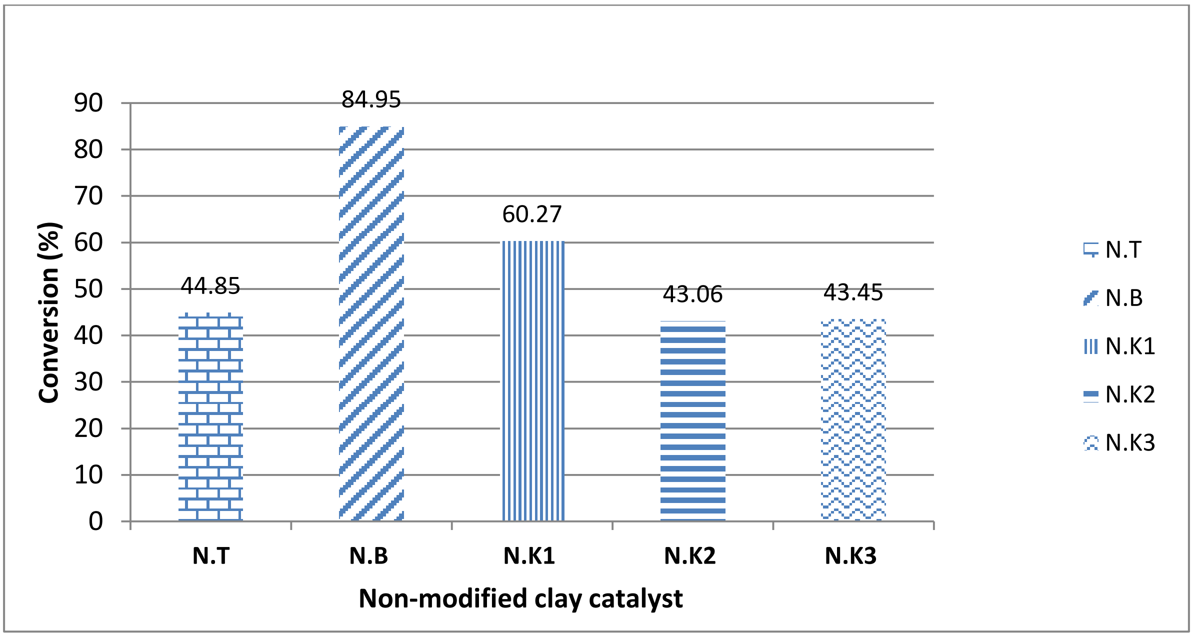


Figure 4.18: Activity of non-modified clay catalysts on bioethanol conversion (At fixed reaction condition of 350 °C and 6 hours)

Such high activity of N.B catalyst in the conversion of bioethanol corresponds to the major phase content of montmorillonite mineral in bentonite clay (Igbokwe et al., 2011). Bentonite and montmorrilonite minerals are potential and predominant catalysts in numerous applications - Such as water purification process (Beall, 2003); benzylation of benzene (Pushpaletha et al., 2005), including little application that open literature has reported on bentonite for the catalytic conversion of bioethanol to hydrocarbons (Widjaya et al., 2013:69).

N.T (Non-modified talc clay), on the other hand, had the lowest conversion of bioethanol (i.e. 44.85 %) compared to the rest of non-modified clay catalysts (Under simlar reaction conditions). For such a low activity but however promising, no work in the open literature has been thus far reported on the use of talc clay for catalytic conversion of bioethanol.

Moreover, the major mineral content in bentonite, montmorrilonite, and kaolin are the two most important clays used in the manufacture of catalysts (Eman, 2012). This information serves as evidence in support to kaolin (Precisely N.K$_1$ for 60.27 % conversion) following bentonite catalyst for best activity in the catalytic conversion of bioethanol (among other non-modified clay catalysts). For this purpose, bentonite (N.B) and kaolin catalysts were further used in this work for subsequent development of clay-based catalysts by various methods.

4.2.2 Effect of beneficiation and acid modification on bioethanol conversion

N.B catalyst as mentioned earlier, was selected for further catalyst modifications, benefication and acid modification. Clay beneficiation (From N.B to B.B catalyst) led to a slight decrease in the activity of the catalyst on bioethanol conversion, from 84.95 to 81.01 % (under fixed reaction conditions of 6 hours and 350 ^{o}C). The performance of various bentonite clays are shown in Figure 4.19.

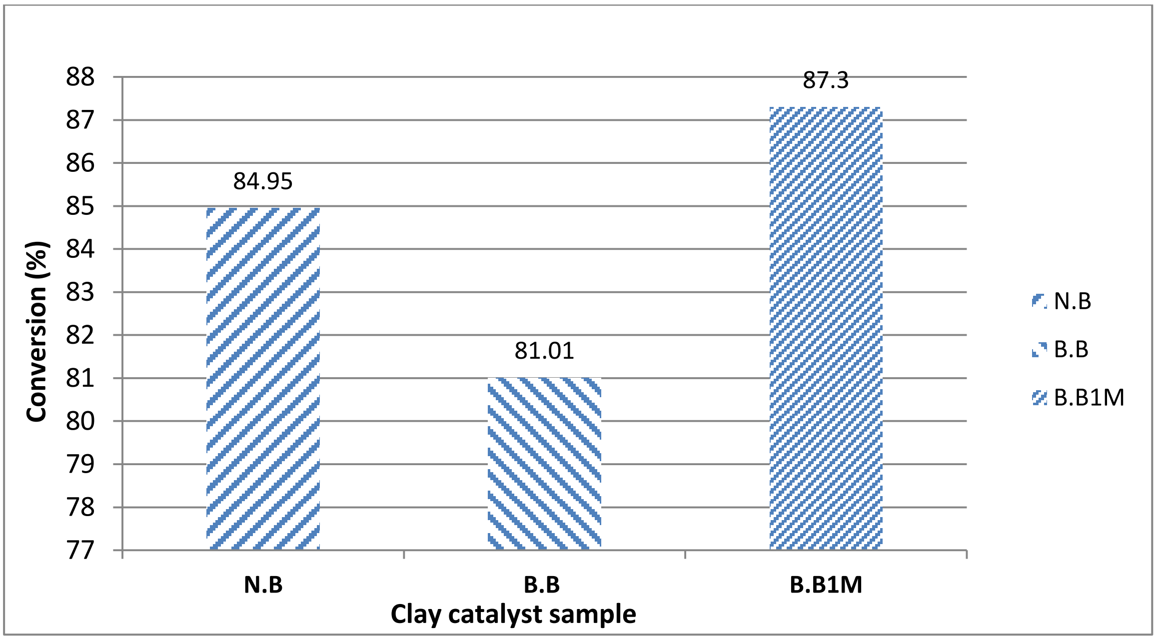


Figure 4.19: Effect of clay beneficiation and acid modification on bioethanol conversion (At fixed reaction condition of 350 ^{o}C and 6 hours)

Acid modification of B.B catalyst further on with the experiment, resulted to increase in the activity of the catalyst on bioethanol conversion (81 to 87.3 %). This increase as also observed in Figure 4.19, compensate for the drop in the catalyst activity that was observed as a result of beneficiation. In other words, acid modification and further enhanced the activity of the clay catalyst in the conversion of bioethanol.it is possible that beneficiation resulted in finer particles but fewer active sites which were further enhanced with acid modification, while there is a possibility of structural changes, active acid sites are likely to have been formed which were active in the bioethanol conversion.

4.2.2.1 Overall effect of beneficiation and acid-modification on bioethanol conversion

Beneficiation and subsequent acid modification of bentonite catalyst viewed as a whole, had therefore led to increased catalytic activity on bioethanol conversion (84.95 to 87.28 %). This increase however as observed in Figure 4.20, was lower than that observed as a result of the subsequent acid modification approach – As observed in Figure 4.19 (i.e. 6.3 % increased bioethanol conversion due acid modification). Hence, modifying the B.B catalyst with sulphuric acid in subsequent to clay beneficiation, was the most effective approach to increased catalytic activity on bioethanol conversion

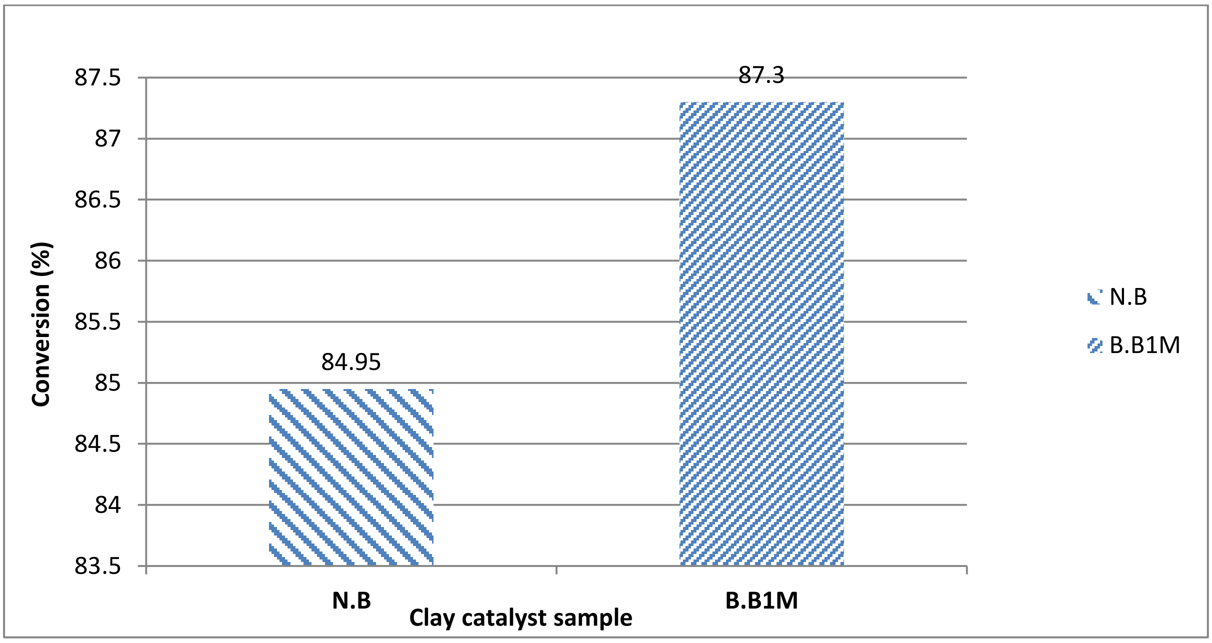


Figure 4.20: Overall effect of catalyst beneficiation and acid-modification on bioethanol conversion (At fixed reaction conditions of 350 ^{0}C and 6 hours).

Hence in contrast to clay beneficiation, such increase in catalytic activity as a result of acid modification, makes it recommending to bypass the beneficiation approach and directly modify the N.B catalyst with acid. This as recommended, is promisingly assumed to also be the most favourable approach to increase the catalytic activity of clay on bioethanol conversion.

4.2.3 Activity of produced clay-based zeolite on bioethanol conversion

The $N.K_2$ and B.B were the clays initially selected for the production of zeolite. These two catalysts were chosen because they contained the highest Si/Al ratio - $N.K_2$ had the highest Si/Al ratio among the non-modified clay materials, followed by N.B as shown in Table 4.1 (pg.72). Zeolite synthesis using B.B however, could not continue due the fact that the bentonite material became hard during drying, following sodium hydroxide fusion. This owes to the binding property of the materials when mixed into sodium hydroxide solution. Bentonite (B.B) was unlike $N.K_2$, which the latter as a kaolinite clay specie, is the most commonly and preferable for zeolite synthesis. Kaolinite have been reported as the purest clay minerals and kaolin when used for zeolite synthesis, contribute to a relatively high thermal stability of zeolite (Emam, 2013:361).

The H-ZeoClay produced from $N.K_2$ clay in adopting the hydrothermal synthesis method led to 99.91 % bioethanol conversion, which exceeds the conversion activity of all the non-zeolite clay-based catalysts produced earlier in this work. This is observed in Figure 4.21 .

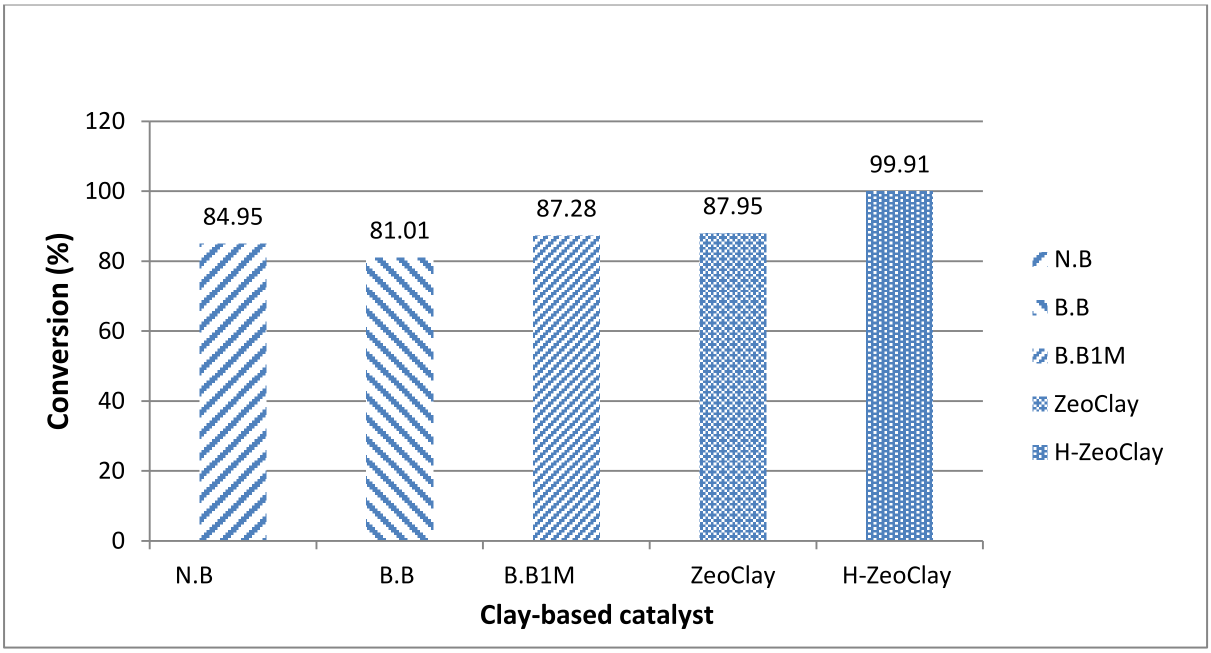


Figure 4.21: Catalytic activity of the H-ZeoClay and other clay-based catalysts on bioethanol conversion (Fixed reaction conditions of 350 ^{0}C and 6 hours).

The finding from Figure 4.21 shows that bioethanol conversion obtained over ZeoClay (Non-protonated clay-based zeolite) is very close comparable to that obtained by $B.B_{1M}$ (Acid-modified catalyst) under fixed reaction conditions (i.e. 87.28 % and 87.95 %). Protonation of the latter catalyst (ZeoClay to H-ZeoClay) with ammonium chloride therefore led to increased activity of ZeoClay (Clay-based zeolite) catalyst on bioethanol conversion (From

87.95 % to 99.91 %). The H-ZeoClay (Protonated clay-based zeolite) therefore in this work was found thus far to have led to highest conversion of bioethanol among the produced clay-based catalysts. This serves as evidence of enhaced acidity of the catalyst due to protonation. Similarly, it was earlier found and as also observed as shown in Figure 4.21 that acid enhancement of a catalyst, $B.B_{1M}$ (bentonite) catalyst in particular (as a result of acid modification), led to higher bioethanol conversion than N.B and B.B catalyst.

The protonation of clay-based zeolite has therefore proven favourable on bioethanol conversion and this outcome similarly corresponds to performance of zeolite catalysts in open literature. Moreover, the use of H-ZeoClay (Protonated clay-based zeolite) in comparison to ZeoClay catalyst for bioethanol conversion, has led to enhanced hydrocarbons distribution and selectivity in both liquid and gaseous product stream from the reaction.

4.2.3.1 Activity of the produced clay-based zeolite and that of other synthesised clay-based catalysts

The clay-based zeolite (H-ZeoClay) led to bioethanol conversion that was very much comparable to that obtained over the H-ZeoCOM (commercial zeolite) in this work (99.91 % ≈ 99.97), for reaction under fixed conditions (6 hours at 350 °C and 2 h^{-1} WHSV). The activity of H-ZeoCOM however, slightly exceeded that of H-ZeoClay .

Nonetheless, the produced H-ZeoClay catalyst thus far and as compared to other clay-based catalysts produced in this work, was found to have led to highest activity in the conversion of bioethanol .

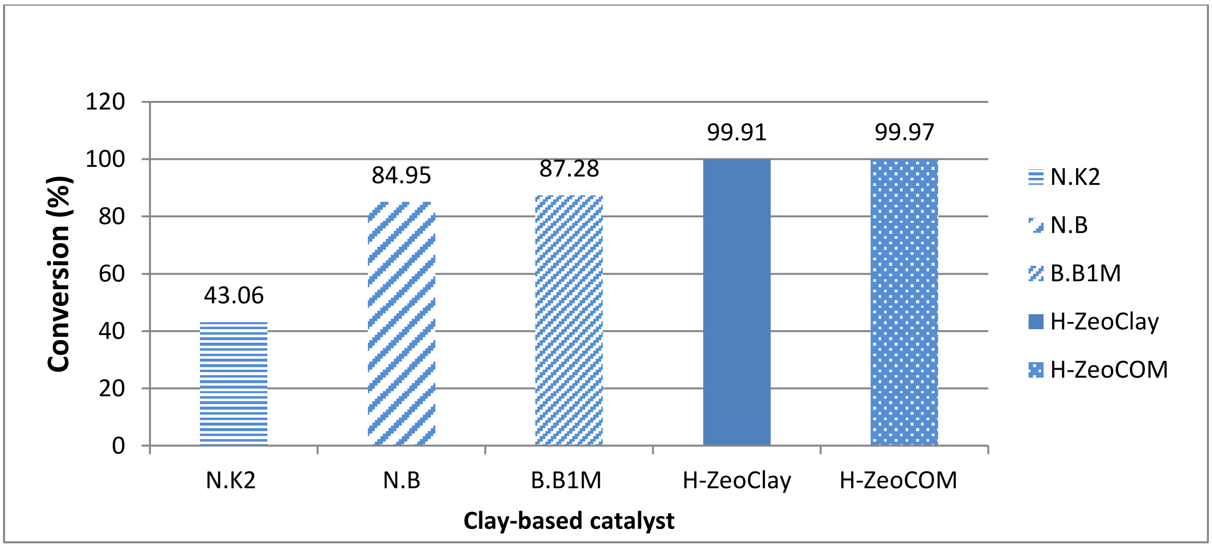


Figure 4.22: Comparative study between clay-based zeolite and other synthesised catalysts (At Fixed reaction conditions of 350 ^{0}C and 6 hours).

4.2.4 Effect of metal promotion on the activity of clay-based zeolite

The H-ZeoClay employed under fixed reaction conditions as other clay-based catalysts (Shown earlier in Figure 4.22), was earlier found to be the most active catalyst in the conversion of bioethanol by 99.91 %. H-ZeoCOM was exceptional to the above as this was rather used as yardstick (for comparison purpose) to H-ZeoClay catalyst.

Promotion (by impregnation) of H-ZeoClay with Nickel, resulted to further and most increased activity of the catalyst on bioethanol conversion to 99.99 % conversion. Hence the resultant catalyst, H-ZeoClay(Ni), thus far (as shown in Figure 4.23) proved to have led to highest conversion of bioethanol in this work.

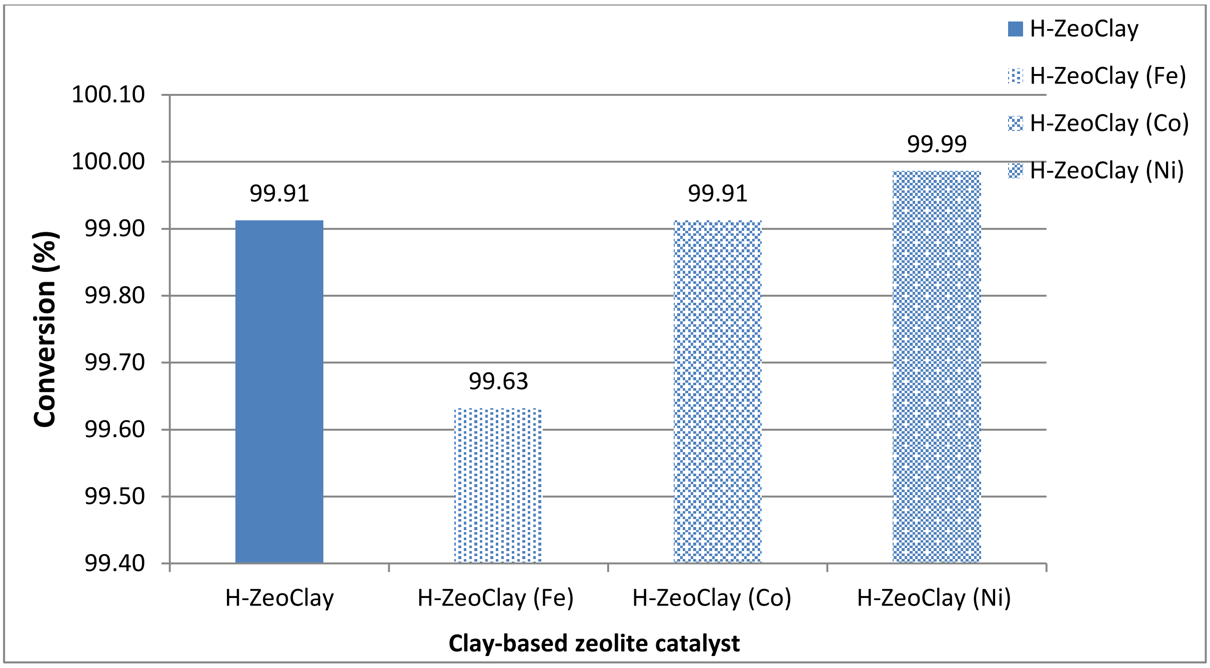


Figure 4.23: Effect of metal promotion on bioethanol conversion (Fixed reaction conditions of 350 °C and 6 hours)

Further on, promotion of H-ZeoClay with Cobalt(Co), resulted to no impact on the conversion of bioethanol, except on product distribution. In other words both H-ZeoClay and H-ZeoClay(Co) led to 99.91 % conversion. Unlike H-ZeoClay(Ni) and H-ZeoClay(Co) , processing of bioethanol over Iron(Fe) promoted clay-based zeolite (H-ZeoClay(Fe)), resulted to further decrease in bioethanol conversion to 99.63 % (As also shown in Figure 23).

Henceforth, the order of increase in bioethanol conversion by metal-impregnated clay-based zeolite is H-ZeoClay (Ni) > H-ZeoClay > H-ZeoClay (Co) > H-ZeoClay (Fe). In target of favourable bioethanol conversion, the use of Cobalt for promotion could be omitted to save on cost of promotion and this will result to the above order of increase as H-ZeoClay (Ni) > H-ZeoClay > H-ZeoClay (Fe).

From the overall observation of the discussion above and precisely made through Figures 4.25 and 4.26, Clay-based zeolite (Such as H-ZeoClay, H-ZeoClay (Fe)) compared to non-zeolite clay-based catalysts (such N.B and B.B_{1M}), were in conclusion found to be the most active clay-based catalysts for the conversion of bioethanol. Much more work to produce these catalyst for bioethanol conversion can therefore be recommended.

4.2.5 Effect of operating conditions on catalytic activity of clay-based catalysts

4.2.5.1 Effect of reaction temperature on bioethanol conversion

Increase in reaction temperature (from 350 to 400 ^oC) over H-Zeoclay, resulted to slight increase on bioethanol conversion as shown in Figure 4.24.

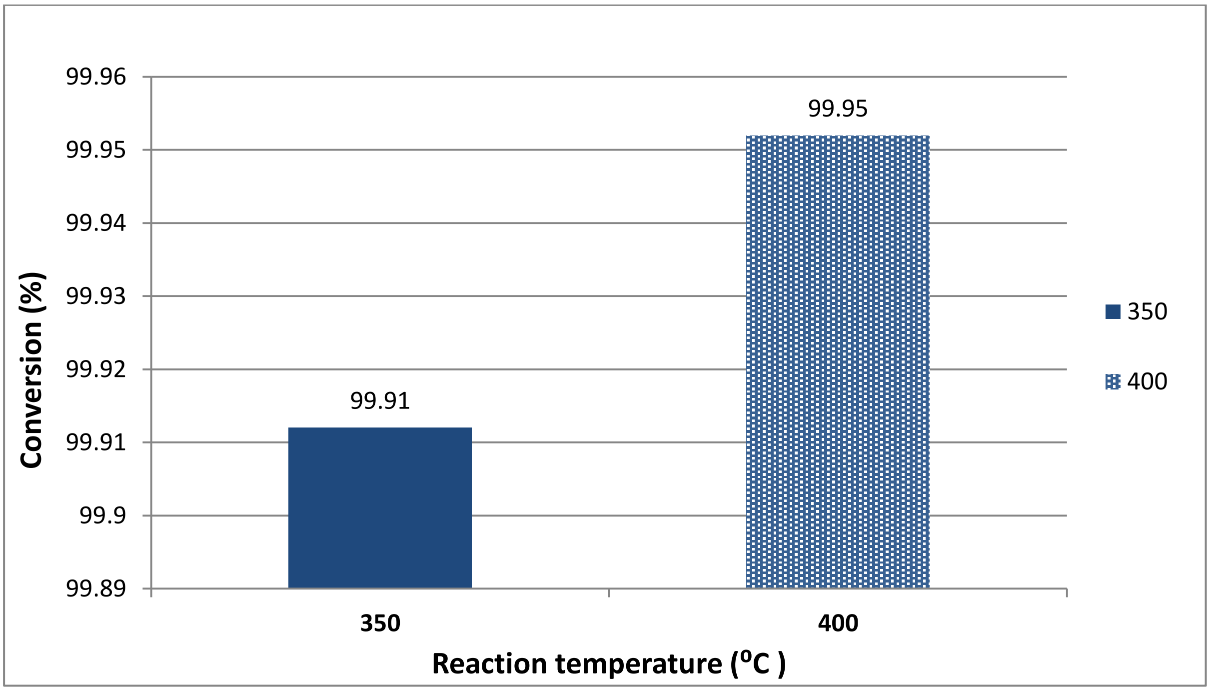


Figure 4.24: Effect of reaction temperature on bioethanol conversion over clay-based zeolite (H-ZeoClay) catalyst (6 hour fixed reaction time)**.**

Bioethanol conversion is an endorthermic process, which normally should corresponds to increased reaction activity as a result of increase in reaction temperature. Catalytic activity therefore in this regard, is assumed to have played a minor role as compared to the rise in reaction temperature condition.

Increase in reaction temperature nevertheless, resulted to catalytic conversion that was comparably higher than that obtained through catalyst promotion with Iron and cobalt for the reaction at 350 °C. This however did not exceed that obtained as a result of catalyst (H-ZeoClay) promotion with Nickel (For the reaction at 350 °C), as shown in Figure 4.25.

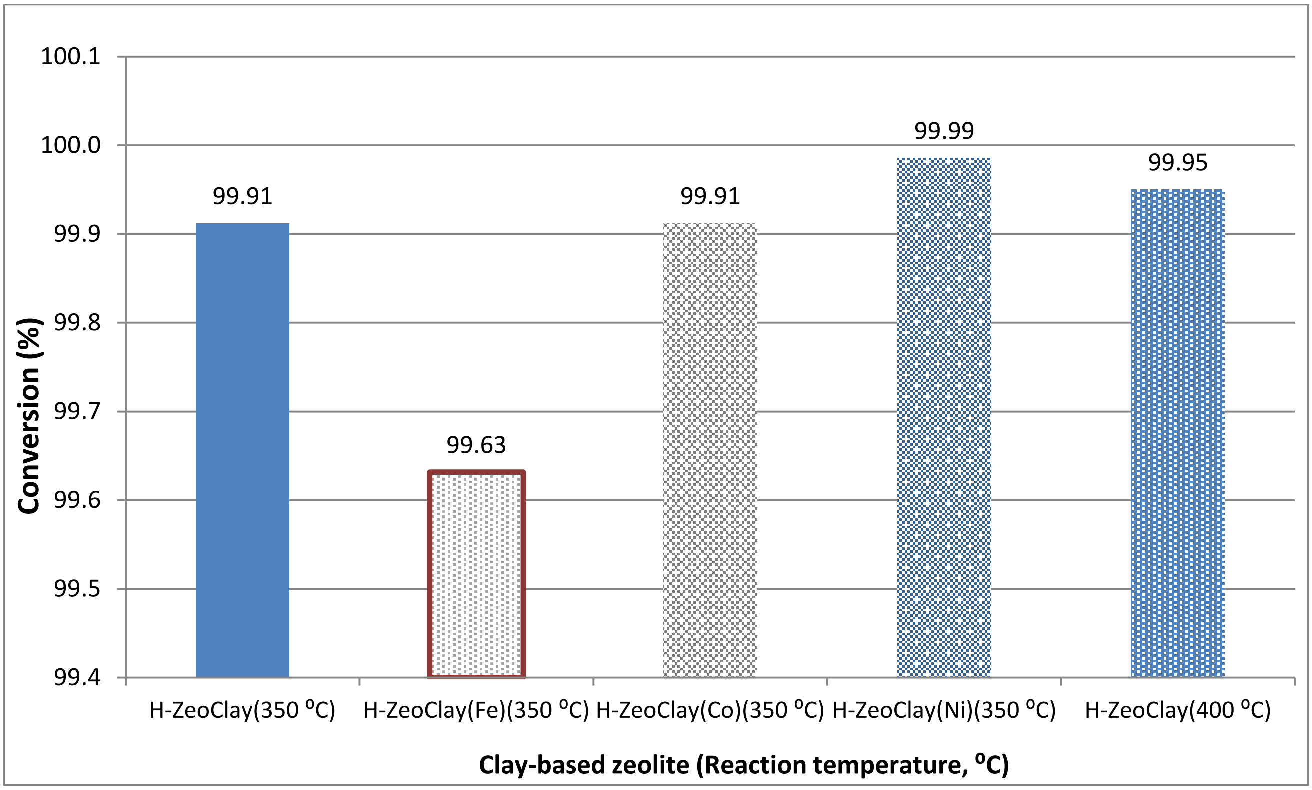


Figure 4.25: Comparison between increase in reaction temperature and catalyst promotion for bioethanol conversion (6 hour fixed reaction time)

From the above observed, it is deduced that all metal promoted catalysts are will result to better activity than H-ZeoClay if these are employed at same increased reaction temperature as the H-ZeoClay catalyst. Thus far however, H-ZeoClay (Ni) catalyst employed at 350 °C still reflectthe relatively highest catalytic activity on bioethanol conversion. It is therefore insignificant to increase the temperature to 400 °C when employing Nickel promoted catalyst. This in turn makes the reaction less energy requiring.

The practical possibility to attain the highest possible or even maximum conversion of bioethanol could be due if the H-ZeoClay (Ni) catalyst were employed at such increased reaction temperature of 400 °C, or even above (Provided fixed reaction time). This is however among the major recommendations.

4.2.5.2 Investigation for optimum reaction time

The catalytic activity of clay-based catalysts in this work was mostly carried out for a period of 6 and 2 hours. Reaction time was then assessed on the non-modified and modified clay catalyst (N.B; B.B; B.B_{1M}), including the zeolite based catalyst in order to determine the optimum operating conditions for the activity of clay-based catalysts on bioethanol conversion. Reaction temperature was investigated at 350 °C and 400 °C.

The overall observation reveals that bioethanol conversion over clay-based catalysts for 6 hour reactions exceeds that obtained for 2 hour reactions. This observation is deducted from Figure 4.26.

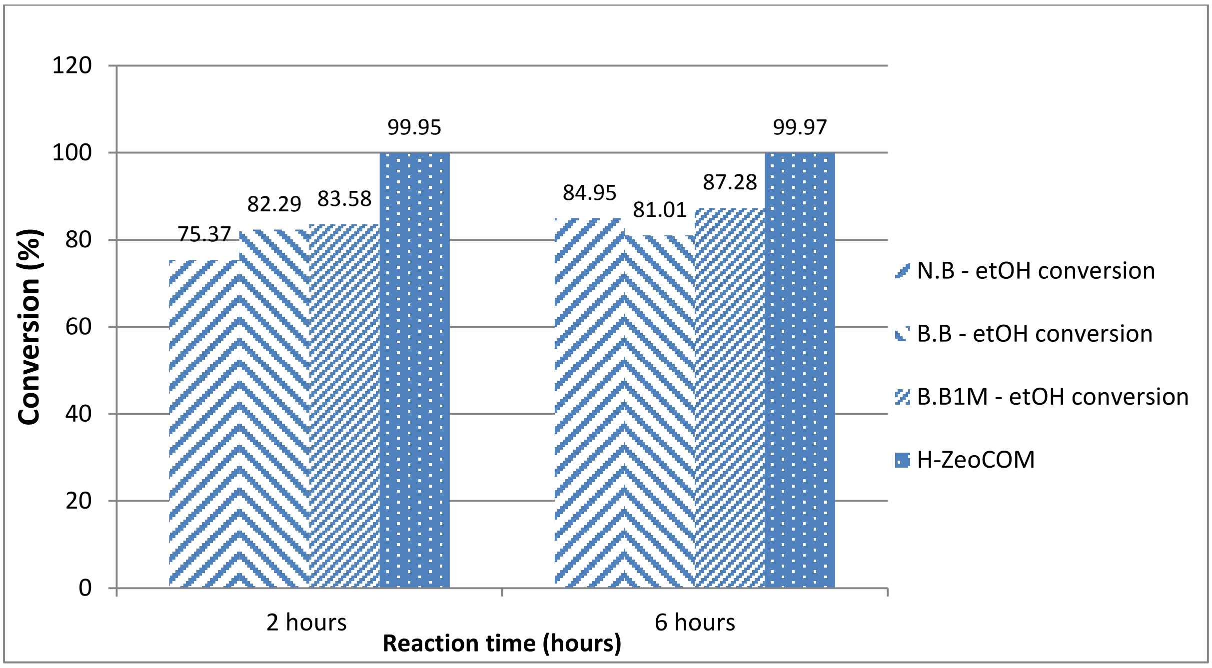


Figure 4.26: Effect of variation in reaction time on bioethanol conversion over the clay-based catalysts (350 °C fixed reaction temperature).

Increasing the reaction time is among the (most) favourable approaches for increased or optimum conversion of bioethanol. This is also an indication that the activity of clay-based catalysts in general, was due for longer reaction time.

The above discussed is particularly supported using B.B_{1M} for additional reaction time of 4 hours as shown in Figure 4.27.

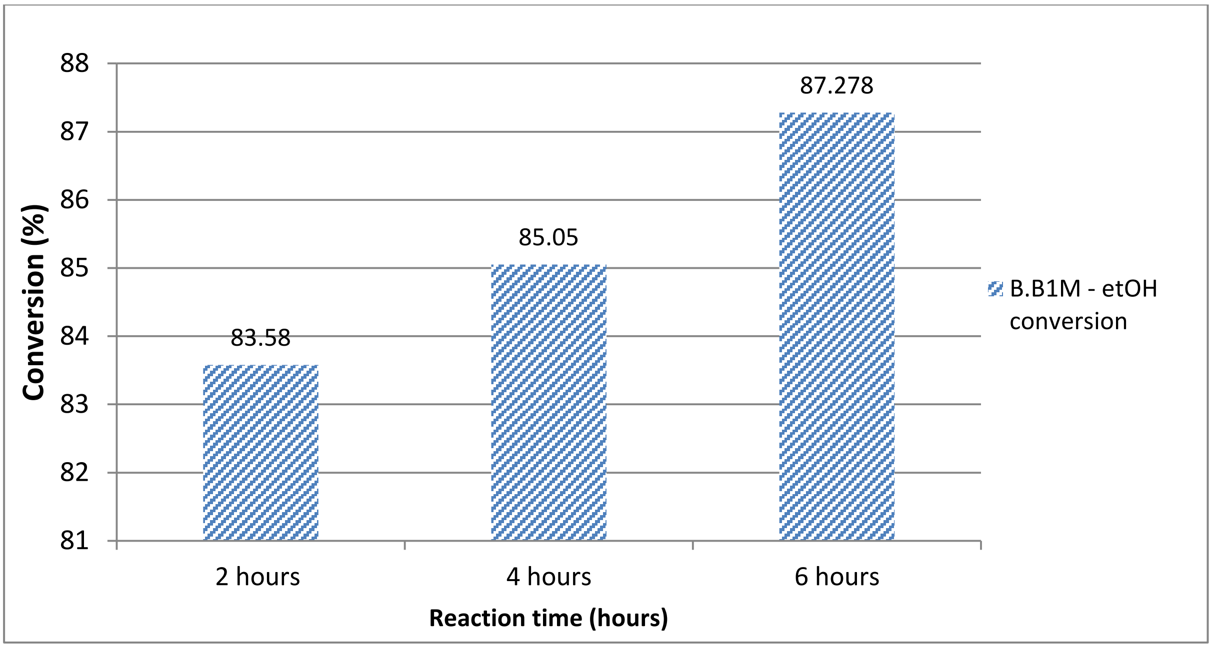


Figure 4.27: Effect of variation in reaction time on bioethanol conversion over $B.B_{1M}$ catalyst (At fixed reaction temperature of 350 ^oC)

In Figure 4.27, it is observed that bioethanol conversion over $B.B_{1M}$ catalyst increased with reaction time; which starting for 2 hour reaction resulted to 83.58 % conversion, then accordingly with increase in reaction time to 4 and 6 hours, increased to 85.05 and 87.28 % conversion respectively. Increase in bioethanol conversion with increase in reaction time, was however in line to gradual increase in the amount of gases produced (As observed in Table 7.2_Appendix 1), as compared to liquid product. In other words, clay-based catalysts with increase in time became more active in the conversion of bioethanol to gases as compared to liquid product.

The above similarly applies to bioethanol conversion over N.B catalyst, which over the reaction period of 2 hours led to 73.37 % conversion; which then by increase in reaction time to 6 hours, further led to increased bioethanol conversion of 84.95 % (See earlier in Figure 4.26). In comparison to 2 and 4 hours, catalytic activity of clay-based catalysts was optimum for reactions of 6 hours. carried out for the period of 6 hours.

In contrast to increase on bioethanol conversion due increase in reaction time, decrease on bioethanol conversion with increase in reaction time (From 2 to 6 hours) was only observed over the B.B catalyst (As also observed earlier in Figure 4.26)**.** Here, unlike other clay-based catalysts, bioethanol conversion slightly dropped from 82.3 to 81.1 %. This also reveals that the activity of B.B catalyst, in contrast to earlier finding, decreased with increase in reaction time. This decrease is however smal and the figures stastically are the same, thereby making the finding to correlates more with increased catalytic activity with increase in reaction time as for other clay-based catalysts. In otherwords, 6.92 %, 3.7%, and 0.02 % increase on bioethanol conversion over N.B catalyst, $B.B_{1M}$ and H-ZeoCOM compared to 3.94 % decrease over B.B catalysts, indicates that increase in reaction time in overall, is favourbale to increased bioethanol conversion. Additional experiments in recommendation, would be more likely to prove for either increased or fixed activity of B.B catalyst on bioethanol conversion.

Table 4.6 reports on variation in the catalyst activity as a result of increase in reaction time.

Table 4.6: Effect of reaction time on catalyst activity (N.B; B.B; $B.B_{1M}$ and H-ZeoCOM)

Reaction time	**N.B** (% Conv.)	**B.B** (% Conv.)	**$B.B_{1M}$** (% Conv.)	**H-ZeoCOM** (% Conv.)
2 hour	75.37 %	82.3	83.58	99.95 %
6 hour	84.95 %	81.01	87.28	99.97 %
Change in conversion	+ 6.92	-3.94	+3.7	+0.02
Variation	Increase	Decrease	Increase	increase

% Conv. : % Conversion

From Table 4.6 above, it is observed that increasing in reaction time is however insignificant when using the H-ZeoCOM and this for as favourable activity on bioethanol conversion as the one obtained from 6 hour reaction, could rather be recommended for 2 hour reaction time. Similarly , without further repetitive experiment to ehance bioethanol conversion over B.B by increase in reaction time, this catalyst (B.B) can thus far as well, with regard to favourable activity on bioethanol conversion, be recommended for 2 hour reaction.

For reaction over clay-based catalysts, it is therefore found in overall that catalyst activity in the conversion of bioethanol was favoured or enhanced with increase in reaction time. In other words, 6 hours thus far was relatively the most optimum reaction time (At fixed reaction temperature of either 350 or 400 ^{o}C)

4.2.5.1.1 Effect of reaction time on hydrocarbons (olefins and paraffins) selectivity

Clay-based zeolites were foun selectivity to olefins and paraffins hydrocarbons at both reaction time of 2 and 6 hours. 2 hour reaction time, precisely using the H-ZeoCOM and H-ZeoClay catalyst, was the most optimum condition with regards to high selectivity of light paraffins in the gas product. 6 hour on the other hand as shown in Figure 4.28, was rather relatively most optimum condition for high olefins selectivity.

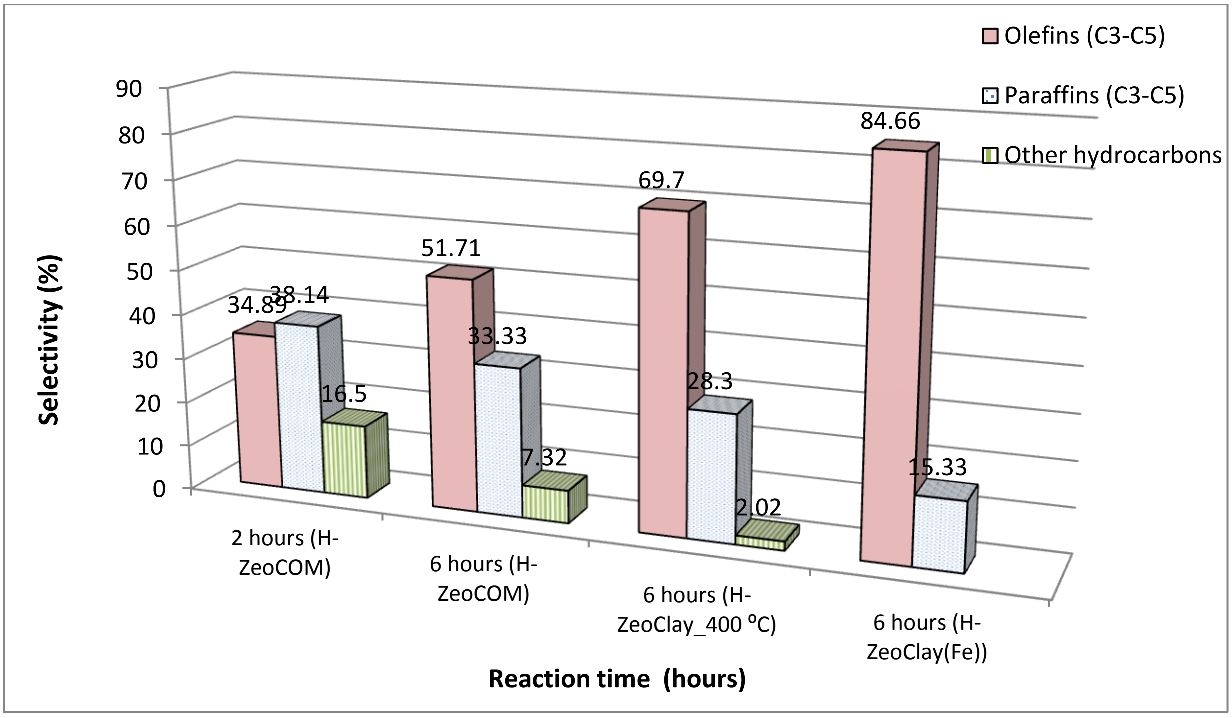


Figure 4.28: Investigation of optimum reaction time for gaseous olefins and parrafins selectivity by zeolite-based catalysts

Likely from 6 hour reaction, the metal promoted clay-based catalysts at 350 °C and the H-ZeoClay at 400 °C as shown in Figure 4.28 were found to be the most selective catalysts to light olefins hydrocarbons (in the gas product) in this work.

For bioethanol conversion over the produced clay-based catalysts, the optimum reaction time and temperature in favour to a relatively high conversion and high olefins selectivity in the gas product, is 6 hour reaction at 400 °C. Reaction period of 2 hours at either temperature (350 or 400 °C) is optimum only to a relatively high paraffins selectivity (or concentration) in the gas product.

Non-zeolite catalysts (N.B, B.B and B.B_{1M}) on the other hand, were in overall most selective to both olefins and parrafins at 2 hour reactions. Figure 4.29 displays the trend of gaseous hydrocarbons selectivity (by non-zeolite clay-based catalysts) with variation in reaction time (under fixed reaction temperature and other conditions).

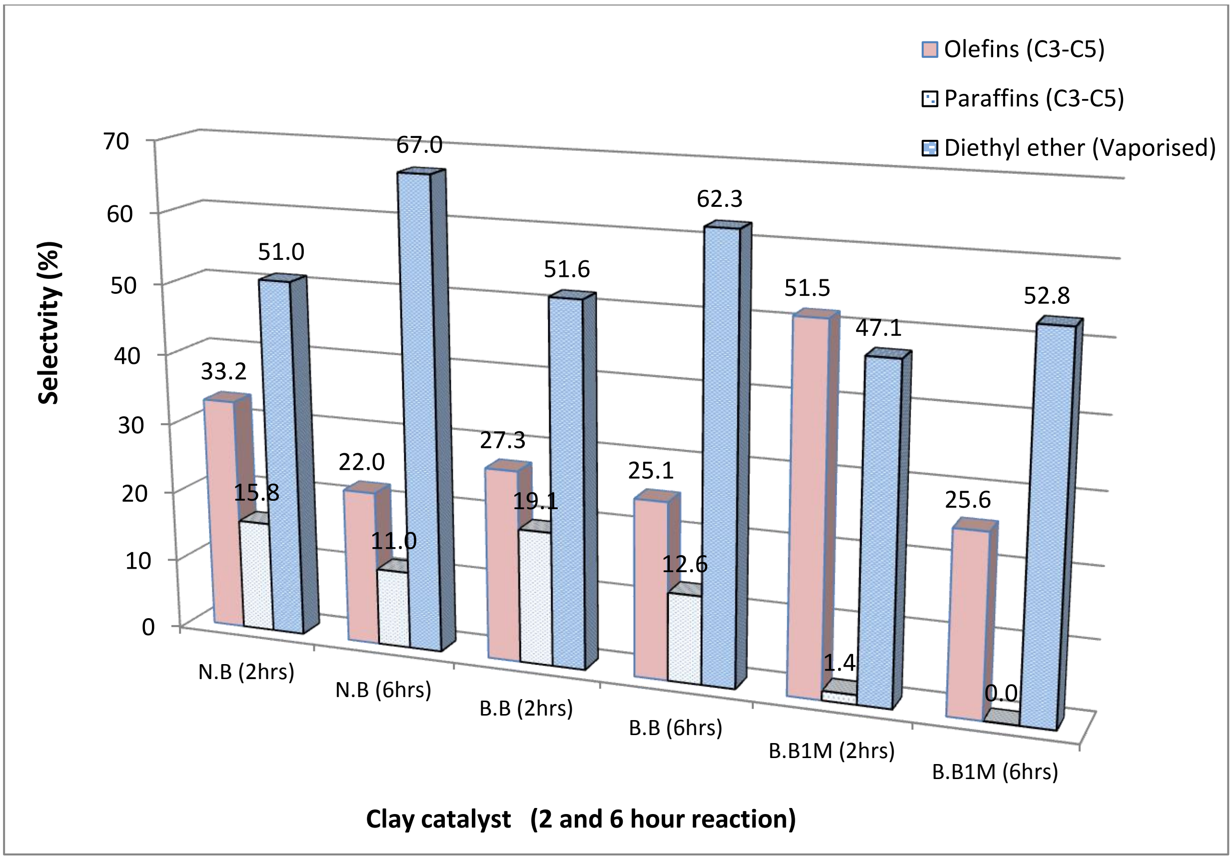


Figure 4.29: Effect of reaction time on gas hydrocarbons selectivity by non-zeolite clay-based catalyst (At 350 °C reaction temperature)

Increase in reaction time as observed in Figure 4.29 over each clay catalyst used for the purpose (N.B, B.B and B.B$_{1M}$), led to decreased selectivity of gaseous paraffins and olefins by both the non-modified (N.B) and modified clay-based catalysts (B.B and B.B$_{1M}$). These however in contrast, resulted to increased selectivity of diethyl ether in the gas product.

The above observed trend is unlike for zeolite and clay-based zeolite catalysts (H-ZeoCOM and H-ZeoClay), which rather by increase in reaction time to 6 hours, led to increase and highest selectivity of olefins in the gaseous product.

2 hour reaction periods therefore over the above clay-based catalysts (Non-modified and modified) at 350 °C, was optimum for a relatively higher selectivity of both olefins and paraffins hydrocarbons in the gas product. Olefins hydrocarbons in each of the above products however, were found to be relatively more selective (selected) than paraffins at both 2 and 6 hour reactions. For example, N.B and B.B catalyst over 2 hour reaction period, resulted to highest selective of olefins and paraffins hydrocarbons, respectively (33.2 % and 19.11 %). N.B with increase in reaction time (i.e. over 6 hour reaction period), resulted to highest selective of diethyl ether (66.96 % selectivity) in the gaseous product.

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Certain volatile liquid hydrocarbons, such as diethyl ether and those with C5 as observed in Figure 4.28 - 4.29 and other various Figure in this work, were collected from the reactor at high temperature (Above their boiling temperature) into gas product in the gaseous state – Since these being passed through the condenser for shorter residence time (Due to shorter length of the condenser), resulted to the relative small amount not to condense but rather were passed through and collected altogether with other gases in the gas product. The gas product, taking into account the above uncondensed hydrocarbons, was analysed immediately after the completion of each reaction.

4.2.6 Product distribution and selectivity by clay-based catalysts

Clay-based catalysts in the catalytic conversion of bioethanol conversion were found dominantly selective to gaseous product as compared to liquid product (hydrocarbons) obtained from the reactions. The overall selectivity of clay-based catalysts to gaseous hydrocarbons in this work ranges most on olefins, followed by diethyl ether and then gaseous parraffins hydrocarbons as shown in Figure 4.30.

For liquid product, the order of high selectivity of hydrocarbons by clay-based catalysts is diethyl ether, toluene, benzene, xylene, methanol as shown in Figure 4.30.

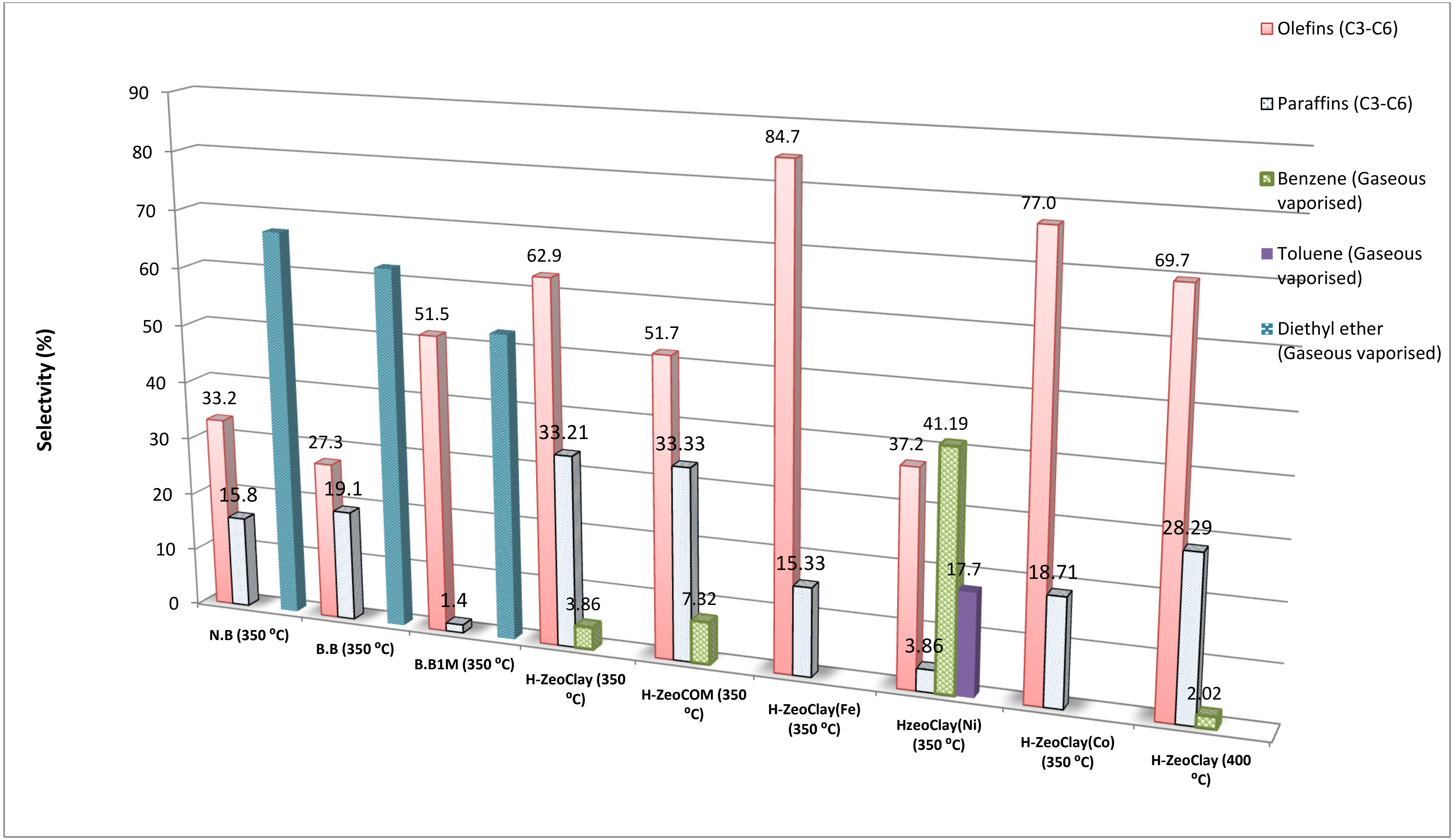

Figure 4.30: Gaseous hydrocarbons selectivity and distribution by clay-based catalysts (6 hour fixed reaction time).

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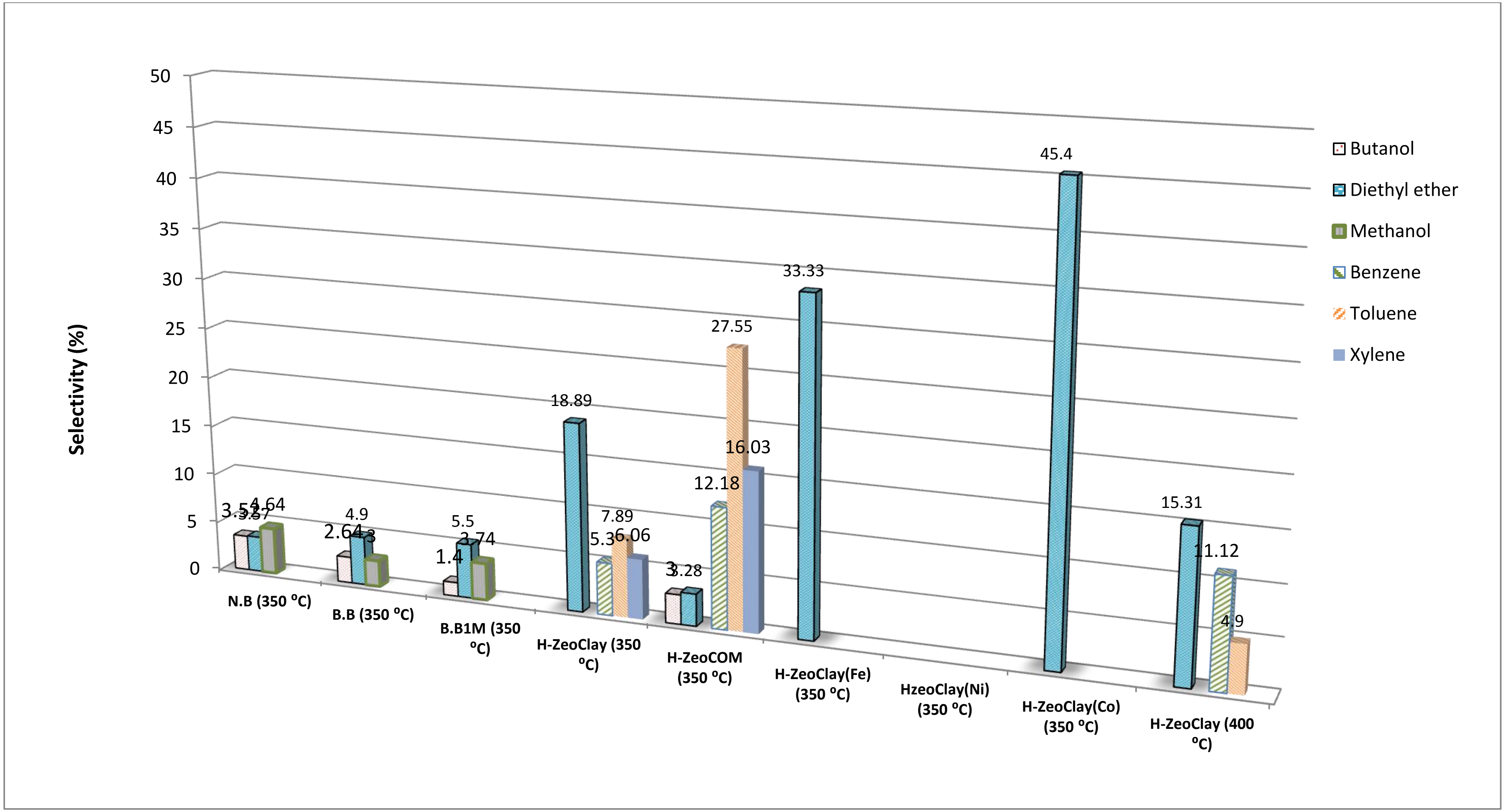


Figure 4.31: Distribution and selectivity of liquid hydrocarbons by produced clay-based catalysts (6 hour fixed reaction time)

4.2.6.1 Selectivity of methanol and butanol by clay-based catalysts

Methanol and butanol in the liquid product were obtained mainly through non-zeolite catalysts (i.e. N.B, B.B and B.B$_{1M}$). Unlike these catalysts, none of the produced clay-based zeolite catalysts in this work (As observed in Figure 4.31) was selective to methanol and butanol in the liquid product. This similarly applies to metal promoted clay-based zeolites. The H-ZeoCOM catalyst (which was used as yardstick to H-ZeoClay), rather was poorly selective to butanol by 3 %.

The N.B catalyst as observed in Figure 4.31, was the most selective clay-based catalyst to methanol and butanol in the liquid product (By 4.64 % and 3.52 %). The order of high selectivity to butanol was then followed by B.B and B.B$_{1M}$ catalyst whereas to methanol was followed by B.B$_{1M}$ and B.B.

4.2.6.2 Selectivity of diethyl ether by clay-based catalysts

Diethyl ether (D.E) in the vaporized form in the gas product, was uniquely and only found selective by non-zeolite clay-based catalysts (N.B, B.B and B.B$_{1M}$). N.B catalyst employed for 6 hour reaction (at 350 ^{o}C), resulted to highest selectivity of diethyl ether by 66.96 %. Beneficiation and acid modification of N.B catalyst to B.B and B.B$_{1M}$ catalyst however, resulted to decreased selectivity of the catalyst to 62.28 % and 52.87 % diethyl ether respectively, as shown in Figure 4.32.

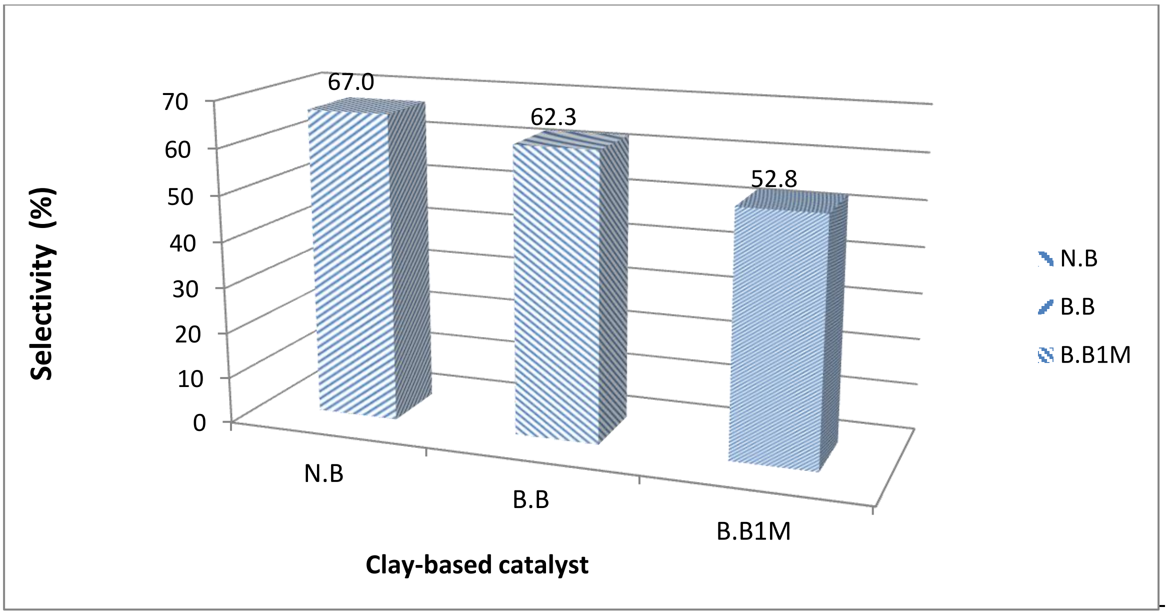


Figure 4. 32: Selectivity of gaseous diethyl ether by non zeolite clay-based catalysts (350 °C reaction temperature).

Unlike the gaseous diethyl ether obtained exclusively by the afore-mentioned catalysts, all the clay-based catalyst in this work were found selective to diethyl ether in the liquid product. H-ZeoClay (Co) as observed in Figure 4.31 earlier, was the most selective clay-based catalyst to liquid diethyl ether by 45.4 % in the liquid product.

4.2.6.3 Selectivity and distribution of liquid hydrocarbons by H-ZeoCOM and H-ZeoClay

The product obtained by bioethanol conversion over H-ZeoClay and H-ZeoCOM consists of liquid and gaseous hydrocarbons. Thus far, this has been obtained through the other clay-based catalysts produced in this work.

Bioethanol conversion over H-ZeoCOM led to higher distribution of hydrocarbons in the liquid product than the H-ZeoClay catalyst. The mentioned distribution proportion was 6 and 5 respectively (6>5)**.**

Both these catalysts however in this work were found exclusively selective to benzene, toluene in both aqueous and gaseous product, whereas to xylene in the aqueous product. Diethyl ether in addition (See Figure 4.30 and Figure 4.31_pg.111-2), were the only hydrocarbons that were found selective by clay-based catalysts in both gaseous (In vapour form) and aqueous product (Liquid product).

According to Figure 4.33, the H-ZeoCOM was however more selective to hydrocarbons in the liquid product than the H-ZeoClay catalyst.

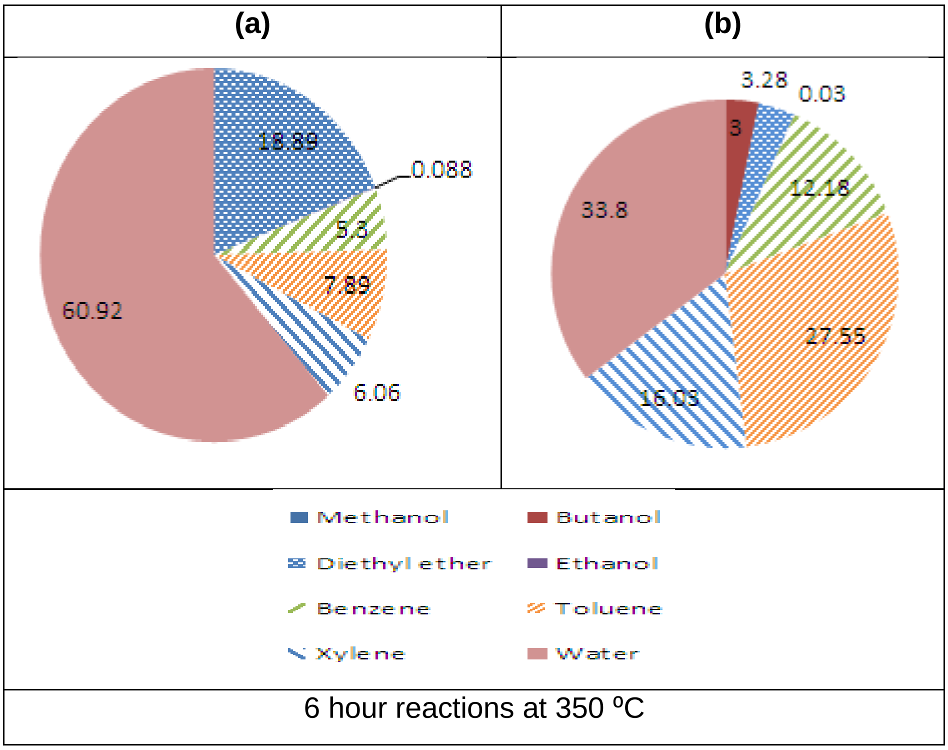


Figure 4.33: Distribution and selectivity of aqueous product by H-ZeoClay (a) and H-ZeoCOM (b) catalyst.

According to Figure 4.33, H-ZeoCOM relative to H-ZeoClay, was more selective to benzene, toluene and xylene at 12.18 %, 27.55 and 16.03 % respectively. In exception, H-ZeoClay was only more selective than H-ZeoCOM with regards to diethyl ether.
Nonetheless, the H-ZeoClay catalyst, followed by H-ZeoCOM, was the most and the only produced clay-based catalyst found selective to liquid toluene (by 7.9 %), at 350 °C.

These two catalysts correspond in terms of product identification in both liquid (aqueous) and gaseous product; such as BTX being exclusively selective by these catalysts. The only difference lies in their selectivity to respective hydrocarbon products.

The slightly higher phase identification of H-ZeoCOM to ZSM-5 as compared to that of H-ZeoClay (Given by XRD Data), as well as the relatively higher Si/Al ratio of H-ZeoCOM, are among the factors to account for difference in product selectivity and distribution as above resulted between these two catalysts.

Further comparison between H-ZeoClay and H-ZeoCOM for their identities as zeolites, was carried out on basis of the physical characteristics of visibility and smell of the aqueous product obtained through these catalysts. The colour and odour of the aqueus product obtained by H-ZeoClay catalyst, was observed to correspond to that obtained by H-ZeoCOM catalyst. These as shown in Figure 4.35, both contains a layer of heavy-like oil suspended on top the product. These similarly possessed same odour, as also applies to odour of the gaseous product obtained by use of these two catalysts. This is additional evidence serving for comparison between the H-ZeoClay and H-ZeoCOM. In other words, this proves that H-ZeoClay is comparable to H-ZeoCOM (Hence zeolites in general), in support to similar phase identity (XRD data) that was observed earlier of both catalysts (In Figure 4.13 and 4.14_pg**.**91-92**).**

Figure 4.34: Comparsion of H-ZeoClay and H-ZeoCOM by physical visibility of liquid product (Closest to the centre: H-ZeoCOM and far end from the centre, H-ZeoClay).

4.2.6.4 Effect of increase in reaction temperature on the selectivity of liquid hydrocarbons

Increase in reaction temperature (from 350 ^{0}C to 400 ^{0}C) for bioethanol conversion over H-ZeoClay catalyst, was found to have a slight effect on hydrocarbons selectivity and distribution in both liquid and gaseous product (6 hour fixed reactiom time). At both temperatures, hydrocarbons such as benzene and toluene aromatics were observed in the liquid product, similarly with olefins and parrafins in the gaseous product.

Increase in reaction temperature however as a result, was found to exclusively enhance the selectivity of benzene from 4 % to 11.2 %. This followed by H-ZeoCOM at 350 ^{0}C, resulted to H-ZeoClay in this work to be the most selective clay-based catalysts to liquid benzene (As observed in Figure 4.36 and also in Figure 4.30). Unlike benzene, the selectivity of the rest of hydrocarbons in the liquid product by H-ZeoClay (Such as diethyl ether and toluene) decreased, while that of xylene was completely suppressed as a result of increase in reaction temperature.

The above observations are made in Figure 4.35.

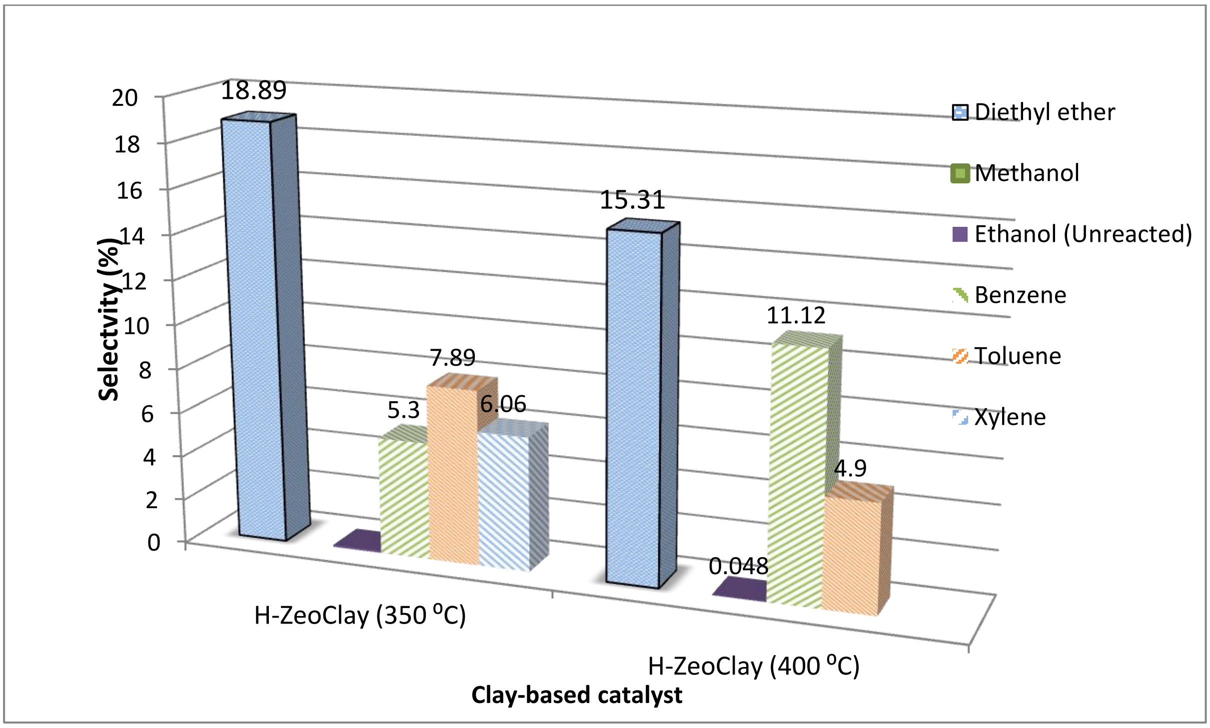


Figure 4. 35: Effect of temperature on hydrocarbon selectivity and distribution in the liquid product (6 hour fixed reaction time).

The selectivity of benzene by H-ZeoClay in the gaseous product (vaporised form) on the other hand (As deducted from Figure 4.30_pg.111), was decreased (from 3.8 to 2.02 %) with increase in reaction temperature (350 to 400 °C).

4.2.6.5 Effect of promotion on selectivity and distribution of liquid and gaseous hydrocarbon products

All the metal promoted clay-based catalysts in this work, like other clay-based catalysts produced in this work (Including their precursor H-ZeoClay), were not found selective to methanol and butanol in the liquid product.

On further view, the promotion of H-ZeoClay with metal elements generally suppressed the selectivity and distribution of hydrocarbons in the liquid (aqueous) product (As observed in

Figure 4.37). This does not correlate with the best catalytic activity obtained by the metal promoted catalysts (H-ZeoClay (Ni) in particular), excep for increase in selectivity of diethyl ether by the H-ZeoClay (Co) and H-ZeoClay (Fe) (From 18.9 %, 33.3 % to 45.4 % selectivity).

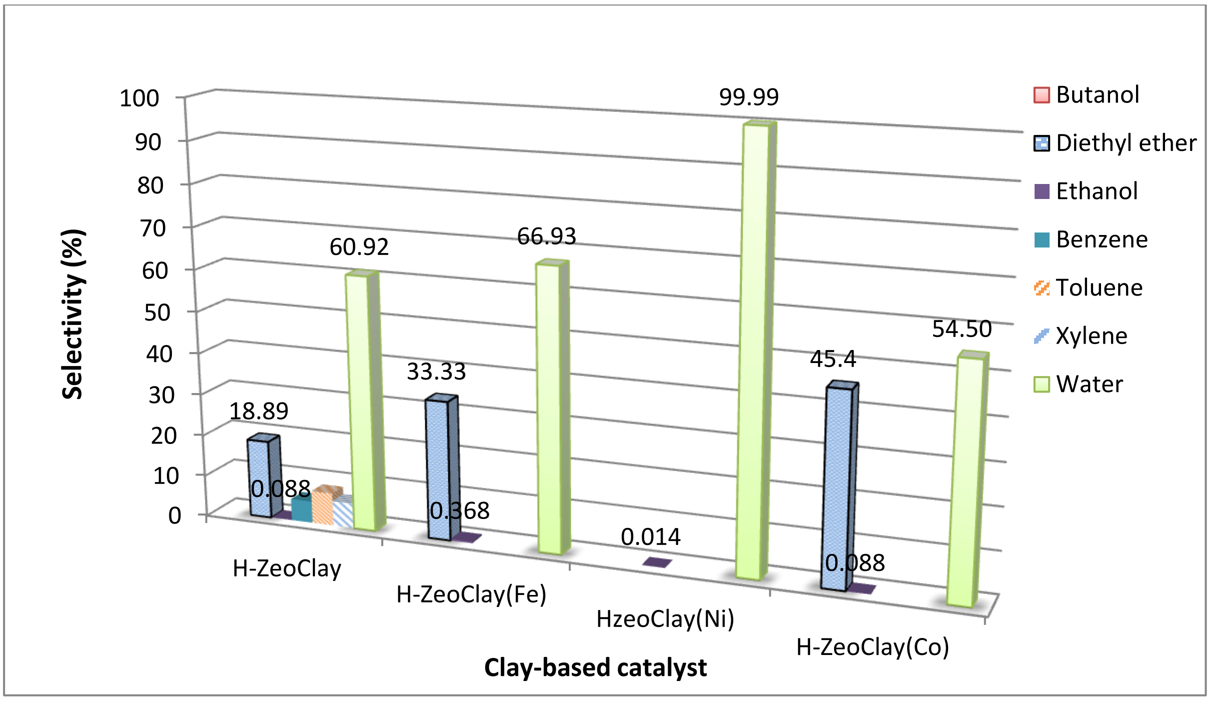


Figure 4. 36: Effect of metal promotion on the selectivity of liquid hydrocarbons (6 hour and 350 °C reaction conditions)

The unreacted ethanol detected in the aqueous product was common for all clay-based catalysts, however only trace amount was detected for promoted clay-based zeolites. For example, the H-ZeoClay (Ni) was the least selective to unreacted ethanol in the liquid product by 0.014 % and this inversely is an indication of its highest activity in the conversion of bioethanol (99.99%) – Figure 4.39. In otherwords, out of the 2.5 mL/hr of bioethanol fed into the reaction over H-ZeoClay (Ni), 99.9 % of the fed amount was converted to gaseous hydrocarbons (in the gas product). From the entire 6 hour reaction, 1.8 mL of the liquid product was recovered, consisting dominantly of water content as observed in Figure 4.36.

Further on with aqueous (liquid) product, H-ZeoClay (Fe) and H-ZeoClay (Co) catalyst, were found selective to diethyl ether by 33.33 % and 45.4 % respectively. H-ZeoClay (Co) thus far by the latter concentration, was the most selective clay-based catalyst to liquid diethyl ether (In the liquid or aqueous product) in this work.

On the other hand, metal promotion on the H-ZeoClay catalyst (i.e. H-ZeoClay (Ni)), also as compared to other clay-based catalysts, led to gaseous product distribution consisting mainly of olefins and paraffins-range hydrocarbons. Produced clay-based zeolites (e.g. H-ZeoClay, HZeoClay (Ni)) among the clay-based catalysts, were the only catalysts found simultaneously selective to aromatics hydrocarbons in the aqueous (liquid) and gaseous product (See Figure 4.30 and Figure 4.31_pg.111-112).

The H-ZeoClay and other produced clay-based zeolites however in overall, were found uniquely selective to benzene and toluene in the gaseous product, of which the H-ZeoClay (Ni) catalyst (As observed in Figure 4.37) was the most in this regards by 41.2 % and 17.7 % respectively.

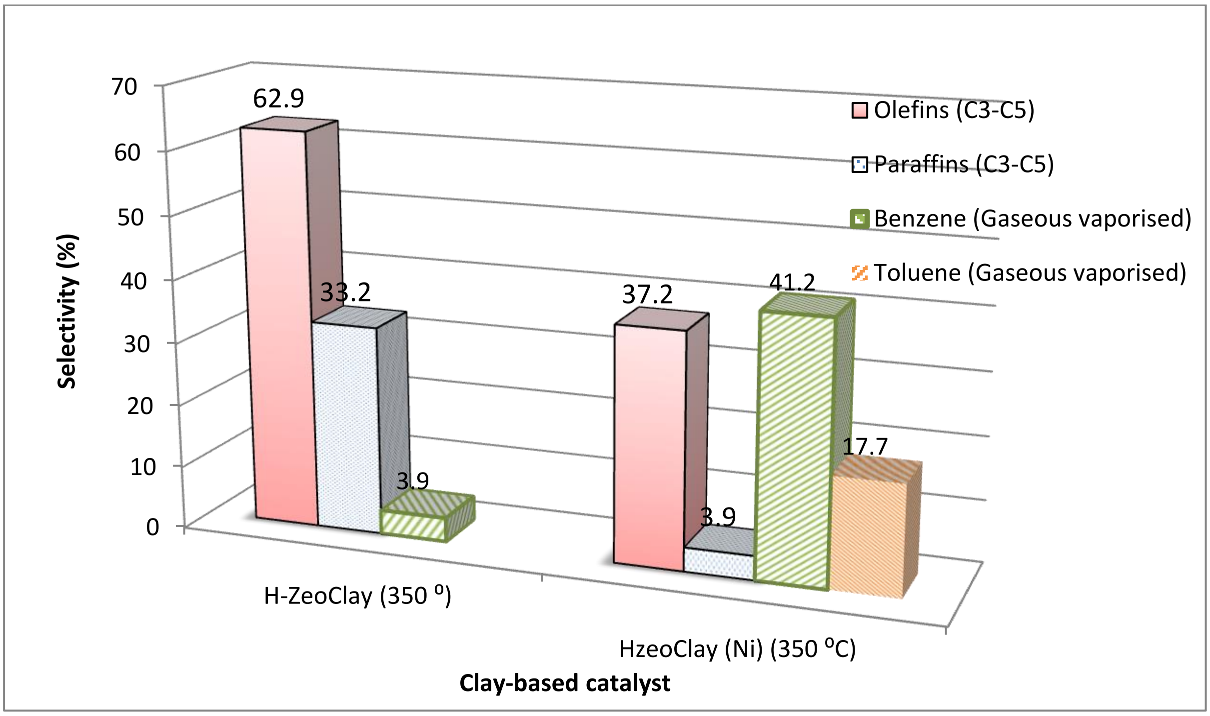


Figure 4.37: Selectivity of gaseous aromatics hydrocarbons by clay-based zeolites (6 hour fixed reaction time)

According to Figure 4.30 (pg.111), the selectivity of benzene and toluene in the gaseous product was enhanced as a result of catalyst (H-ZeoClay) promotion with Nickel (Under fixed reaction conditions of 6 hours and 350 ^{0}C).

4.2.6.6 Selectivity of gaseous olefins and paraffins by non-zeolite clay-based and clay-based zeolite catalysts

All clay-based catalysts produced in this work were found to be commonly selective to olefins and parraffins hydrocarbons in the gas product. These include the non-modified, modified clay-based catalyst and the clay-based zeolites.

The produced clay-based zeolites were however found in overall to lead to highest selectivity-range of olefins and parraffins–hydrocarbons in the gas product (As reported in Figure 4.38). Among these precisely, H-ZeoClay (Fe) catalyst was the most selective to light olefins in this work by 84.7 %, followed by H-ZeoClay (Co) by 76.8 %. The H-ZeoClay catalyst similarly resulted to highest selective of light paraffins in the gas product by 33.21 %. Catalyst promotion with metal elements on the other hand, relative to H-ZeoClay, resulted to decrease to lowest selectivity of parrafins-range hydrocarbons (3.86 %). In other words, H-ZeoClay (Fe) catalyst could therefore be recommended for favourable selectvity of olefins whereas the non-promoted H-ZeoClay, for parrafins-hydrocarbons in the gas range.

B.B catalyst resulted to highest selectivity of parraffins-range hydrocarbons among the non-zeolite catalyst (19.11 %), whereas this was relatively lower that for H-ZeoClay (Under fixed reaction conditions). Further with acid modification, the B.B$_{1M}$ in contrast led to lowest selectivity of paraffins-range hydrocarbons by 1.36 % and to a relatively increased selectivity to olefins-range hydrocarbons by 51.54 %. This yet was lower compared to clay-based zeolites, precisely H-ZeoClay (Fe) as reported earlier and observed in Figure 4.31 (pg.112).

Selectivity of olefins in the gas product by H-ZeoClay catalyst, was enhanced from 62.88 to 69.7 % with increase in reaction temperature (from 350 ^{o}C to 400 ^{o}C), as also observed in Figure 4.41. This however was still lower than olefins selectivity obtained through catalyst promotion with Iron (H-ZeoClay (Fe)) at 350 ^{o}C (i.e. 84.7 %) and ranks the second highest in this regard. Increase in reaction temperature on the other hand resulted to slight decrease on paraffin hydrocarbons (28.3 %), which nonetheless was relatively higher than that obtained through metal promotion of the catalyst (H-ZeoClay).

This approach however as observed in Figure 4.38, was not favourable to increase in the selectivity of parraffins hydrocarbons in the gas product. Hence increase in reaction temperature, neither metal promotion of the clay-based zeolite (H-ZeoClay) can be recommended for favourable and improved selectivity of parraffins range hydrocarbons in the gas product.

Catalyst beneficiation as earlier discussed in this work, was found to have enhaced the structural porosity of N.B catalyst, which then favoured the selectivity of parraffins hydrocarbons by the resultant B.B catalyst. Acid modification on the other hand as reported earlier in this work through SEM in Figure 4.4 (pg.78), led to decreased catalyst porosity. Hence the resultant less porous catalyst ($B.B_{1M}$) was rather favourably selectivity to olefins other than to parraffins hydrocarbons. This simply indicate that parraffins hydrocarbons could not go through the catalyst and as result these were rather mostly cracked over the catalyst to olefins, in account to the resultant high selectivity of light olefins in the gas product.

From the above discussed, the order of clay-based catalysts for decrease selectivity to olefins hydrocarbons in the gas product is H-ZeoClay (Fe)> H-ZeoClay(400 ^{0}C) > H-ZeoClay (Co) > H-ZeoClay > H-ZeoCOM > $B.B_{1M}$. This order for paraffins hydrocarbons is H-ZeoCOM > H-ZeoClay > H-ZeoClay (400 ºC) > B.B > H-ZeoClay (Co) > H-ZeoClay (Fe).
(NB: All catalysts above were employed at 350 ºC reaction temperature, except for the one indicated at 400 ºC).

Figure 4.38 graphically reports on variation in paraffins and olefins selectivity by various clay-based catalysts produced in this work.

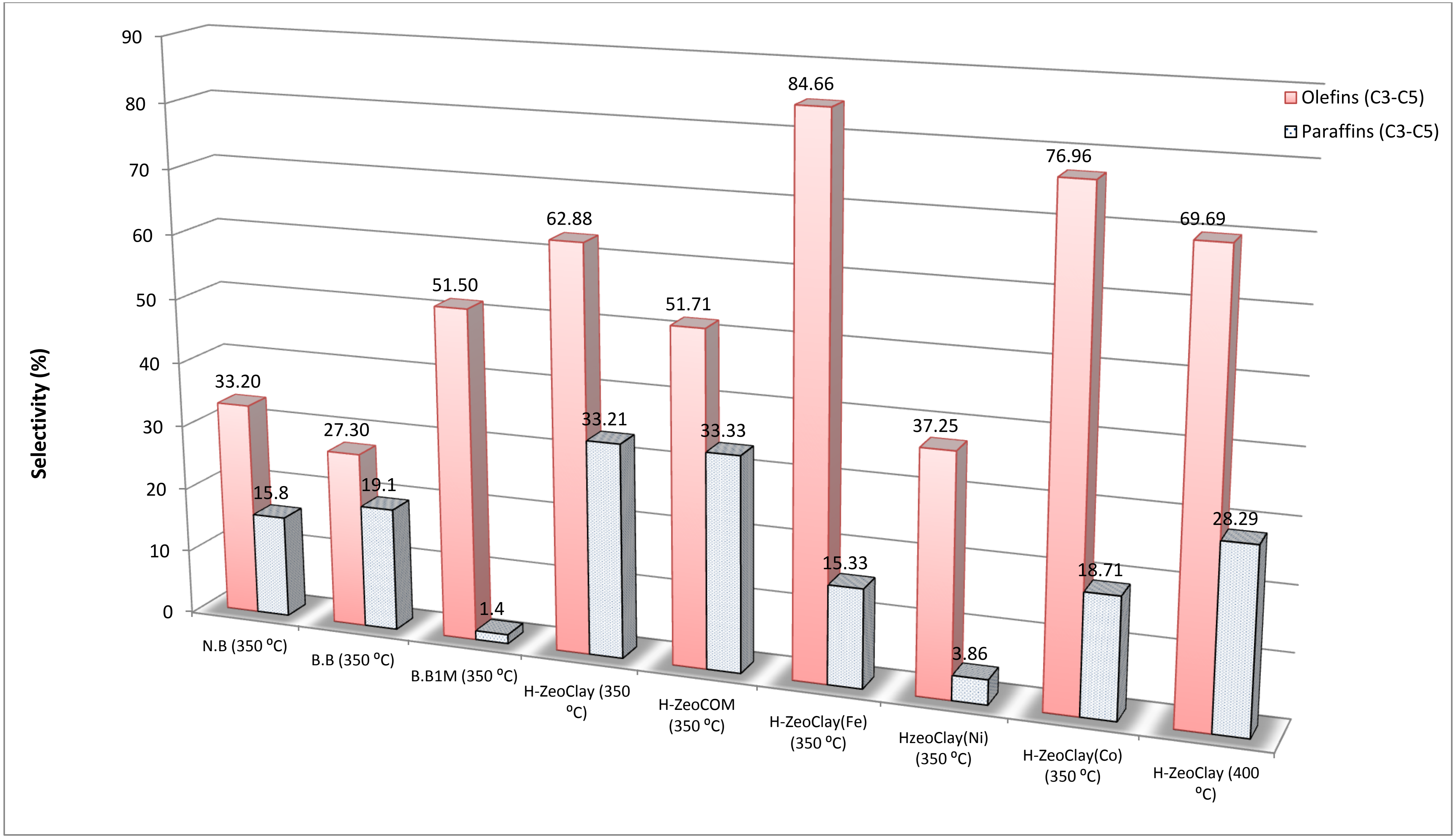


Figure 4. 38: Olefins and parrafins distribution and selectivity by produced clay-based catalysts (6 hour fixed reaction, 350 – 400 °C)

Selectivity and distribution of hydrocarbon products by clay-based catalysts in the entire above finding and discussion section, was reported separately for liquid and gas product as observed. Unlike the above, product selectivity as reported in the upcoming Table 4.7 and corresponding to conversion of each clay-based catalyst evaluated in this work, was collectively reported for both liquid and gas product in mol %. Table 4.7 in extension is reported in Appendix 4. Note that the trends of hydrocarbons selectivity or variation in either liquid or gas product was at most observed to be the same for selectivity reported in concentration v/v % and that in mole %. Figure 4.30 and 4.30 (a) in correspondence to the above comparision are also displayed in Appendix 4.

Table 4.7: Catalytic evaluation of bioethanol conversion over clay-based catalysts (**6 hour reaction time**)

Clay-based catalysts	**EtoH conv. (%)**	**Selectvity of hydrocarbons in liquid and gas product (Mole %)**													**Fraction distribution**	
		Alcohols			**Diethyl ether**		**Olefins** (C3-C5)	**Paraffins** (C3-C5)	**BTX**						**Mole %**	
									Benzene		**Toluene**		**Xylene**			
		EtOH	BuOH	MeOH	Liquid	Gaseous			Liquid	Gaseous	Liquid	Gaseous	Liquid	Water	**Liquid**	**Gas**
N.B	**84.95**	7.99	1.87	2.47	1.9	31.4	10.33	5.16	-	-	-	-	-	38.89	53.1	46.9
B.B	**81.01**	5.28	0.73	0.73	1.36	44.97	18.15	9.08	-	-	-	-	-	19.69	27.8	72.2
B.B$_{1M}$	**87.28**	5.29	0.76	2.03	2.98	30.86	17.37	2.68	-	-	-	-	-	30.53	**41.6**	58.4
H-ZeoClay	**99.91**	0.035	-	-	7.51	-	37.89	21.73	2.11	2.33	3.135	-	**2.41**	24.56	**39.75**	60.25
H-ZeoCOM	**99.97**	0.017	1.8	-	1.9	-	22.71	14.64	**7.13**	3.21	**16.12**	-	-	19.78	56.1	43.9
H-ZeoClay (Fe)	**99.63**	0.08	-	-	7.5	-	**65.74**	11.9	-	-	-	-	-	14.82	22.35	77.65
H-ZeoClay (Ni)	**99.99**	0.001	-	-	-	-	33.58	3.48	-	37.14	-	15.96	-	9.83	9.83	90.17
H-ZeoClay(Co)	**99.91**	0.017	-	-	8.9	-	61.89	15.05	-	-	-	-	-	10.68	19.59	80.41
H-ZeoClay (400 ^{o}C)	**99.95**	0.018	-	-	5.6	-	44.13	17.92	4.08	1.28	1.8	-	-	11.51	**36.57**	63.33

EtOH conv.: Bioethanol conversion

EtOH: Ethanol (Unreacted in the liquid product)

BuOH: Butanol in the liquid product

MeOH: Methanol in the liquid product

Olefins (C3-C5): These consist of both straight-chained IsoOlefins

Paraffins (C3-C5): These consist of both straight-chained Isoparaffins

N.B: Non-modified bentonite catalyst

H-ZeoClay (Fe): Iron Promoted/impregnated Clay-based zeolite catalyst

B.B: Modified Beneficiated Bentonite catalyst

H-ZeoClay (Ni): Nickel Promoted/impregnated Clay-based zeolite catalyst

B.B$_{1M}$: Acid modified bentonite catalyst

H-ZeoClay (Co): Cobalt Promoted/impregnated Clay-based zeolite catalyst

H-ZeoClay: Clay-based Zeolite catalyst

H-ZeoCOM: Commercial zeolite catalyst (Protonated)

Gaseous: These are non-condensate vaporised reaction hydrocarbon products

H-ZeoClay (400 ^{o}C): Clay-based Zeolite catalyst evaluated at 400^{o}C

N.B: All the above catalytic activity were evaluated at **350 ^{o}C**, except H-ZeoClay (400 ^{o}C)

4.3 The effect of catalytic properties on bioethanol conversion

The catalytic performance of clay-based catalysts on bioethanol conversion was assessed based on their catalytic properties, which as discussed earlier, were varied as a result of catalyst modifications (Beneficiation and acid modification) , production and promotion of clay-based zeolites.

4.3.1 The effect of Si/Al ratio of (non-modifed) clay catalysts on bioethanol conversion

The difference in the proportion of Si/Al ratio in clays, was among the properties investigated to assess for their catalytic performance on bioethanol conversion. In various literature such as Madeira et al.(2012) where zeolite (Precisely ZSM-5) was used for catalytic conversion of bioethanol, the Si/Al ratio of the catalyst had been reported to have influence on catalytic performance. Increase or decrease in Si/Al ratio to 40, at fixed reaction conditions, was reported to increase and maintain the catalytic activity of zeolite on ethanol conversion. The Si/Al ratio considered as catalytic property, has also been investigated to assess the performance of the clay catalysts (non-modified and modified) on bioethanol conversion.
Among the non-modified clay catalysts, N.B catalyst as reported in Figure 40 had the second lowest Si/Al ratio of 1.07, followed by N.K$_3$ with slightly lowest Si/Al ratio of 1.01. In accordance to zeolites as mentioned above, N.K$_2$ with highest Si/Al ratio of 3.06, could have resulted to highest activity than N.B (and other clays) in the conversion of bioethanol. In contrast however, N.K$_2$ Si/Al ratioinstead resulted to lowest activity in the conversion of bioethanol.

For clay catalyst (The various non-modified) , It is therefore not conclusive to relate the trend of increase on bioethanol conversion with increase in Si/Al ratio ratio. The best fit to the trend however as reported in Figure 4.40 (i.e. ≈ 80 % fit), correlates increase in the Si/Al ratio of clay catalystswith decrease in their activity on bioethanol conversion (Under fixed reaction conditions). The 20 % contradiction to the trend which shows increase in catalytic activity with increase in Si/Al ratio, was deduced mainly due to variation in categories of the clayused (Particular N.K$_3$ to N.B) and not due to Si/Al ratio. In otherwords, the very comparable Si/Al ratio of N.K$_3$ and N.B Si/Al ratio (i.e. 1.01 and 1.07) is not subject to difference in their activity on bioethanol conversion.

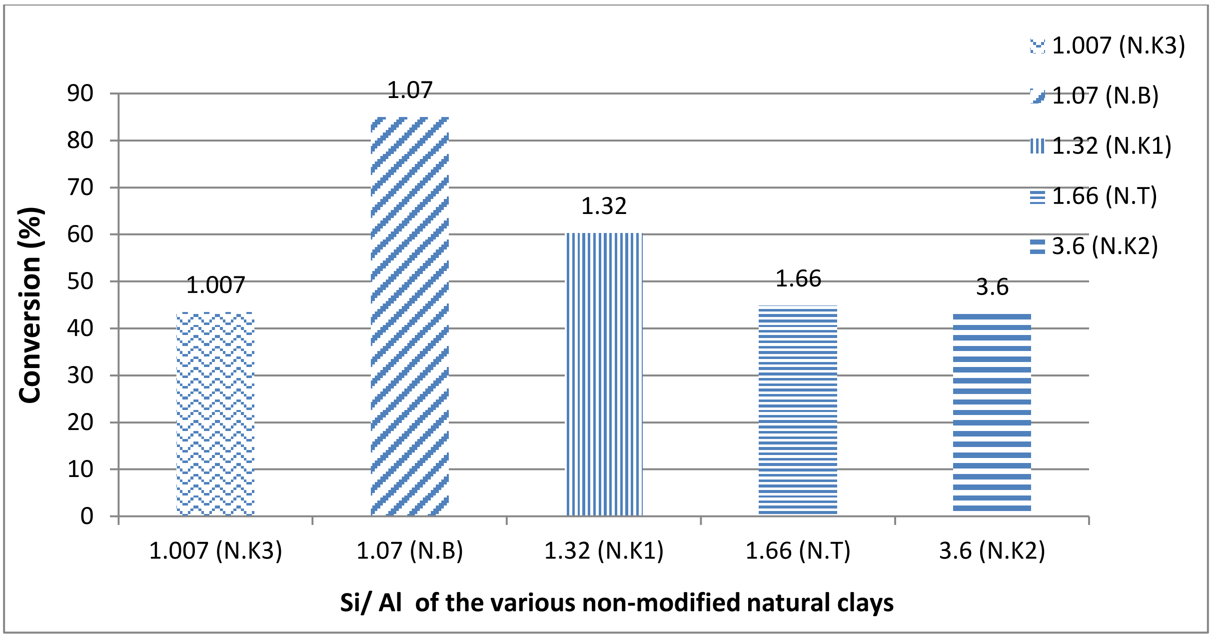


Figure 4.39: Correlation between bioethanol conversion and Si/Al ratio of various non-modified clay catalysts (6 hour reaction at 350 °C).

The trend exhibiting decrease in bioethanol conversion is 80 % fit with increase in Si/Al ratio. This trend however, is more reliable in correspondence to variation in nature or category of clay used. Hence N.B (Bentonite catalyst) was most active catalyst, followed by kaolin (N.K_1) and then N.T (Talc clay catalyst specie) in bioethanol conversion. This finding also supports the use of bentonite and kaolin as most important clays employed or to be employed in the manufacture of catalysts (For bioethanol conversion or other industrial applications such petroleum profuction).

4.3.1.1 Effect of Si/Al ratio and clay classification on bioethanol conversion

Classification of clays and their catalytic properties as separately, can therefore serve as basis to assess for difference in their catalytic perfomance on bioethanol conversion.
In otherwords, the performance of clays on bioethanol conversion, can be dependent either on their categories or catalytic properties. For example, N.K_2 and N.K_3 kaolin catalysts are classified under same categories and these as a result, while exhibiting differents Si/Al ratio, led to comparable conversion of bioethanol (i.e. 43.45 and 43.06 %).

In addition to XRD data given through Figure 7.22-7.24 (Appendix 2), the comparable outcome in the activity of the above kaolin clays on bioethanol conversion, reflect the evidence of them being of the same clay category (i.e. kaolinite group of clay as reported in literature section, Table 2.1_ pg.12).

The difference in Si/Al ratio ratio of N.K_1 relative to N.K_2 and N.K_3 catalyst, is still however a more significant factor (than the category to which they belong) in accounting for the difference observed in their relative activity on bioethanol conversion (60.2 % and 43.06 %). In otherwords, It has been found that clays may be classified under the same category but if these are mined from different geological sources (or simply different boreholes), their resultant catalytic properties and hence catalytic performance on bioethanol conversion, will more likely differ. Difference in Si/Al ratio of clays even applies to clay layers obtained from same geological borehole, yet at different depth (Below the earth surface). This finding was supported by Jacob et al. (2004:563), whom reported on differences in Si/Al ratio of kaolin clay samples mined at different depth of one particular borehole.

Hence variation on catalytic activities of clays of same category based on difference in Si/Al ratio, is shown in Figure 4.40.

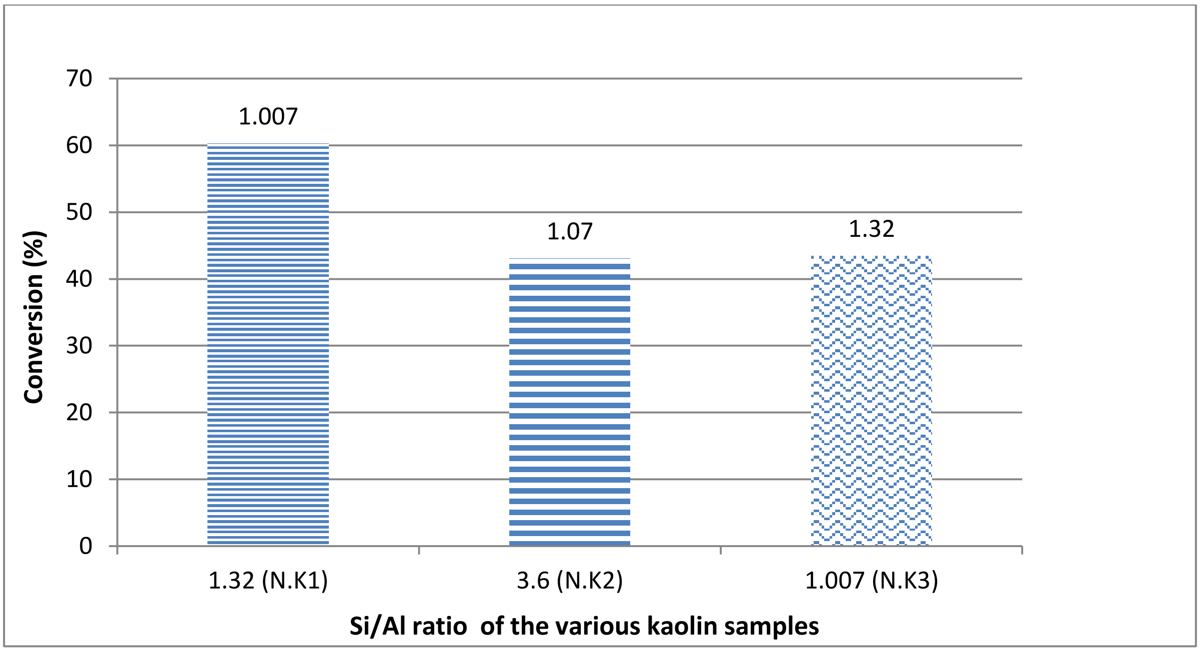


Figure 4.40: Effect of Si/Al ratio of kaolinite samples on bioethanol conversion (6 hour reaction at 350 ^{0}C).

4.3.1.2 Effect of beneficiation and acid modification on Si/Al ratio and bioethanol conversion

It was earlier discovered among the non-modified clay that increase in Si/Al ratio of clay catalyst, was corresponding to decrease in their activity on bioethanol conversion. This was similarly observed as a result of clay beneficiation. Clay beneficiation as observed in Figure

4.41, resulted to increase in Si/Al ratio of the catalyst from from 1.7 to 2.8. This as a result, led to decreased catalyst activity on bioethanol conversion from 84.95 to 81.01 %.

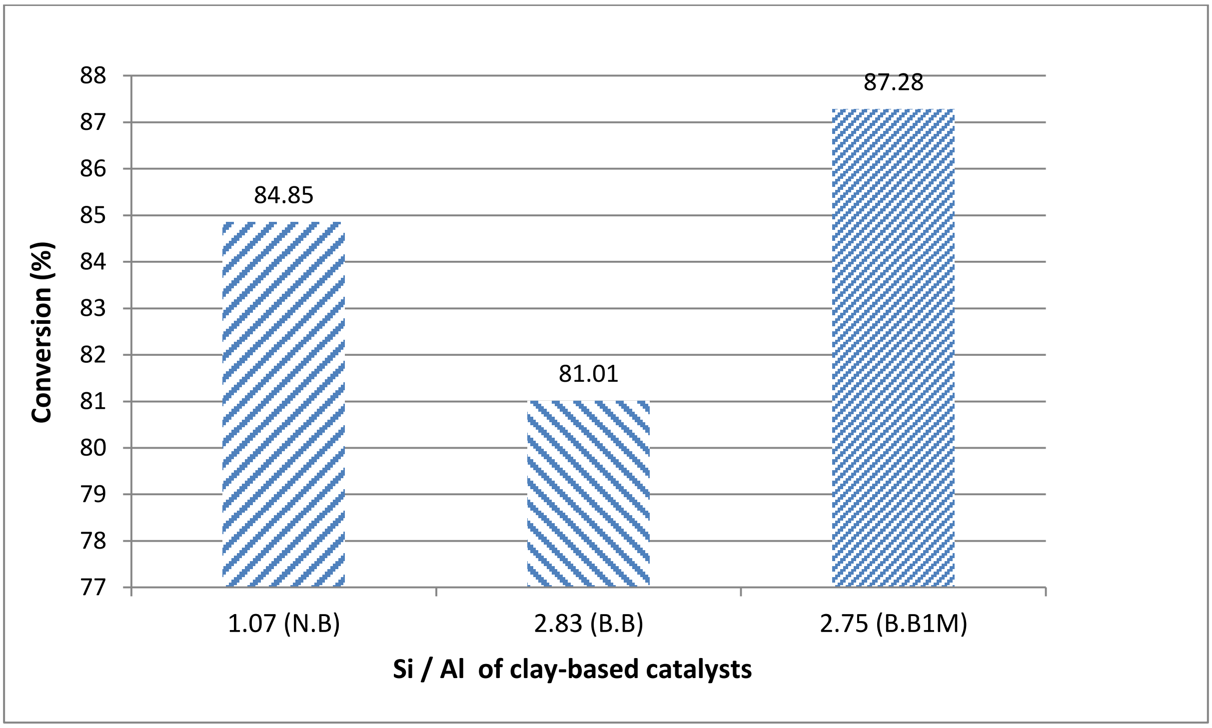


Figure 4. 41: Effect of Si/Al ratio of modified clay samples on bioethanol conversion

Acid modification on the beneficiated catalyst further on (As observed in Figure 4.41), resulted to increased activity of the catalyst on bioethanol conversion. This increase as observed relatively from B.B to B.B$_{1M}$, corresponds to decrease in Si/Al ratio of the catalyst. This result is reversal to that obtained due catalyst beneficiation (N.B relative to B.B) and that observed among the various non-modified clay catalysts (Figure 4.39_pg**.**126).Decrease on bioethanol from the above mentioned was observed with increase in Si/Al ratio of the catalyst (Under fixed conditions of 6 hours and 350 ^{0}C).

For clay catalysts therefore, as slightly similar to zeolite as reported by Madeira et al., (2012) for referenced Si/Al ratio of 40, It is found in overall that increase or decrease in Si/Al ratio to 2.75 was observed with increase in their activity on bioethanol conversion..

The view of clay beneficiation and acid modification as a whole (N.B → B.B$_{1M}$) if simplified from Figure 4.41, indicates that increase in Si/Al ratio of clay leads to increased activity of the catalyst in bioethanol conversion.

4.3.2 The effect of catalyst morphology on bioethanol conversion (Catalyst activity)

The morphology of N.B catalyst (As earlier discussed through SEM in Figure 4.1_pg.74), was observed to consist dominantly of quadrilateral, with relatively small proportion of pentagonal cuboidal particles. This was extended to hexagonal shapes of particles for other non-modified clays (N.T, N.K_1, N.K_2 and N.K_3)

The relatively highest activity of N.B catalyst on bioethanol conversion, was therefore also accounted due to its less geometrical extended morphology than other non-modified clay materials. This observation serves to indicate that the smaller the structural morphology (Decreased geometry or morphological planar of particles) of clay catalysts (Less sided), the lower the catalyst activity observed in the conversion of bioethanol.

The above observation also corresponds to clays materials on basis on their categories. N.B catalyst found to consist of least extended geometrical morphology, is classified under smectite group of clays, while N.T and N.K_1-N.K_2 classified as Talc and kaolinite group of clays, were found to consist of more extended geometrical morphology.

4.3.2.1 Effect of morphology and catalyst size on bioethanol conversion

The investigation t of the catalyst morphology as discussedin section 4.3.2, also served to account for estimate catalyst particle size. According to popular literature of zeolites (Viswanadham et al., 2012), increase in activity of zeolites in the conversion of ethanol has corresponded to reduced or smaller particle size of the catalyst.

Hence, N.B catalyst resulting to relatively high activity in the conversion of bioethanol, is an indication of this catalyst to have dominantly consisted of smaller particle size than the other non-modified clay catalysts employed in this work. In other words, the morphology of N.B consisting of less geometrical extended particles, is estimate to the fact that these particles were smaller relative to those of other non-modifided clay samples. Therefore the smaller the particle size of (the non-modified) clay catalysts, the higher the catalyst activity in the conversion of bioethanol

Further on, reduction of the catalyst particle size was at most observed as a result of catalyst beneficiation followed by acid moficiation (Figure 4.5_pg.79). Hence the increase in catalyst activity on bioethanol conversion as a result of beneficiation and acid modification, correspond to reduced particle size of the resultant catalyst sample.

4.3.2.2 Effect of porosity on bioethanol conversion

Catalyst porosity is also among the catalyst properties that has been possibly estimated or observed through SEM data to account for various activity of clay-based catalysts on bioethanol conversion. This was estimated through the extent of closeness, particle intergration or extent of particle overlapping given through SEM images.

It was earlier found that non-modified clays resulted to different activities upon their application on bioethanol conversion, and this is believed to be affected by different morphology and porosity observed of these catalysts (As observed through Figure 4.42 and Figure 4.43). N.B catalyst was at most observed and estimated to be relatively less porous than the other non-modified clay materials used in this work. The observed least porosity of N.B catalyst sample in turn, corresponds to the relatively high activity of this catalyst in the conversion of bioethanol.

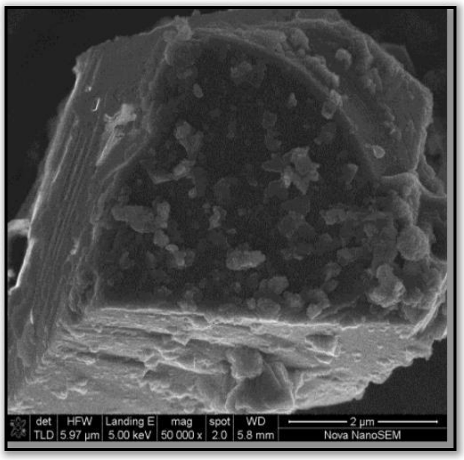
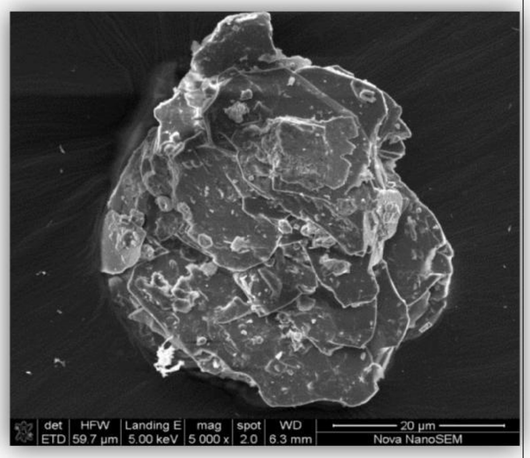
N.B	N.T
	
Bioethanol Conversion (%)	
84.95	44.85

Figure 4. 42: Effect of morphology and porosity of clay catalysts (N.B and N.T) on bioethanol conversion

According to Figure 4.42, catalyst activity on bioethanol conversion was then decreased by varying the catalyst from the N.B to N.T catalyst. This accordingly, was resulted due to the estimate increased porosity of N.T relative to N.B catalyst. In other word, the low porosity of N.B relative to N.T, was accounted by relatively non overlapping particles as observed.

Bentonite as clay material is prominently known for its higher binding property which during the experiment of beneficiation in aqueous suspension, was observed to be stronger than that of other clay materials used in this work (Figure 7.8-7.9_Appendix 2). The high binding property of bentonite clay is also reflective of its lower porosity as a catalyst sample. In other words, this indicates the possibility of high retention period of ethanol fed onto the catalyst during the reaction and hence resulting to favourable or relatively high activity in the conversion of bioethanol. or greater conversion.

N.K$_1$ catalyst in comparison to N.K$_2$ and N.K$_3$ catalyst , led to a relatively high bioethanol conversion and this according to Figure 4.43, was most possibly observed to be relatively less porous.

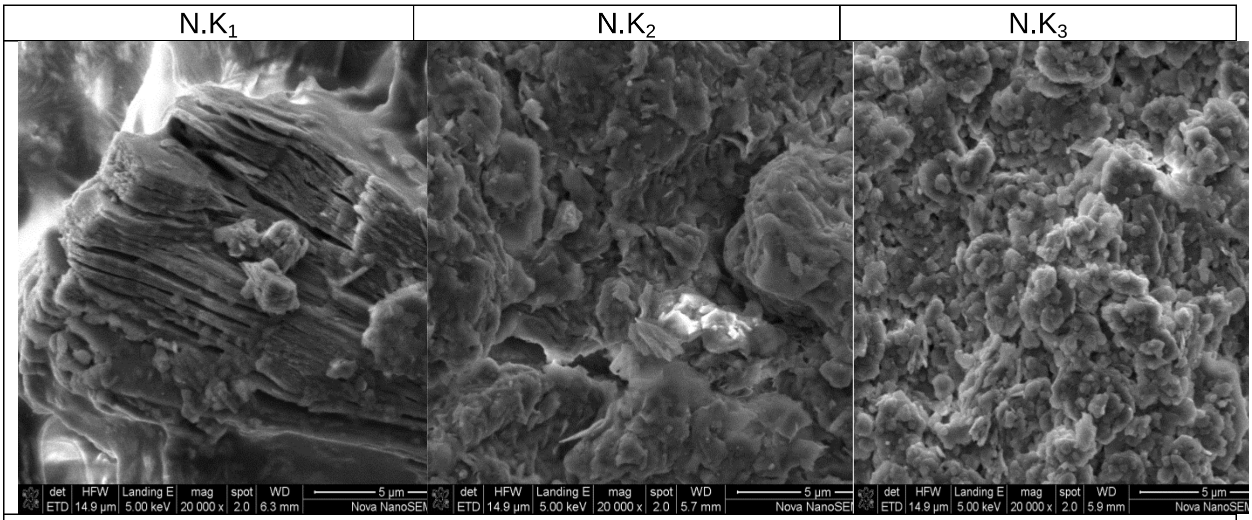
<table>
<tr><td>N.K$_1$</td><td>N.K$_2$</td><td>N.K$_3$</td></tr>
<tr><td colspan="3">
</td></tr>
<tr><td colspan="3">Bioethanol conversion (%)</td></tr>
<tr><td>60.27</td><td>43.06</td><td>43.45</td></tr>
</table>

Figure 4. 43: Effect of morphology and porosity of kaolin catalysts (N.K$_1$; N.K$_2$ and N.K$_3$) on bioethanol conversion

N.K$_2$ catalyst in turn, was observed to be slightly more porous than N.K$_3$ and hence relatively resulted to slight lower activity in the conversion of bioethanol (than N.K$_3$). A less porous catalyst sample is normally expected to retain bioethanol feed for longer time as soon as this is reached over the catalyst during the course of the reaction. Hence as a result, the less porous a clay catalyst sample (by estimation), the high the possibility of increased activity in the conversion of bioethanol.

4.3.2.3 Effect of porosity and Si/Al ratio of H-ZeoClay and H-ZeoClay on bioethanol conversion

In the afore discussion, N.B was most possibly estimated as the least porous catalyst among the non-modified clay samples. This as a result, led to this sample to be relative more active in the conversion of bioethanol.

Te H-ZeoCOM was earlier revealed to consist of particles that were closely overllaped and hence was found to be most possibly less porous than the H-ZeoClay catalyst (As observed through SEM image A2 and B2 in Figure 4.7_pg.81). The activity of H-ZeoCOM in the conversion of bioethanol as a result, was higher than that obtained by the H-ZeoClay under same reaction conditions (99.97 > 99.91 %).

More over in support to high activity of bioethanol by H-ZeoCOM, this sample (Commercial zeolite) as supplied by Zeolyst international, was reported to have a Si/Al ratio of 50. This further through protonation with ammonium chloride, was reduced to Si/Al ratio of 45.8 (Figure 7.3_Appendix 2). The prepared H-Zeoclay on the other hand, as revealed by EDS result in Figure 7.2 (Appendix 2), was found to have a Si/Al ratio of 23.

4.3.2.4 Effect of metal promotion on morphology and activity of catalyst on bioethanol conversion

Promotion of H-ZeoClay with Nickel, was earlier found to have led to enhanced and highest catalytic activity on bioethanol conversion as compared to other clay-based promoted catalyst, H-ZeoClay (Fe) and H-ZeoClay (Co). This resulted due the fact that H-ZeoClay (Ni) was found to consist of smaller particle size than H-ZeoClay (Fe) and H-ZeoClay (Co) catalyst (99.96 %). The trend in metal promotion on H-ZeoClay revealed that the smaller the catalyst particle size, the smaller the estimate porosity observed of the promoted catalyst. In other words, The highest activity of H-ZeoClay (Ni) relative to other promoted catalysts, correspond to the relatively low porosity of this catalyst sample.

H-ZeoClay (Ni) was as well found to be less porous than H-ZeoClay catalyst. This as a result, was among the factors to have led to reduced and suppressed selectivity of this catalyst to liquid hydrocarbons product, as well to olefins and parraffins-range hydrocarbons in the gaseous product. Nonetheless, the relatively low porosity of H-Zeoclay(Ni) led to unique and highest selectivity of toluene by this catalyst (This was earlier discussed through Figure 4.36_pg.120).

General observation from the above reveals that the less porous the sample of the clay-based zeolites, the higher will be the activity of this catalyst in the conversion of bioethanol and vice versa. This observation was also made among the non-modified clay catalysts (Non-zeolite clay-based catalysts)

4.3.3 Effect of mineralogical composition of clay catalyst (non-zeolite) on bioethanol conversion (non-zeolite)

The mineralogical composition of clays as mentioned earlier, are believed to among the possible properties to account for their catalytic performance on bioethanol conversion.

The core mineralogical content (phase) identified in bentonite catalyst were montmorrilonite, silica quarts and an aluminium-silicate based content. These initially amounted to 42.6 %, 48.8 % and 8.6 % composition in the non-modified clay (N.B).

Upon beneficiation (N.B → B.B), the phase content of silica quarts was enhanced (to 89.4 %), while that of montmorrilonite and silica-based content were decreased in the catalyst sample, B.B (to 4.4 and 6.2 % respectively). This as a result as obseverd in Table 4.8, led to decreased activity of the (B.B) clay catalyst on bioethanol conversion (At fixed reaction time of 6 hours). This slight catalyst deactivation was therefore found to correspond to large decreased amount of montmorillonite mineral in the catalyst sample (B.B), as well to decrease amount in the aluma silica-based mineral. The increased concentration of silica quartz in the catalyst sample (B.B) was among the inhibiting factors on catalyst activation (as a result of beneficiaton) in the conversion of bioethanol. The above discussed are observed In Table 4.8.

Table 4.8: Effect of beneficiation and acid-modification on mineralogical composition of bentonite clay catalyst

Clay-based catalysts	**Mineralogical composition** (%, w/w)			**Conversion , %**
	Montmorrilonite	Silica Quartz	Aluminium silicate content	
N.B	42.6	48.8	8.6	84.85
B.B	4.4	89.4	6.2	81.01
B.B1M	32.9	64.6	2.5	87.28

Further modification of clay catalyst with sulphuric acid as observed in Table 4.8, led to significant recovery of montmorrilonirte percentage phase content by 28.5 % (4.4 to 32.9 %), decrease in silica quarts content by 24.8 % (89.4 to 64.6 %) and further decrease in the phase composition of alumina-silica based mineral to 2.5 %. The sudden recovery and significant increase in the activity of the clay catalyst (B.B$_{1M}$) on bioethanol (81 to 87.28 % conversion), was therefore impacted by the increased amount of montmorrilonite content in the clay sample and decrease in the phase composition of silica quarts. In otherwords, the montmorrilnote mineral content in (bentonite) clay was among the determining properties for favourable catalyst activity in the conversion of bioethanol. Many literature have reported that montmorrilonite is a chief mineral content in bentonite and is a potential and predominant mineral used in various catalytic applications (Igbokwe, 2011). This clay mineral, in addition to kaolin mineral , are known as the most important clays used in the manufacturing of catalysts (Eman, 2013). This then reveals the potential of this mineral concentration in favour to bioethanol conversion. Silica quarts content on the other hand, was found not to be a active content in clay activity towards bioethanol conversion. Further reduction of this material can be achieved through additional investigation on acid modification approach. Variation in aluminasilica-based mineral content on the other hand, was insginicant as a result of catalyst beneficiation and acid modification. This mineral as a result, seemed to have impacted insignifcatntly in catalyst activity on bioethanol conversion.

Bioethanol conversion observed with variaition in catalyst mineralogical content, as discussed above, is graphically reported in Figure 4.44.

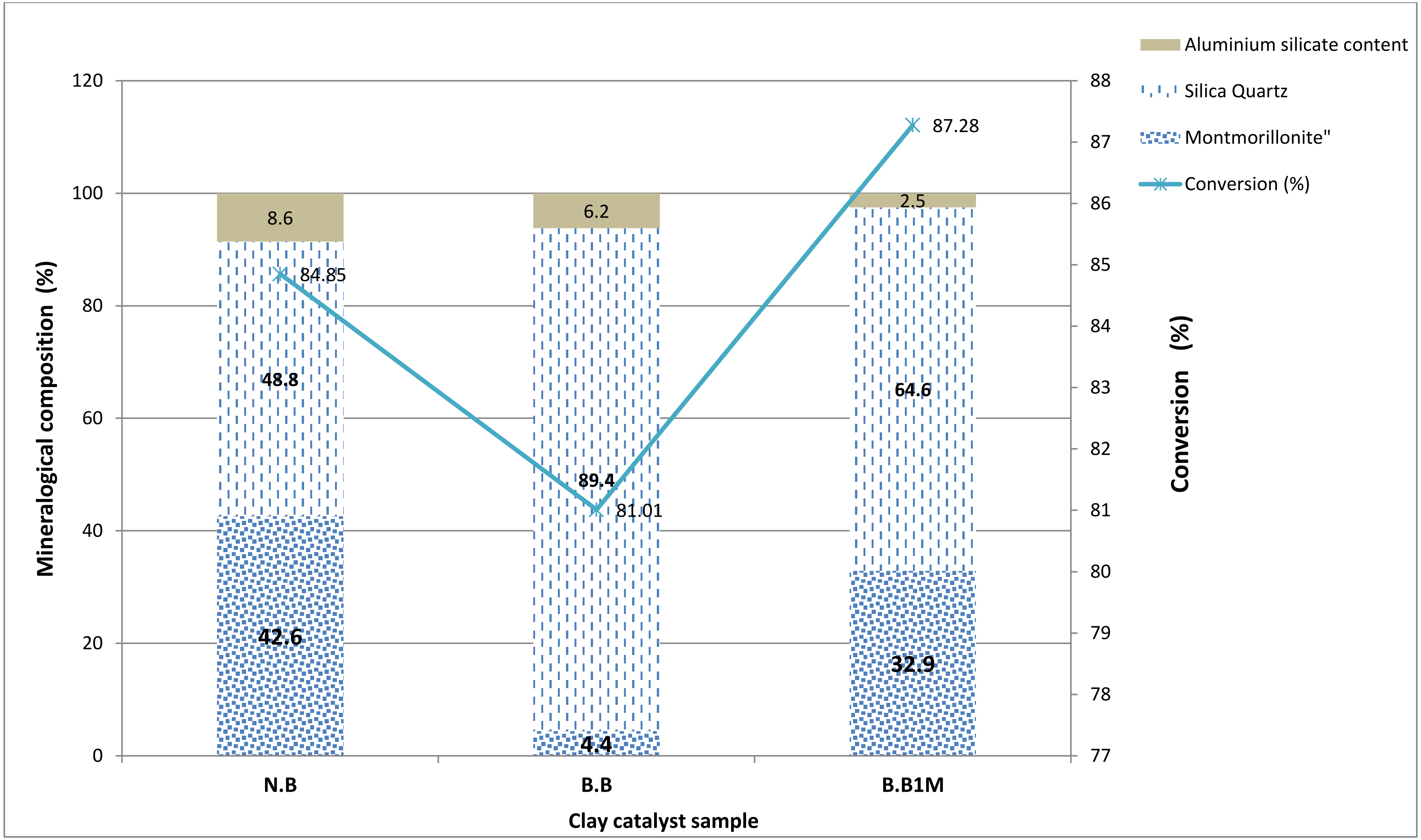


Figure 4.44: Effect of clay mineralogical composition on bioethanol conversion (At 350 ^{o}C and 6 hour fixed reaction conditions).

4.4 Possible assumptions, deviations, errors and challenges

4.4.1 Deviation from literature

The analysis (as well as the collection) of gas product and liquid product in this work was carried out separately (in two separate Gas Chromatography equipments), making the distribution and selective of hydrocarbons in the liquid and gas product to be calculated and reported separately throughout the discusssion and finding section. Certain literature reports on the selectvity of liquid and gas product collectively, and this attempt (collective selectivity in mol or mass %) to justify for mass or mole balance in alignment to bioethanol conversion (obtained over each clay-based catalyst), was then reported earlier in Table 4.7 (pg.127) – whch was deducted from the detailed Table 4.7 in Appendix 4.

The gas molecules in the gas product (as reported in Table 7.1-7.6_ Appendix 1) appeared as triplet per distribution. The three molecules per distribution were assumed to be in equimolar amount (Each constitute one third of the distribution) – See Table 7.7 (Appendix 1)

Due to large amount and random distribution of gas molecules observed in the gaseous product as given by the GC data (Table 7.1-7.6_ Appendix 1); gas hydrocarbon molecules were classified according their respective categories (Mainly olefins and paraffins) and the collective selectivity of each category by clay-basedcatalysts or respective concentration in the liquid or gas product (i.e. either olefins, parrafins or others) was then the one reported through the figures. Hydrocarbons detected in trace amount (or uncommon) in the gas products were not reported neither discussed through the selectivity figures of this work.

It was observed that certain hydrocarbon molecules evaporate at all temperatures. Hence these were detected in both liquid and gas product in this work. These include such as diethyl ether, benzene and toluene, and the C_5 olefins and parraffins. These were collected from the reactor into the gas product at higher tempetarure in their gaseous state (Above their boiling temperature) and immediately analysed after the completion of the reaction. Certain amount of the above hydrocarbons collected in the gaseous state, was as a result of them not to have condensed due to shorter residence time in the condenser and hence were collected altogether with other gases (as liquid content) in the gas product.

4.4.2 Lack of accuracy or further findings due lack of resources

Certain findings in this work were restricted due to lack of equipments, reagents and sources to investigate and identify them. These include not evualating and assessing the clay-based catalysts at temperature above 400 ºC; inability to identify certain hydrocarbon in the obatined products due to lack of adequate GC calibration standards; Inability to carry out additional characterisation techniques for accurate measurement of certain catalytic properties (Catalyst surface area, porosity and acidity) ; and limited supportive sources / literarture work to reference for or in line with the use of clay materials or clay-based catalysts for bioethanol conversion. These are further discussed below.

The capped regulated temperature supplied by the furnace was 400 ºC. This due lack of technical assistance for adjustment, limited the research for possible reactions beyond 400 ºC. A rise in temperature from 350 to 400 ºC did not affect conversion; this however showed a forecasted trend for increased bioethanol conversion with increase in reaction temperature, as well catalysts selectivity towards dominant hydrocarbons in the liquid and gas product.

4.4.2.1 Limitation to findings and supportive information (Hence exclusive findings to this work)

Very little work and sources have been reported on clay materials or clay-based catalysts for bioethanol conversion. From the few obtained (Gruver et al., 1995; Corma et al., 2012; Widjaya et al., 2012; etc.), limited information is due to relate or support this work. For example certain of these sources report on the use of sepiolite clay as a catalyst for bioethanol dehydration at lower reaction temperatures (200 – 250 ºC). Unlike this work, the application of catalysts such as kaolin, talc clay including bentonite (In the natural non-modified to modified state) have been investigated for bioethanol conversion at higher temperature (350 ˚C). More over, none of open literature has reported on both synthesis and clay-based catalysts (clay-based zeolites in partcular) application for the conversion of bioethanol conversion. This makes such findings exclusive to this work.

5. Conclusion and Recommendations

5.1 Conclusions

All clay-based catalysts prepared and employed in this work were found active for catalytic conversion of bioethanol. Bentonitic clay in the non-modified state and among non-zeolite clay-based catalysts, initially led to bioethanol conversion of 84.9 %. Clay beneficiation followed by acid modification of this sample, resulted inreduction in catalyst particle size,increase in sides and increase in Si/Al ratio of the clay catalyst. These as a result, led to activity of the bentonite catalyst to enhance to 87.3 % bioethanol conversion

Further on, the research and experimental finding revealed that the catalyst developed from clay (H-ZeoClay) in this work was identical to ZSM-5 zeolite. The H-ZeoClay in question was found to represent the structural framework of ZSM-5 zeolite in similar manner as the XRD data in literature, for a doublet at 6-10^0 2θ along with a triplet at 22-25^0. Dominance in cuboidal morphology of crystal units of the H-ZeoClay was also found to correspond to the morphology of those of zeolites reported in literature. The above similarly applied for commercial zeolite (H-ZeoCOM) which was used as yardstick to H-ZeoClay. The average EDS result of the H-ZeoClay catalyst revealed the Si/Al ratio of 23, while that of H-ZeoCOM was 46. The clay-based zeolite (H-ZeoClay) through the above finding led to further increased to 99.91 % bioethanol conversion, which in this regard under similar conditions is comparable for most zeolites in literature. The yardstick H-ZeoCOM as also comparable to H-ZeoClay, closely led to 99.97 % bioethanol conversion. From statiscally viewpoint, the H-Zclay and H-ZeoCOM have achieved the same conversion and H-Zclay recommendly and subtly compared, could lead to the exact or even greater conversion than H-ZeoCOM if it is re-synthesized with the same Si/Al ratio ratio as the H-ZeoCOM.Si/Al ratio

Increase in reaction temperature over the H-ZeoClay slightly led to increased bioethanol conversion of 99.95 %. Nonetheless Promotion (by impregnation) of H-ZeoClay with Nickel at fixed temperature of 350 ^{0}C, resulted to further and most increased activity of the catalyst on bioethanol conversion of 99.99 %. The highest activity of H-ZeoClay (Ni) relative to precursor and other promoted catalysts, corresponded to the relatively smaller particle size and low estimate porosity of this catalyst sample.

Product selectvity and distribution by clay-based catalysts was most dominant towards gaseous hydrocarbons as compared to liquid hydrocarbons. The dominance in liquid or gaseous hydrocarbon product obtained in literature through zeolite catalysts, has been observed to be inconsistent(Sometimes liquid product more dominant than gas product and vice versa). Light olefins (C_3-C_5), gaseous diethyl ether and light paraffins were the gaseous hydrocarbons obtained in this work by order of high selectivity in the product. This for liquid products includes diethyl ether, toluene, xylene, benzene, methanol and butanol. The clay-based zeolite in common to commercial zeolite, was exclusively selective to xylene by low proportion in the liquid product. This catalyst from major to decrease proportion was selective to light olefins, light paraffins, liquid benzene and toluene. The identity of hydrocarbons product and the trend of their selectivity and distribution by clay-based zeolite, makes the clay-based zeolite comparable to the yardstick commercial zeolite, as well as to various zeolite (H-ZSM-5) catalysts reported in literature. Benzene and toluene aromatics, including paraffins hydrocarbons obtained above are gasoline constituents, which in litearure the zeolite H-ZMS-5 has been successfully exploited for their production from ethanol.

The selectivity of butanol by Bentonite clay catalyst at relatively higher proportion makes this catalyst through this work comparable to one in literature in this regards. Moreover, the selectivity of Bentonite catalyst to light hydrocarbons such as butadiene and diethyl ether, also makes it comparable to Bentonite and other clay-based catalysts in literature.Clay-based catalysts (precisely the H-ZeoClay) in this work were found to be mainly selective to light olefins and paraffins in the range C_3-C_6. This has been similarly observed in literature for H-ZSM-5 catalyst, except for simultansous selectivity of light and heavier olefins and paraffisn hydrocarbons by certain zeolites (C_3^+).

The distinct selectivity of aromatic hydrocarbons by clay-based zeolites and that of light alcohols by non-zeolite clay-based catalysts, revealed that the latter mainly served for catalytic cracking of bioethanol. Clay-based zeolites on the other hand led to both cracking followed by actual catalytic conversion of bioethanol to aromatics hydrocarbons (Cyclization of intermediate hydrocarbons). Hence the non-zeolite clay-based catalysts can be recommended for the production of butanol and methanol from bioethanol; whereas the clay-based zeolites could be favourabiliy recommended for the production of light olefins and aromatic hydrocarbons.

Bioethanol conversion using the non-modified clay, modified clay and clay-based zeolites was found averagely optimum for reactions of 6 hours.

The application of clay catalysts in their very natural non-modified state, followed by their modification and evaluation on bioethanol conversion, was to the best of author's knowledge. Like wise, development of the valuable clay-based zeolites , followed by evaluation of these catalysts on bioethanol conversion, was to the best of author's knowledge.

5.2 Recommendations

Direct modification of clay catalyst with acid and omitting the clay beneficiation approach in prior, is rather recommended in order to have obtained the same catalytic activity as that through clay beneficiation. A further investigation to modify other variety of clay samples (Non-zeolite clay-based catalyst) with sulphuric acid is recommended so as to assess and compare their catalytic properties and performance to that of bentonite clay employed in this work.

Investigation of catalyst regeneration and reusability is a further study recommended using the optimum clay-based catalyst and reaction conditions (clay-based catalytic system from this work) obtained from this work

Additional characterisation techniques on the various catalysts synthesised in this work (mainly the clay-based zeolite and acid-modified catalyst), are recommended to determine the accuracy of certain of their catalytic properties – Such as the surface and porosity measurement by BET, acidity measurement by TPD-NH_3 measurement and thermal stability assessment by TGA measurement.

Targeting this work mainly towards the production of high value hydrocarbons (such as gasoline-range) will make it more beneficial and recommended. This will be viable if the overall focus of this work is refrained from non-zeolite clay-based catalysts and rather orientated only towards developing clay-based zeolites, that will be competitive to commercial zeolite catalysts (for bioethanol conversion).

The application of clay-based zeolite at much higher reaction temperatures minimally from 400 ^{o}C, is well recommended. This is due to the least favourable outcome (average increase) that was observed in the conversion of bioethanol and proportional selectivity of hydrocarbons (In both liquid and gas product) that was also observed by mere increase in reaction temperature from 350 ^{o}C to 400 ^{o}C. The capped regulated temperature supplied by the furnace , was however 400 ^{o}C.

Employing the metal-promoted clay-based zeolite catalysts at the increased reaction temperature of 400 °C and above (other than 350 °C as in this work) is also recommended in anticipation for increased bioethanol conversion and hydrocarbons selectivity in the product. The application of the above mentioned catalysts simply at 350 °C led to the most favourable selectivity of olefins, toluene and benzene in the gas product.

Promotion of the non-zeolite clay-based catalysts (e.g N.B) with metal elements can also be investigated so as to assess their outcome performance on bioethanol conversion. Other methods of metal promotion such as ion exchange (the popular used in literature for zeolite promotion) is recommended due its popularity by various researchers and most regardingly improvement of catalyst performance

Throughout this work, clay-based catalysts employed for bioethanol conversion, were found to be dominantly selective to gaseous hydrocarbon products as compared to liquid product. Hence to settle a balance between the selectivity of liquid and gaseous product in this regard, additional reactions could be carried out or investigated at temperature range below 300 °C. Similarly, the performance of clay-based catalysts could be as well investigated at the above temperature range.

Bioethanol conversion over clay-based catalysts was relatively optimum at 6 hour reactions. Additional experiments over clay-based zeolites are recommended for 2 hours and longer reaction period than 6 hours so as to assess for the activity of these catalysts with time.

6. Bibliography

6.1 Journal articles

Blanchard, R., Richardson, D.M., O'Farrell, P.J. & Von Maltitz, G.P. 2011. Biofuels and biodiversity in South Africa. South African Journal of Science, 107: May/June

Calsavara, V., Baesso, M.L. & Fernandes-Machado, N.R.C. 2008. Transformation of ethanol into hydrocarbons on ZSM-5 zeolites modified with iron in different ways. *Fuel*, 87(8-9): 1628–1636.

Chantawong V., H., N.W. 2003. Synthesis of Zeolite from Thai Kaolin for Wastewater Treatment. *2nd Regional Conference on Energy Technology Towards a Clean Environment*: 9–024.

Choudhary, R.P., Sheoran, A.S. & Trivedi, S,K. 2012. A Small Benefitiation Unit: State of Art. *International Journal of Earth Sciences And Engineering*, 775-781, August.

Corma, A., Iborra, S. & Velty, A. 2007. Chemical Routes for the Transformation of Biomass into Chemicals. *Chemical Reviews*, 107(6): 2411–2502.

Corma, A., Mengual, J. & Miguel, P.J. 2012. Stabilization of ZSM-5 zeolite catalysts for steam catalytic cracking of naphtha for production of propene and ethene. *Applied Catalysis A: General*, 421-422: 121–134.

Corma, A. & Perez-Pariente, J. 1987. Catalytic activity of modified silicates: I. Dehydration of ethanol catalysed by acidic sepiolite. *Clay Miner*, 22(4): 423–433.

Ekosse, G.-I.E. 2010. Kaolin deposits and occurrences in Africa: Geology, mineralogy and utilization. *Applied Clay Science*, 50(2): 212–236.

Emam, E.A. 2013. Clays as catalysts in petroleum refining industry. *ARPN Journal of Science and Technology*, 3(4): 356–375.

Gayubo, A.G., Aguayo, A.T., Atutxa, A., Prieto, R. & Bilbao, J. 2004. Deactivation of a HZSM-5 Zeolite Catalyst in the Transformation of the Aqueous Fraction of Biomass Pyrolysis Oil into Hydrocarbons. *Energy & Fuels*, 18(6): 1640–1647.

Gruver, V., Sun, A. & Fripiat, J.J. 1995. Catalytic properties of aluminated sepiolite in bioethanol conversion. *Catalysis letters*, 34(3-4): 359–364.

Guo, F. & Fang, Z. 2011. Biodiesel production with solid catalysts. *Biodiesel, Feedstocks and ProcessingTechnologies*. https://www.researchgate.net/profile/Margarita_Stoytcheva/publication/275885801_Biodiesel_Feedstocks_and_Processing_Technologies/links/554881850cf2e2031b387ba7.pdf#page=352 30 March 2016.

Heckroodt, R.O. 1991. Clay and clay materials in South Africa. *J. South. Afr. Inst. Min. Metall*, 91: 343–363.

Hillier, S. 2003. Clay Mineralogy. Encyclopaedia of sediments and sedimentary rocks: Kluwer Academic Publishers, Dordrecht: 139-142.

Hoang, T.Q., Zhu, X., Danuthai, T., Lobban, L.L., Resasco, D.E. & Mallinson, R.G. 2010. Conversion of Glycerol to Alkyl-aromatics over Zeolites. *Energy & Fuels*, 24(7): 3804–3809.

Igbokwe, P.K, N., M.S. 2011. Effect of activation parameters on conversion in clay catalysed esterification of acetic acid. *International Journal of Basic & Applied Sciences IJBAS-IJENS*, 11(5): 1–8.

Inaba, M., Murata, K., Saito, M. & Takahara, I. 2006. Ethanol conversion to aromatic hydrocarbons over several zeolite catalysts. *Reaction Kinetics and Catalysis Letters*, 88(1): 135–141.

Jacob, R.E., Mitha, V.R. & MacPherson, D. 2004. The kaolinitic clay deposits on Beaconsfield, north of Grahamstown. *South African journal of science*, 100. http://search.ebscohost.com/login.aspx?direct=true&profile=ehost&scope=site&authtype=crawler&jrnl=00382353&AN=16509273&h=IoYYc5grhqUaYWaSuI%2Bxcas1Jwo9d%2BcCf3c9x0fI6bq61P4KRNQgWx7y9x6MmD3gHeiCYkwt4%2BpyWKmFfAPj%2Bw%3D%3D&crl=c 30 March 2016.

Khatamian, M. & Irani, M. 2009. Preparation and characterization of nanosized ZSM-5 zeolite using kaolin and investigation of kaolin content, crystallization time and temperature changes on the size and crystallinity of products. *Journal of the Iranian Chemical Society*, 6(1): 187–194.

Kim, K.S., Park, J.O. & Nam, S.C. 2013. Synthesis of Iron-loaded Zeolites for Removal of Ammonium and Phosphate from Aqueous Solutions. *Environmental Engineering Research*, 18(4): 267–276.

Lee, D.-W., Park, Y.-M. & Lee, K.-Y. 2009. Heterogeneous Base Catalysts for Transesterification in Biodiesel Synthesis. *Catalysis Surveys from Asia*, 13(2): 63–77.

Machado, N.R.C.F., Calsavara, V., Astrath, N.G.C., Matsuda, C.K., Paesano(Jnr), A. & Baesso, M.L. 2006. Hydrocarbons From ethanol Using [Fe,Al]ZSM-5 Zeolites Obtained By Direct Synthesis. *Applied Catalysis A: General*, 311:193-198, June.

Machado, N.R.C.F., Calsavara, V., Astrath, N.G.C., Matsuda, C.K.,Junior, A.P., A. & Baesso, M.L. 2005. Obtaining Hydrocarbons From ethanol Over Iron-Modified ZSM-5 Zeolites. *Fuel*, 84: 2064-2070, May.

Madeira, F.F., Tayeb, K.B., Pinard, L., Vezin, H., Maury, S, & Cadran, N. 2012. ethanol Transformation Into Hydrocarbons On ZSM-5 Zeolites: Influence of Si/Al ratio Ratio On Catalytic Performances And Deactivation Rate. Study of The Radical Species Role. *Applied Catalysis A: General*, 443-444: 171-180, August

Madeira, F.F., Gnep, N.S., Magnoux, P., Vezin, H., Maury, S. & Cadran, N. 2010. Mechanistic insights on the ethanol transformation into hydrocarbons over HZSM-5 zeolite. *Chemical Engineering Journal*, 161(3): 403–408.

Manos, G., Yusof, I.Y., Papayannakos, N. & Gangas, N.H. 2001. Catalytic Cracking of Polyethylene over Clay Catalysts. Comparison with an Ultrastable Y Zeolite. *Industrial & Engineering Chemistry Research*, 40(10): 2220–2225.

Mezni, M., Hamzaoui, A., Hamdi, N. & Srasra, E. 2011. Synthesis of zeolites from the low-grade Tunisian natural illite by two different methods. *Applied Clay Science*, 52(3): 209–218.

Mills, G.A., Holmes, J. & Cornelius, E.B. 1950. The Acid Activation of Some Bentonite Clays. *The Journal of Physical Chemistry*, 54(8): 1170–1185.

Mori, K., Matsubara, H., Kitagawa, K., Kubota, Y. & Takahashi, R. STUDY ON BIO-DIESEL FUEL PRODUCTION FROM COFFEE GROUNDS BY SOLID CATALYST METHOD. http://paginas.fe.up.pt/clme/icem15/ICEM15_CD/data/papers/2997.pdf 30 March 2016.

Mravec, D., Strestikova, E., Ilavsky, J., Hrabe, Z., & Majling, J. 1987. Preparation Of Synthetic Zeolite ZSM-5. *Chem. Papers*, 41(3): 335-341, August.

Musyoka, N.M., Missengue, R., Kusisakana, M. & Petrik, L.F. 2014. Conversion of South African clays into high quality zeolites. Applied Clay Science, 97-98: 182–186.

Onal, M., Sarikaya, Y., Alemdaroglu, T. & Bozdogan, İ. 2002. The effect of acid activation on some physicochemical properties of a bentonite. *Turkish Journal of Chemistry*, 26(3): 409–416.

Rahimi, N. & Karimzadeh, R. 2011 *Catalytic cracking of hydrocarbons over modified ZSM-5 zeolites to produce light Olefins*. Applied Catalysis A: General 398 (2011) 1–17.

Rinaldi, R. & Schüth, F. 2009. Design of solid catalysts for the conversion of biomass. *Energy & Environmental Science*, 2(6): 610.

Robertson, M.A., F.G.S., R.H.S, 1991. *Clay minerals as catalysts*.

Rownaghi, A.A., Rezaei, F. & Hedlund, J. 2011. Yield of gasoline-range hydrocarbons as a function of uniform ZSM-5 crystal size. *Catalysis Communications*, 14(1): 37–41.

Schwarz, J.A., Contescu, C. & Contescu, A. 1995. Methods for preparation of catalytic materials. *Chemical Reviews*, 95(3): 477–510.

Silva, V.J., Rodrigues, J.J., Soares, R.R., Napolitano, M.N. & Rodrigues, M.G.F. 2013. Cobalt supported on zsm-5 zeolite using kaolin as silicon and aluminun sources for fischer-tropsch synthesis. *Brazilian Journal of Petroleum and Gas*, 7(2): 83–94.

Sivasamy, A., Cheah, K.Y., Fornasiero, P., Kemausuor, F., Zinoviev, S. & Miertus, S. 2009. Catalytic Applications in the Production of Biodiesel from Vegetable Oils. *ChemSusChem*, 2(4): 278–300.

Temuujin, J., Jadambaa, T., Burmaa, G., Erdenechimeg, S., Amarsanaa, J. & MacKenzie, K.J.D. 2004. Characterisation of acid activated montmorillonite clay from Tuulant (Mongolia). *Ceramics International*, 30(2): 251–255.

Viswanadham, N., Saxena, S.K., Kumar, J., Sreenivasulu, P. & Nandan, D. 2012. Catalytic performance of nano crystalline H-ZSM-5 in ethanol to gasoline (ETG) reaction. *Fuel*, 95: 298–304.

Wang, P., Shen, B., Shen, D., Peng, T. & Gao, J. 2007. Synthesis of ZSM-5 zeolite from expanded perlite/kaolin and its catalytic performance for FCC naphtha aromatization. *Catalysis Communications*, 8(10): 1452–1456.

Weitkamp, J. 2000. Zeolites and catalysis. *Solid State Ionics*, 131(1): 175–188.

Widjaya, R.R., Soegijono, B. & Rinaldi, N. 2012. Characterization of Cr/bentonite and HZSM-5 zeolite as catalysts for bioethanol conversion to biogasoline. *Makara J. Sci.*, 16(1): 65–70.

Yahiaoui, A., Belbachir, M. & Hachemaoui, A. 2003. An acid exchanged montmorillonite clay-catalyzed synthesis of polyepichlorhydrin. *International Journal of Molecular Sciences*, 4(10): 548–561.

Zhang, R. 2010. The Elemental Composition of Atmospheric Particles at Beijing during Asian Dust Events in Spring 2004. *Aerosol and Air Quality Research*. http://www.aaqr.org/Doi.php?id=8_AAQR-09-05-OA-0038&v=10&i=1&m=2&y=2010 30 March 2016.

Zhou, C.H. 2011. Clay mineral-based catalysts and catalysis. *Applied Clay Science*, 53(2): 85–86.

6.2 Books

Academy of Science of South Africa (ASSAf). 2015. *The State of Green Technologies in South Africa.*November 2014.

Cape Peninsula University of Technology (CPUT). 2013. *Research, Technology Innovation and Partnerships (RTI)*. 10-year blueprint: November 2012.

Chapman, J.H. & Anderson, D.1980. Method of clay beneficiation. USA

Chorkendorff, I. & Niemantsverdriet, J.W. 2007. *Concepts of Modern Catalysis and Kinetics*. 2nd revised and enlarged Ed.

Dr. Wilczura-Wachnik, H. 2006. *Catalytic dehydration of alcohols.* University of Warsaw: Faculty of Chemistry.

First, E. L., Gounaris, C. E., Wei, J., and Floudas, C. A. 2011. *Computational characterization of zeolite porous networks: an automated approach*. Physical Chemistry, Chemical Physics, 13(38), 17339-17358.

Grim, R. E. & Grimshaw R.W*.* 2012*.* Clay Mineralogy*. The Columbia Electronic Encyclopedia.* 6th ed.: Columbia University Press.
© 2000–2015 Sandbox Networks, Inc., publishing as Infoplease.
13 Aug. 2016 <http://www.infoplease.com/ce6/people/A0844662.html>.

Hagen, J. 2006. *Industrial catalysis*. A practical approach.”Wiley-VCH Verlag GmbH, Weinheim, Germany.

Kettha. 2009. *National Green Technology Policy and Government Initiatives*.pdf.

Lancashire Pr. R.J, 1995- 2013. *Conversion of ethanol to gasoline-range hydrocarbons*. Jamaica: The department of Chemistry, University of the West Indies,Mona Campus.

Marcus, Bonnie K., Cormier and William E. June 1990. "*Going Green with Zeolites*": Chemical Engineering Progress.

Milliken, T.H, Oblad, A.G & and Mills, G.A.1950. *Use of clays as petroleum cracking catalysts*.

Petani, S., Barrett, A. Huynh, T. & Pham, H. 2013. *Methanol to Gasoline conversion*. University of California San Diego.

Pushpaletha, P., Rugmini, S. & Lalithambika, M. 2005. *Correlation between surface properties and catalytic activity of clay catalysts*. India: Regional Research Laboratory (CSIR) & Industrial Estate (PO), Thiruvananthapuram

Yuan, J., Everett, B.E & Andrews, W.R.1997. *Method for beneficiating discoloured kaolin to produce high brightness coating clay*. USA

6.3 Websites

Art 186. 2014*. Intro to ceramics.* **http://seco.glendale.edu/-rkibler/clay.html** *[December 24].*

Burgess Pigment Company. 2012*. What is Kaolin?* **http://www.burgesspigment.com/burgesswebsite.nsf.html[n.d]**

Chemical engineering tools and information. 2011. *Green Chemistry with Zeolite Catalysts.* **http://www.cheresources.com/zeolitezz.shtml** [n.d].

Greener industry, 2015. Ethanol: *Production Methods Summary*. **http://www.greener-industry.org.uk/pages/ethanol/ethanol4PMS.htm**

Infoplease. 2005. *Clay: Properties and Classification.* **http://www.infoplease.com/encyclopedia/science/clay-properties-classification.html** [October 2014].

Mindat.org. 2014. *Kaolinite*. **http://mindat.org/min-2156.html** [March 30, 2014].

Mineral Gallery, 2006.*The clay mineral group.* **http://www.galleries.com/Clays_Group** [February 2007]

ALS Environmental.n.d. *Petroleum hydrocarbon ranges_Flyer*.. **http://www.alsglobal.com/environmental/services/north-america-environmental-services/usa/petroleum-hydrocarbons.aspx** [2014]

P & G. 2014. Zeolite. http://scienceinthebox.com/what-are-zeolites.html *[10 April 2014].*

USDC. n.d. *Methanol to Gasoline conversion.* **http://chemelab.ucsd.edu/mbioethanol/indexMTG/main.html** *[November 2014].*

Lancashire. 2013. *Conversion of ethanol to gasoline-range hydrocarbons*. **http://wwwchem.uwimona.edu.jm/lectures/synfuel.html** [November 2014].

7. Appendix

NB: Tables, Figures, equations or calculations for Appendix 1, Appendix 2 and Appendix 3 as mentioned below, were obtained and extracted from excel's spreadsheets.

Appendix 1

7.1 Product distribution of liquid and gaseous hydrocarbons from bioethanol conversion over several clay-based catalysts **(Table 7.1 - Table 7.6)**

Table 7. 1: Product Distribution of liquid and gaseous hydrocarbons from bioethanol conversion over natural (non-modified) clay catalysts

	Rxn no.	Rxn.4	Rxn.1	Rxn.3	Rxn.2	Rxn.5	Rxn.6	Rxn.7
	Synthesis method -->	**Natural or non-modified clays**						
	Clay-based Catalyst -->	N.T (75-212 um)	N.B (75-212 um)	N.K1 (75-212 um)	N.K2 (75-212 um)	N.K3 (75-150 um)	N.B (75-212 um)	N.B (75-212 um)
	Reaction time	**6 hours reaction**					2 hours reaction	4 hours reaction
	Ethanol conversion (%) -->	**44.85**	**84.95**	**60.27**	**43.06**	**43.45**	**75.37**	**47.87**
Product distribution & selectivity (Conc.-selectivity / %)	**Hydrocarbon liquid fraction**	**R.T (Component)** % Composition	**R.T (Component)** % Composition	**R.T (Component)** % Composition	**R.T (Component)** % Composition	R.T (Component) % Composition	**R.T (Component)** % Composition	**R.T (Component)** % Composition
		10.852 (BuOH) 6.66 %	10.862 (BuOH) 3.52 %	10.877 (BuOH) 10.4 %	10.88 (BuOH) 13.05 %	10.906 (BuOH) 6.84 %	10.858 (BuOH) 4.4 %	10.873 (BuOH) 6.31 %
		11.168 (D.E) 5.07 %	11.144 (D.E) 3.57 %	11.167 (D.E) 50.01 %	11.172 (D.E) 5.03 %	11.193 (D.E) 4.85 %	11.144 (D.E) 6.01 %	11.162 (D.E) 4.19 %
		11.507 (MeOH) 0.29 %	11.482 (MeOH) 4.64 %	11.501 (MeOH) 0.29 %	11.509 (MeOH) 0.28 %	11.53 (MeOH) 0.47 %	11.481 (MeOH) 4.53 %	11.497 (MeOH) 0.80 %
		11.681 (EtOH) 55.15 %	**11.674 (EtOH) 15.049 %**	**11.688 (EtOH) 39.73 %**	**11.695 (EtOH) 56.938 %**	**11.723 (EtOH) 56.55 %**	**11.674 (EtOH) 24.6 %**	**11.677 (EtOH) 52.13 %**
		N/a **(Water) 27.12 %**	N/a **(Water) 73.22%**	N/a **(Water) 44.45 %**	N/a (Water) 24.62 %	n/a **(Water)** 31.23 %	n/a **(Water)** 60.27 %	n/a **(Water)** 36.49 %
	Total liquid produced (ml)	≈23.5 ml	≈ 14.25 ml	≈19.8 ml	24 ml	17.5 ml	≈ 5.2 ml	≈ 15 ml
	Hydrocarbon liquid fraction	**R.T Area (%) Quality (%)**	**R.T Area (%)** Qlty	**R.T Area (%)** Qlty	**R.T Area (%)** Qlty	**R.T Area (%) Qlty**	**R.T Area (%)** Qlty%	**R.T Area (%)** Qlty%
		1.935 48.15%	**1.935 33.04%**	**1.935 11.73%**	**1.939 10.09%**	1.936 26.06%	**1.935 47.46%**	**1.934 42.68%**
		Bicyclo[1.1.0]butane	Bicyclo[1.1.0]butane	Bicyclo[1.1.0]butane	Bicyclo[1.1.0]butane (45)	Bicyclo[1.1.0]butane (40)	Bicyclo[1.1.0]butane (45)	Bicyclo[1.1.0]butane
		1,3-Butadiene	1-Methylcyclopropene	1,3-Butadiene	1,3-Butadiene (9)	1,3-Butadiene (9)	1-Methylcyclopropene (9)	1-Methylcyclopropene
		1-Methylcyclopropene	1,3-Butadiene	1,3-Butadiene	1-Methylcyclopropene (9)	1,3-Butadiene (9)	1,3-Butadiene (9)	1,3-Butadiene
		2.118 51.85%	**2.115 66.96%**	**2.112 88.27%**	**2.118 89.91 Qlty**	2.114 73.94%	**2.114 50.99%**	**2.115 57.32%**
		Ethyl ether	Ethyl ether	Ethyl ether	Ethyl ether (78)	Diethylether	Ethyl ether	Ethyl ether
		Ethyl ether	Ethyl ether	Ethyl ether	Ethyl ether (64)	Diethylether	Ethyl ether	Ethyl ether
		Ethyl ether	Ethyl ether	Ethyl ether	Ethyl ether (64)	Diethylether	Ethyl ether	Ethyl ether
							2.160 1.55%	
							2-Butene, 2-methyl-	(86)
							2-Pentene	(86)
							2-Butene, 2-methyl-	(86)
	Average Total gas produced	3802.9	12579.5	10287.7	8823.4	15992.79	5114.4	5909.5

7.2 Interpretation of GC area concentration to % concentration, to mole and weight selectivity of hydrocarbons in the liquid and gas product (Table 7.1.1 _ below)

Table 7.1. 1: Interpretation of GC area concenration to % concentration, mole and weight % hydrocarbon products

Liquid fractions		N.B (6 hrs rxn)	(Rxn No.1)						
Peak number	Retention Time	Area (∫)	GC Area Concentration (%)	Hydrocarbon Identity	Actual concentration (%) (a)	Mole (b)	Mole (%)	Mass (g) = n(b)* Mr	Mass % (wt %)
1	-	-	-	-	96	40.8			
2	10.862	716.6	3.52	Butanol	3.52	0.50	1.869	37.16	3.4360
3	11.144	726.7	3.57	Diethyl ether	3.57	0.51	1.895	37.68	3.48438
4	11.482	945.6	4.64	Methanol	4.64	0.66	2.466	21.20	1.9599
5	11.674	**17 979.80**	88.27	Ethanol	**15.05**	2.14	7.993	98.64	9.12
6	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-
Total ------->	n/a	**20368.7**	100		26.777	3.82	14.222	194.68	18.0015
	n/a	n/a	n/a	Water content in liquid product	73.22	10.43	38.891	187.82	17.36675
Total (liquid concentration)	-	-	-	-	100	**14.25**	**53.113**	**382.50**	**35.3682**
Total volume of liquid produced (ml) = 14.25						-	-	-	-
Gas fraction (GC/MS	**RT**	**Area (%)**	**Quality**	**Gas amount produced** (ml)	**Actual concentration (%)**	**Gas amount produced** (mole)	-	-	-
	1.935	**33.04%**		4156.27	**33.04%**	**4.16**	**15.491**	**74.65**	**6.902**
		Bicyclo[1.1.0]butane	45			1.39	5.164	24.89	2.301
		1-Methylcyclopropene	9			1.39	5.164	24.88	2.301
		1,3-Butadiene	9			1.39	5.164	24.88	2.301
	2.115	**66.96%**		8423.25	**66.96%**	**8.42**	**31.395**	**624.33**	**57.73**
		Diethylether	**86**			2.81	10.465	208.11	19.243
		Diethylether	78			2.81	10.465	208.11	19.243
		Diethylether	64			2.81	10.465	208.11	19.243
Average gas flow rate (ml/s)				0.58239			-		-
Total Gas produced (ml / 6 hours)				**12579.52**	**100.00%**	**12.58**	**46.887**	**698.98**	**64.63**
							-		-
	NB				Total mole = Mole of liquid product + gas of product		-		-
	Concentration (GC Area)	Concentration GC Area in (%)			-	**26.83**	**100**	1081.48	**100**

7.3 Conversion Calculation (Calculation 1)

	NB Concentration (GC Area)	Concentration GC Area in (%)
EtOH in	**119477.9**	96
EtOH out	**17 979.80**	15.05

15.048 % of the initial conc. The remaining are conc. of the other components.

Meaning Water = 100 - 15.0486 = 84.95 %

Conversion (%)		
EtOH in (%) as 100 % - EtOH outlet (%) as 15.05 %		84.95
Using Area Concentration (GC Area)	84.95	
Using Area Concentration (%)		84.32
Using % Conc.		

Concentration of ethanol in the product (EtOH % out)

EtOH % out = (GC area concentration of EtOH in the product / GC Area Concentration of EtOH in the feed) * 100

NB: 15 % EtOH out is 15 % to 96 %. Therefore 96 % in this case is 100 %

Conversion

$$\text{Conversion (X)} = \frac{n_{C^0} - n_C}{n_{C^0}} \text{ X } 100$$ (Silva, V.J et al., 2013:86)

Where n_C^0 and n_C are the initial and final concentrations of C in the reactor

In otherwords,

$$\text{Conversion} = \frac{Concentration\ of\ EtOH\ in\ the\ Feed\ - Concentration\ of\ EtOH\ in\ the\ product}{Concentration\ of\ EtOH\ in\ the\ Feed} \text{ X } 100$$

$$\text{Or } = \frac{Initial\ Concentration\ of\ EtOH - Final\ Concentration\ of\ EtOH}{Initial\ Concentration\ of\ EtOH} \text{ X } 100$$

$$= \frac{EtOH\ in\ (\%) - EtoH\ out\ (\%)}{EtOH\ in\ (\%)} \text{ X } 100$$

E.g. Ethanol conversion from N.B

$$= \frac{96\ (\%) - \ 15.05\ (\%)}{96\ (\%)} \text{ X } 100 \quad = 84.32\ \%$$

Alternatively in terms of mole

$$Conversion = \frac{Actual\ mole\ of\ \ EtOH\ \ fed - Actual\ mole\ of\ unreacted\ ethanol\ in\ \ the\ product}{Actual\ \ mole\ of\ EtOH\ fed} \text{ X } 100$$

	Experiment pump calibration	Change in ethanol amount in the feed tank	Actual fed	Actual loss while feeding (ml)	Actua mole unreacted in the product
Ethanol fed	5.5 ml / hour	225 - 182.5			
EtOH fed for 6 hours	33	42.5	14.81	19-28.3	
Mole			14.22		2.145

$$Conversion = \frac{14.22 - 2.145}{14.22}\ X\ 100 \quad = \quad 84.\ 95\ \%$$

Objective 2 (Data results): Investigate the effect of clay beneficiation and treatment on catalyst composition and morphology

Table 7.2: Product Distribution of liquid and gaseous hydrocarbons from ethanol conversion over beneficiated and/or acid-modified clay catalysts

	Rxn no.	**Rxn.8 & 16**	**Rxn.16**	**Rxn.10**	**Rxn.11**	
	Synthesis method -->	**Beneficiated clay**		**Acid-modified clays**		
	Clay-based Catalyst -->	B.B (<53 um)	B.B (<53 um)	B.B1M	B.B1M	B.B1M
	Reaction time	2 hours reaction	6 hours reaction	2 hours reaction	4hours	6 hours
	Ethanol conversion (%) --->	**82.29**	**81.01**	**83.58**	**85.05**	**87.28**
Product distribution & selectivity (Conc.-selectivity / %)	**Hydrocarbon liquid fraction**	**R.T (Component)** % Composition	**R.T (Component)** % Composition	**R.T (Component)** % Composition	**R.T (Component)** % Composition	R.T (Component) % Composition
		10.852 (BuOH) 1.78 %	10.84 (BuOH) 2.64 %	10.878 (BuOH) 0.56 %	10.882 (BuOH) 1.03 %	10.883 (BuOH) 1.4 %
		11.138 (D.E) 6.14 %	11.125 (D.E) 4.90 %	11.158 (D.E) 12.02 %	11.162 (D.E) 5.21 %	11.163 (D.E) 5.5 %
		11.471 (MeOH) 4.90 %	11.457 (MeOH) 2.64 %	11.498 (MeOH) 1.8 %	11.501 (MeOH) 3.63 %	11.502 (MeOH) 3.74 %
		11.67 (EtOH) 17.71 %	**11.65 (EtOH) 18.9 %**	**11.706 (EtOH) 16.42 %**	**11.705 (EtOH) 14.95 %**	**11.709 (EtOH) 12.72 %**
		n/a **Water 69.47 %**	n/a **Water 70.83 %**	**Water** (+impurities) **69.2 %**	**Water 74.68 %**	**Water 76.21 %**
	Total liquid produced (ml)	Not recorded	5.95 ml - 6ml	≈ 3.1-2 ml	≈ 12 ml	≈14.25 ml
	Hydrocarbon liquid fraction	**R.T Area (%)** Quality%	**R.T Area (%)** Qlty%	**R.T Area (%)** Qlty%	**R.T Area (%)** Qlty%	R.T Area (%) Qlty%
		1.935 39.34%	**1.935 37.716%**	**1.940 48.83%**	**1.940 37.35%**	**1.940 38.46%**
		Bicyclo[1.1.0]butane (45)	Bicyclo[1.1.0]butane (42)	2-Butene, (E) - (7)	1 - Propene, 2-methyl- (7)	1-Propene, 2-methyl (7)
		1-Methylcyclopropene (9)	1-Methylcyclopropene (9)	2-Butene (7)	2-Butene, (E) - (7)	2-Butene, (E) - (7)
		1,3-Butadiene (9)	1,3-Butadiene (9)	1-Butene (7)	2-Butene, (E) - (7)	2-Propenal (7)
		2.114 51.61%	**2.114 62.284%**	**2.115 47.09%**	**2.115 51.41%**	**2.115 52.84%**
		Diethyl ether (86)	Diethyl ether (86)	Diethyl ether (78)	Diethyl ether (86)	Diethyl ether (78)
		Diethyl ether (78)	Diethyl ether (78)	Diethyl ether (64)	Diethyl ether (78)	Diethyl ether (64)
		Diethyl ether (64)	Diethyl ether (78)	Diethyl ether (64)	Diethyl ether (64)	Diethylether (64)
		2.160 1.57%		**2.161 4.07%**	**2.161 1.81%**	**2.161 1.81%**
		Cyclopropane, 1,2-dimethyl-, cis- (86)		2-Methyl-1-butene (90)	2-Butene, 2-methyl- (86)	2-Methyl-1-butene (86)
		2-Pentene (86)		2-Butene, 2-methyl- (90)	2 - Pentene, (Z) - (86)	2- Pentene (86)
		2-Butene, 2-methyl- (86)		Cyclopropane, 1,2-dimethyl-, cis (90)	Cyclopropane, 1,2-dimethyl-, cis- (86)	2-Butene, 2-methyl- (86)
		4.001 8.99%			**2.604 1.07%**	
		Ethane, 1,1-diethoxy- (9)			Ethyl acetate (50)	
		Ethane, 1,1-diethoxy- (9)			Ethyl acetate (50)	
		1-Propanamine, N1-methyl-2-methoxy (4)			Pentanoic acid, 3-methyl-4-oxo (39)	
					4.003 8.35%	**4.004 6.88%**
					Ethane, 1,1-diethoxy- (9)	Ethane, 1,1-diethoxy- (9)
					Ethane, 1,1-diethoxy- (9)	Ethane, 1,1-diethoxy- (9)
					Trimethylsilylmethanol (4)	Ethanamine, 2,2-diethoxy- (4)
	Average Total gas produced (ml/h)	**2882.1**	2597.8	4396.62	3700.91	3335.81

7.4 Concentration selectivity of gas hydrocarbons molecules (Objective 1 - 7) ---> (Calculation 2)

The concentrations of hydrocarbons molecules in the liquid product (presented as selectivity in terms of concentration of each individual hydrocarbon present in the liquid), were directly deducted from the values given in Table 7.1-33 (in this Appendix). These are then reported as concentration selectivity of each in Figure such as Figure 4.34 (pg.115) - See below

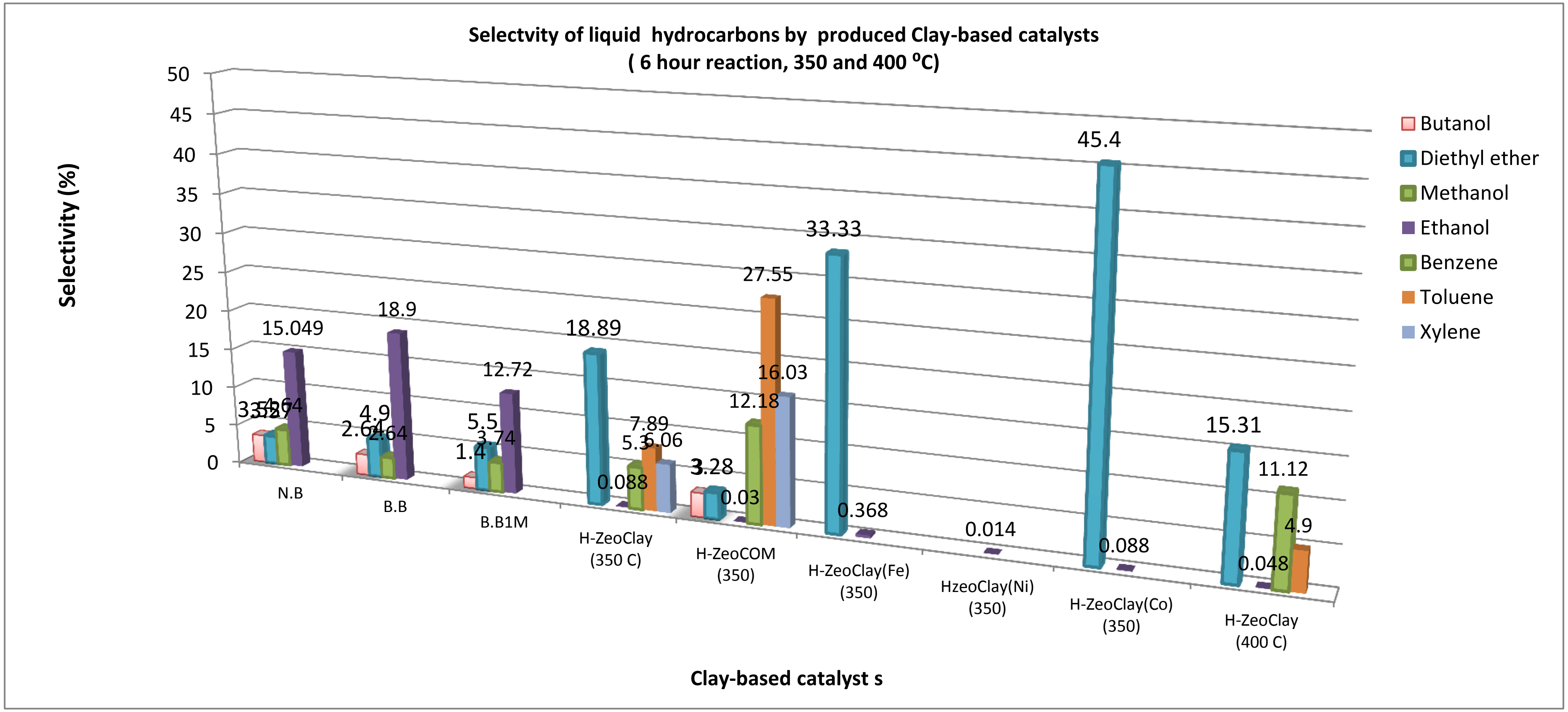


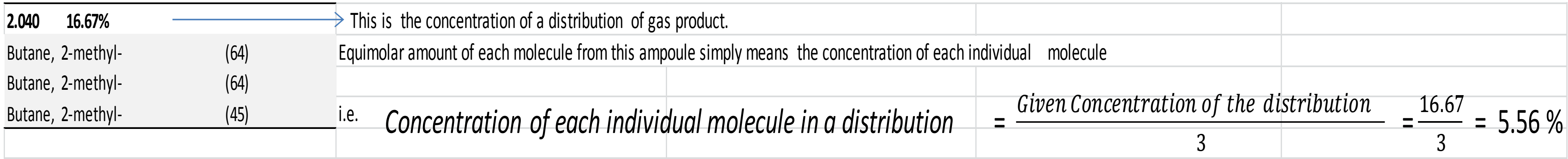
Figure 4.34 (pg.115): Distribution and selectivity of liquid hydrocarbons by produced clay-based catalysts

7.4.1 Distribution of gas molecules in the gas product (Equivalent to hydrocarbons distribution in this product)

The gas molecules unlike liquid were detected in distribution or set of three hydrocarbons per distribution as observed in Table 7.1 - 7.6. Seeing that the hydrocarbons in the gas product appear in diverse amount and cannot be possibly accounted for individually (in terms of concentration) , these were grouped and presented according their classification such as olefins, paraffins and Diethyl ether (Vaporised form).

A set consisting of three molecules represents a single hydrocarbon distribution in the gas product. For example the gas product obtained by reacting ethanol over the produced catalyst (H-ZeoClay) is distributed into 10 set (group) of hydrocarbons. In other words it is said that the hydrocarbons (Molecules) distribution in the gas product is 10.

It was then assumed that the three hydrocarbon molecules that make up each distribution are in equimolar amount of the concentration obtained for entire distribution. For example as presented below for a distribution of molecules obtained by the produced catalyst (H-ZeoClay).



2.040	**16.67%**	This is the concentration of a distribution of gas product.
Butane, 2-methyl-	(64)	Equimolar amount of each molecule from this ampoule simply means the concentration of each individual molecule
Butane, 2-methyl-	(64)	
Butane, 2-methyl-	(45)	i.e.

$$Concentration\ of\ each\ individual\ molecule\ in\ a\ distribution = \frac{Given\ Concentration\ of\ the\ distribution}{3} = \frac{16.67}{3} = 5.56\ \%$$

7.4.2 Grouping and calculating the collective concentration of olefins, parraffins, diethyl ether or any other hydrocarbon molecule in the gas product

Knowing the concentration of a molecule in an ampoule of gas, the concentration of each olefins or parraffins hydrocarbons in various ampoules were calculated (as show above). These were then summed up to give the collective concentration of olefins or paraffins as presented in this work.

Note that olefins or parraffins as presented in this work, are the collective representation of straight-chained, branched (Iso) or cyclo olefins or parraffins. Straight-chained or lighter olefins are highlighted in light pink and heavier gas olefins (branched and cycloOlefins) in dark pink. Parrafins (from lighter to heavier) are highlighted in light-dark grey colour --> See as highlighted below. Diethyl ether Mostly in Table 7.1 far above, is highlighted in light green colour as Diethyl ether

For example, given a gas distribution or the 4th ampoule below obtained from the produced catalyst (See table 30), the equimolar amount (concentration) of each molecule is 11 /3 = 3.67 %. This ampoule consists of 2 olefins and 1 parraffins hydrocarbons. Hence the percentage olefins in this is 7.34 % (3.67+3.67) and that of paraffins is 3.67 %

Table 7.2.1: Equimolar concentration of hydrocarbon molecules per distribution in the gas product and determination of collective concentration of olefins, paraffins or other hydrocarbon range in the gas product.

H-ZeoClay clay-based catalyst - 6 hour reaction			
4th Ampoule	Equimolar amount of molecules	Olefins concentration	Paraffins concenration
2.093 11%	**11%**		
2-Methyl-1-butene	3.67%	3.67%	
Cyclopropane, 1.1 - dimethyl-	3.67%	-	3.67%
2-Pentene (Z)-	3.67%	3.67%	
6th Ampoule			
2.160 19.02%	**19.02%**		
2-Butene, 2-methyl- (90)	6.34%	6.34%	
Cyclopropane, 1.2 - dimethyl-, cis (90)	6.34%	-	6.34%
2-Pentene (Z)- (90)	6.34%	6.34%	
Total (4 & 6th Ampoule of gas molecules)	30.02%	**20.02**	**10.01**
And so on			
1-3 Ampoule		Similarly calculated	Similarly calculated
7-11 Ampoule			
Total (1-11 Ampoule)			
TOTAL		**62.88**	**33.21**

The concentration of olefins and paraffins hydrocarbons (including other molecules) in the gas product using various clay-based catalysts, was calculated in the same manner as above. Hence Figure such as Figure 4.33 (pg.144) was generated as shown below.

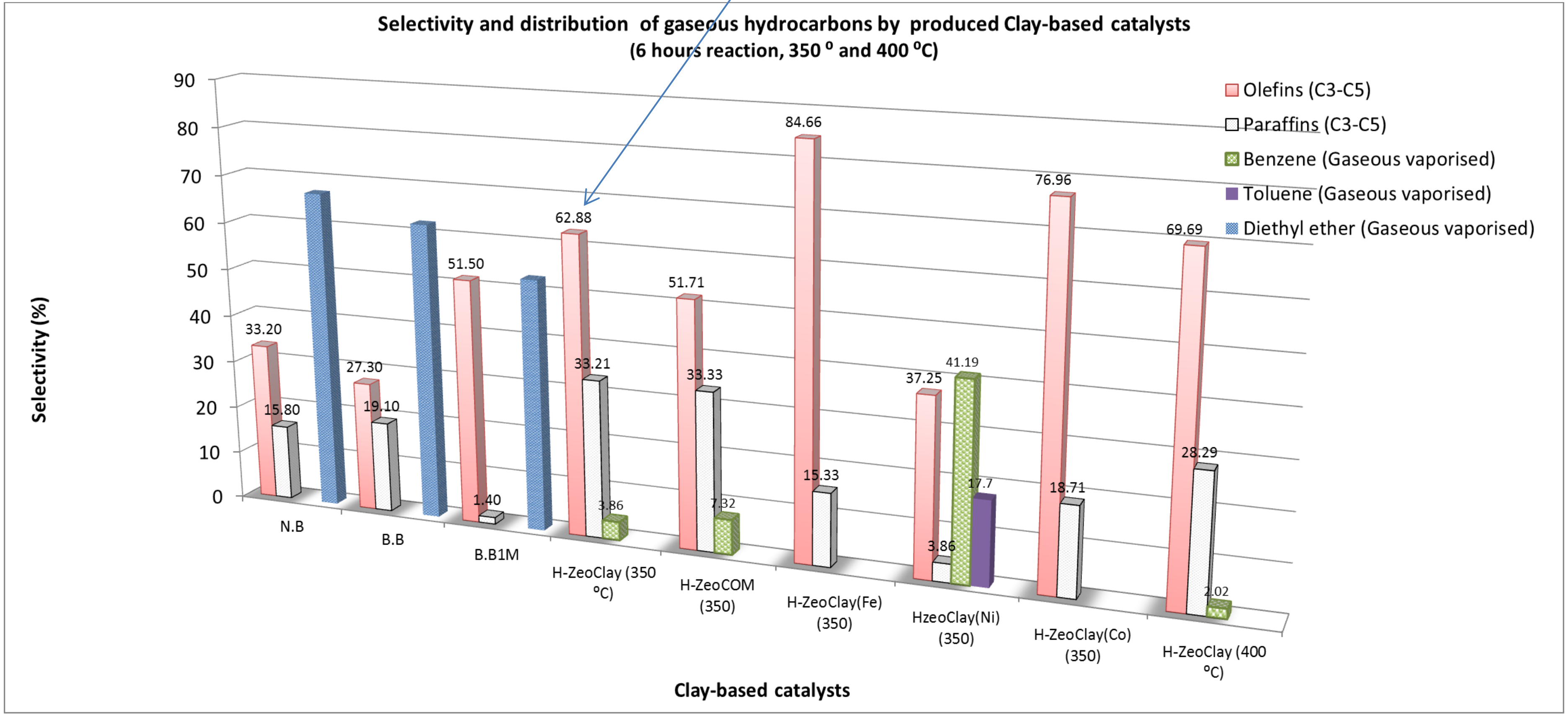


Figure 4.33 (pg.114): Gaseous hydrocarbons selectivity by produced clay-based catalysts

Objective 3 (Data results): Produce catalyst from clay

Objective 4 (Data results): Carry out comparative studies of ethanol conversion over clay-based catalyst and other synthesised zeolites

Table 7.3: Product Distribution of liquid and gaseous hydrocarbons from ethanol conversion over the produced clay-based catalyst and commercial zeolite catalysts

	Rxn no.		**Rxn.14**		**Rxn.14**		**Rxn.15**		**Rxn.17**
	Synthesis method -->	**Catalyst from clay**							
	Clay-based Catalyst -->	H-ZeoCOM				H-ZeoClay @ 350 C		ZeoClay	
	Reaction time	2 hours		6 hours		6 hours (@ 350 C)		6 hours	
	Ethanol conversion (%)		**99.95**		**99.97**		**99.91**		**87.95**
Product distribution & selectivity (Conc-Selectivity / %)	**Hydrocarbon liquid fraction**	**R.T (Component)**	% Composition	**R.T (Component)**	% Composition	**R.T (Component)**	% Composition	**R.T (Component)**	% Composition
			-	10.738 (BuOH)	3 %		-	10.85 (BuOH)	2.0 %
		11.137 (D.E)	5.23 %	11.137 (D.E)	3.28 %	11.136 (DE)	18.89 %	11.13 (D.E)	7.6 %
		11.566 (MetOH)	5.1 %		-		-	11.466 (MetOH)	3 %
		11.694 (EtOH)	**0.052 %**	**11.688 (EtOH)**	**0.03 %**	**11.69 (EtOH)**	**0.088 %**	**11.667 (EtOH)**	**12.05 %**
		11.985 (Benzene)	4.74 %	11.986 (Benzene)	12.18 %	12.129 (Benzene)	5.3 %		-
		12.717 (Toluene)	5.35 %	12.735 (Toluene)	27.55 %	12.742 (Toluene)	7.89 %		-
		-		14.007 (Xylene)	16.03 %	13.935 (Xylene)	6.06 %	13.946 (Xylene)	0.4 %
		Water	**75.9 %**	**Water**	**33.8 %**	**Water** (+Other impurities)	**60.92 %**	**Water** (+Other impurities)	**74.97 %**
	Volume of liquid produced (ml)		Not Recorded		≈ 12.25 ml		≈ 8.9 ml (+0.1 ml loss)		≈ 13 ml
	Hydrocarbon gas fractions	**R.T** **Area (%)**	Qlty%	**R.T** **Area (%)**	Quality%	**RT** **Area (%)**	Qlty%	**R.T** **Area (%)**	Quality %
		1.897 **7. 31 %**		**1.925** **22.85%**		**1.922** **18.07%**		**1.934** **28.69%**	
		Borane, compd. With dimethylamine (1:1)	(7)	1-Butene	(9)	1-Propene, 2-methyl-	(42)	Bicyclo [1.1.0]butane	(50)
		Isobutane	(5)	1-Butene	(9)	1-Butene	(9)	1,3-Butadiene	(9)
		Isobutane	(5)	Borane, compd. With dimethylamine (1:1)	(9)	2-Butene (Z)-	(9)	1-Methylcyclopropene	(9)
		1.925 **17.52%**		**1.950** **17.69%**		**1.952** **18.53%**		**2.115** **47.17%**	
		Borane, compd. With dimethylamine (1:1)	(9)	1-Butene	(45)	1-Propene, 2-methyl-	(72)	Ethyl ether	(78)
		2-Butene, (Z)-	(7)	1-Butene	(45)	1-Butene	(50)	Ethyl ether	(64)
		Cyclopropylamine	(7)	1-Butene	(45)	1-Butene	(50)	Ethyl ether	(64)
		1.946 **17.55%**		**2.049** **26.76%**		**2.040** **16.67%**			
		1-Propene, 2-methyl-	(45)	Butane, 2-methyl-	(64)	Butane, 2-methyl-	(64)		
		1-Butene	(9)	Butane, 2-methyl-	(64)	Butane, 2-methyl-	(64)		
		1-Propene, 2-methyl-	(9)	Butane, 2-methyl-	(45)	Butane, 2-methyl-	(45)		
		2.041 **27.52%**		**2.095** **7.52%**		**2.093** **11%**			
		Butane, 2-methyl-	(64)	Cyc loprapane, 1,2-dimethyl-, trans	(50)	2-Methyl-1-butene	(64)		
		Butane, 2-methyl-	(64)	2-Methyl-1-butene	(49)	Cyclopropane, 1.1 - dimethyl-	(64)		
		Butane, 2-methyl-	(45)	2-Pentene	(47)	2-Pentene (Z)-	(64)		
		2.096 **8.671%**		**2.122** **2.06%**		**2.123** **5.08%**			
		Cyc loprapane, 1,2-dimethyl-, trans	(47)	2-Pentene, (E)-	(86)	2-Pentene (Z)-	(90)		
		2-Methyl-1-butene	(46)	Cyc loprapane, 1,2-dimethyl-, cis	(86)	2-Pentene (Z)-	(90)		
		1-Butene, 3-methyl	(43)	2-Butene, 2-methyl	(86)	2-Butene, 2-methyl-	(90)		
		2.161 **8.575%**		**2.161** **9.553%**		**2.160** **19.02%**		**2.161** **7.29%**	
		Cyc loprapane, 1,2-dimethyl-, cis	(90)	2-Pentene, (Z)-	(90)	2-Butene, 2-methyl-	(90)	2-Butene, 2-methyl-	(90)
		2-Pentene, (Z)-	(90)	2-Pentene	(90)	Cyclopropane, 1.2 - dimethyl-, cis	(90)	Cyclopropane, 1,2-dimethyl-, cis	(90)
		2-Pentene	(90)	2-Butene, 2-methyl	(90)	2-Pentene (Z)-	(90)	2-Butene, 2-methyl-	(90)
				2.306 **0.59%**		**2.305** **1.19%**			
				Cyclopentene	(86)	Cyclopentene	(80)		
				Cyclopentene	(86)	Cyclopentene	(80)		
				Cyclopentene	(86)	Cyclopentene	(80)		
		2.344 **2.95%**		**2.344** **3.39%**		**2.342** **3.64%**			
		1-Heptene, 4-methyl-	(50)	Cyclopropane, 1,2-dimethyl-, trans	(50)	Hexane, 2,3-dimethyl	(45)		
		1-Heptene, 5-methyl-	(42)	1-Heptene, 4-methyl-	(50)	Cyclopropane, 1,2-dimethyl-, trans	(43)		
		Cyclopropane, 1,2-dimethyl-, trans	(40)	1-Heptene, 5-methyl-	(42)	Trans-3-Penten-2-ol	(35)		
		2.412 **0.81%**		**2.412** **1.1%**		**2.411** **1.18%**			
		Pentane, 3-methyl-	(90)	Pentane, 3-methyl-	(90)	Pentane, 3-methyl-	(90)		
		Pentane, 3-methyl-	(90)	Pentane, 3-methyl-	(90)	Pentane, 3-methyl-	(90)		
		Pentane, 3-methyl-	(90)	Pentane, 3-methyl-	(90)	Pentane, 3-methyl-	(90)		
		2.734 **0.89%**		**2.734** **1.15%**		**2.734** **1.75%**		**2.944** **3.23%**	
		Cyclopentane, methyl-	(91)	Cyclopentane, methyl-	(91)	Cyclopentane, methyl-	(91)	Cyclopentene, 1-methyl-	(81)
		Cyclopentane, methyl-	(86)	Cyclopentane, methyl-	(90)	Cyclopentane, methyl-	(90)	2,4-Hexadiene	(81)
		Cyclopentane, methyl-	(83)	Cyclopentane, methyl-	(90)	Cyclopentane, methyl-	(90)	1,3-Pentadiene, 2-methyl-, (E) -	(81)
		3.056 **8.2%**		**3.055** **7.32%**		**3.054** **3.86%**		**2.62** **2.62%**	
		Benzene	(91)	Benzene	(91)	Benzene	(91)	Benzene	(91)
		Benzene	(91)	Benzene	(91)	Benzene	(91)	Benzene	(91)
		Benzene	(91)			Benzene	(91)	Benzene	(91
	Average Total gas produced (ml/h)		1831.43		1598.26	2273.92			3818.72

Objective 5 (Data results): Investigate the effect of promotion on clay-based catalysts.

Table 7.4: Product Distribution of liquid and gaseous hydrocarbons from ethanol conversion over metal promoted clay-based catalysts

Rxn no.		Rxn.**15**		Rxn.**18**		Rxn.**19**		Rxn.**20**
Synthesis method -->			**Metal promotion of clay-based catalyst**					
Clay-based Catalyst -->	H-ZeoClay @ 350 C		H-ZeoClay+Fe		H-ZeoClay+Ni		H-ZeoClay+Co	
Reaction time	6 hours (@ 350 C)		6 hours		6 hours		6 hours	
Ethanol conversion (%)		**99.91**		**99.63**		**99.986**		**99.91**
Hydrocarbon liquid fraction	**RT (Component)**	% Composition	**R.T (Component ID)**	% Composition	**R.T (Component ID)**	% Composition	**R.T** (Compodent ID)	% Composition
		-		-		-		-
	11.136 (D.E)	18.89 %	11.134 (D.E)	33.33 %		-	11.13 (D.E)	45.40 %
		-		-		-		-
	11.69 (EtOH)	**0.088 %**	**11.69 (EtOH)**	**0.368 %**	**11.724(EtOH)**	**0.014 %**	**11.686 (EtOH)**	**0.088%**
		-						-
	12.129 (Benzene)	5.3 %		-		-		
	12.742 (Toluene)	7.89 %		-		-		
	13.935 (Diethyl ether)	6.06 %		-		-		
	Water (+Other impurities)	**60.92 %**	**Water** (+Other impurities)	**66.63 %**	**Water** (+impurities)	**99.986 %**	**Water** (+impurities)	**54.5 %**
Total liquid produced (ml)		≈ 8.9 ml (+0.1 ml loss)		≈ 3.5 ml		≈ 1.8 ml		≈ 3 ml
Hydrocarbon gas fractions	**RT Area (%)**	**Qlty%**	**R.T Area (%)**	**Quality%**	**R.T Area (%)**	**Qlty%**	**RT Area (%)**	**Qlty%**
	1.922 18.07%		**1.927 49.05%**		**1.930 29.52%**		**1.927 46.04%**	
	1-Propene, 2-methyl-	(42)	1 - Butene	(72)	1-Butene	(80)	2-Butene, (Z)-	(72)
	1-Butene	(9)	1- Butene	(72)	1-Butene	(80)	1-Propene, 2-methyl-	(72)
	2-Butene (Z)-	(9)	2- Butene, (Z) -	(72)	2-Butene (Z)-	(80)	1-Butene	(72)
	1.952 18.53%		**2.043 4.94%**		**2.165 11.59%**		**2.043 8.72%**	
	1-Propene, 2-methyl-	(72)	Butane, 2-methyl-	(72)	Cyclopropane, 1,2-dimethyl-, cis	(90)	Butane, 2-methyl-	(72)
	1-Butene	(50)	Butane, 2-methyl-	(72)	2-Pentene	(90)	Butane, 2-methyl-	(72)
	1-Butene	(50)	Butane, 2-methyl-	(50)	2-Butene, 2-methyl-	(90)	Butane, 2-methyl-	(50)
	2.040 16.67%		**2.094 11.61%**		**3.059 41.19%**		**2.040 10.94%**	
	Butane, 2-methyl-	(64)	2-Pentene, (Z)-	(86)	Benzene	(91)	2-Pentene (Z)-	(80)
	Butane, 2-methyl-	(64)	2-Pentene, (Z)-	(86)	Benzene	(90)	2-Pentene	(80)
	Butane, 2-methyl-	(45)	1-Butene, 3-methyl	(86)	Benzene	(90)	2-Pentene (Z)-	(80)
	2.093 11%		**2.125 6.55%**		**4.859 17.7%**		**2.093 5.89%**	
	2-Methyl-1-butene	(64)	2-Pentene, (E)-	(86)	Toluene	(91)	2-Butene, 2-methyl-	(90)
	Cyclopropane, 1.1 - dimethyl-	(64)	2-Methyl-1-butene	(86)	Toluene	(91)	2-Methyl-1-butene	(90)
	2-Pentene (Z)-	(64)	Cyclopropane, 1,2-dimethyl-, trans	(86)	Toluene	(91)	Cyclopropane, 1,2-dimethyl-, cis	(90)
	2.123 5.08%		**2.162 24.62%**				**2.162 24.08%**	
	2-Pentene (Z)-	(90)	Cyclopropane, 1,2-dimethyl-, cis	(90)			2-Pentene	(90)
	2-Pentene (Z)-	(90)	2-Pentene, (Z)-	(90)			2-Pentene (Z)-	(90)
	2-Butene, 2-methyl-	(90)	2-Pentene	(90)			Cyclopropane, 1,2-dimethyl-, cis	(90)
	2.160 19.02%		**2.944 3.22%**				**2.340 4.33%**	
	2-Butene, 2-methyl-	(90)	Cyclopentene, 1-methyl-	(90)			2-Ethyl-1-butanol, trifluoroacetat	(59)
	Cyclopropane, 1.2 - dimethyl-, cis	(90)	Cyclopentene, 1-methyl-	(90)				
	2-Pentene (Z)-	(90)						
	2.305 1.19%							
	Cyclopentene	(80)						
	Cyclopentene	(80)						
	Cyclopentene	(80)						
	2.342 3.64%							
	Hexane, 2,3-dimethyl	(45)						
	Cyclopropane, 1,2-dimethyl-, trans	(43)						
	Trans-3-Penten-2-ol	(35)						
	2.411 1.18%							
	Pentane, 3-methyl-	(90)						
	Pentane, 3-methyl-	(90)						
	Pentane, 3-methyl-	(90)						
	2.734 1.75%							
	Cyclopentane, methyl-	(91)						
	Cyclopentane, methyl-	(90)						
	Cyclopentane, methyl-	(90)						
	3.054 3.86%							
	Benzene	(91)						
	Benzene	(91)						
	Benzene	(91)						
Average Total gas produced (ml/h)	2273.92			2025.59		2751.06		2053.13

Objective 6 (Data results): Determine the optimum operating conditions for ethanol conversion process over clay-based catalysts

Table 7.5: Product Distribution of liquid and gaseous hydrocarbons from ethanol conversion over the produced catalyst at 400 ˚C

	Rxn no.	Rxn.15			Rxn.21		
	Synthesis method -->	Operating conditions					
	Clay-based Catalyst -->	H-ZeoClay @ 350 ˚C			H-ZeoClay @ 400 ˚C		
	Reaction time	6 hours (@ 350 ˚C)			6 hours (@ 400 ˚C)		
	Ethanol conversion (%)			99.91			99.95
Product distribution & selectivity (Conc.-selectivity / %)	Hydrocarbon liquid fractions	RT (Component)	% Composition		RT (Component)	% Composition	
			-			-	
		11.136 (D.E)		18.89 %	11.132 (D.E)		15.31%
			-			-	
		11.69 (EtOH)	0.088 %		11.681 (EtOH)	0.048 %	
			-			-	
		12.129 (Benzene)		5.3 %	12.118 (Benzene)		11.12%
		12.742 (Toluene)		7.89 %	12.716 (Toluene)		4.9 %
		13.935 (Xylene)		6.06 %		-	
		Water (+Other impurities)	60.92 %		Water	68.61 %	
	Total liquid produced (ml)	≈ 8.9 ml (+0.1 ml loss)			≈ 4.5 ml		
	Hydrocarbon gas fractions	RT	Area (%)	Qualilty	R.T	Area (%)	Qlty
		1.922	18.07%		1.924	23.11%	
		1-Propene, 2-methyl-		(42)	1-Butene		(42)
		1-Butene		(9)	1-Propene, 2-methyl-		(42)
		2-Butene (Z)-		(9)	1-Butene		(42)
		1.952	18.53%		1.948	22.34%	
		1-Propene, 2-methyl-		(72)	1-Butene		(50)
		1-Butene		(50)	1-Butene		(50)
		1-Butene		(50)	2-Butene, (Z)-		(50)
		2.040	16.67%		2.042	11.72%	
		Butane, 2-methyl-		(64)	Butane, 2-methyl-		(64)
		Butane, 2-methyl-		(64)	Butane, 2-methyl-		(64)
		Butane, 2-methyl-		(45)	Butane, 2-methyl-		(45)
		2.093	11%		2.094	10.74%	
		2-Methyl-1-butene		(64)	Cyclopropane, 1,1 - dimethyl-		(72)
		Cyclopropane, 1.1 - dimethyl-		(64)	2-Pentene (Z)-		(72)
		2-Pentene (Z)-		(64)	Cyclopropane, 1.2 - dimethyl-, trans		(72)
		2.123	5.08%		2.124	5.35%	
		2-Pentene (Z)-		(90)	2-Pentene (E)-		(90)
		2-Pentene (Z)-		(90)	2-Butene, 2-methyl-		(90)
		2-Butene, 2-methyl-		(90)	2-Butene, 2-methyl-		(90)
		2.160	19.02%		2.161	20%	
		2-Butene, 2-methyl-		(90)	2-Pentene (Z)-		(90)
		Cyclopropane, 1.2 - dimethyl-, cis		(90)	2-Pentene		(90)
		2-Pentene (Z)-		(90)	Cyclopropane, 1,2 - dimethyl-, cis		(90)
		2.305	1.19%		2.306	1.15%	
		Cyclopentene		(80)	Cyclopentene		(86)
		Cyclopentene		(80)	Cyclopentene		(86)
		Cyclopentene		(80)	Cyclopentene		(86)
		2.342	3.64%		2.346	2.47%	
		Hexane, 2,3-dimethyl		(45)	Cyclopropane, 1,2-dimethyl-, tran		(64)
		Cyclopropane, 1,2-dimethyl-, trans		(43)	1-Heptene, 5-methyl		(64)
		Trans-3-Penten-2-ol		(35)	Butane, 2-cyclopropyl-		(42)
		2.411	1.18%		2.735	1.1%	
		Pentane, 3-methyl-		(90)	Cyclopentane, methyl-		(90)
		Pentane, 3-methyl-		(90)	Cyclopentane, methyl-		(86)
		Pentane, 3-methyl-		(90)	Cyclopentane, methyl-		(80)
		2.734	1.75%		3.056	2.02%	
		Cyclopentane, methyl-		(91)	Benzene		(91)
		Cyclopentane, methyl-		(90)	Benzene		(90)
		Cyclopentane, methyl-		(90)	Benzene		(90)
		3.054	3.86%				
		Benzene		(91)			
		Benzene		(91)			
		Benzene		(91)			
	Average Total gas produced (ml/h)	2273.92					1295.28

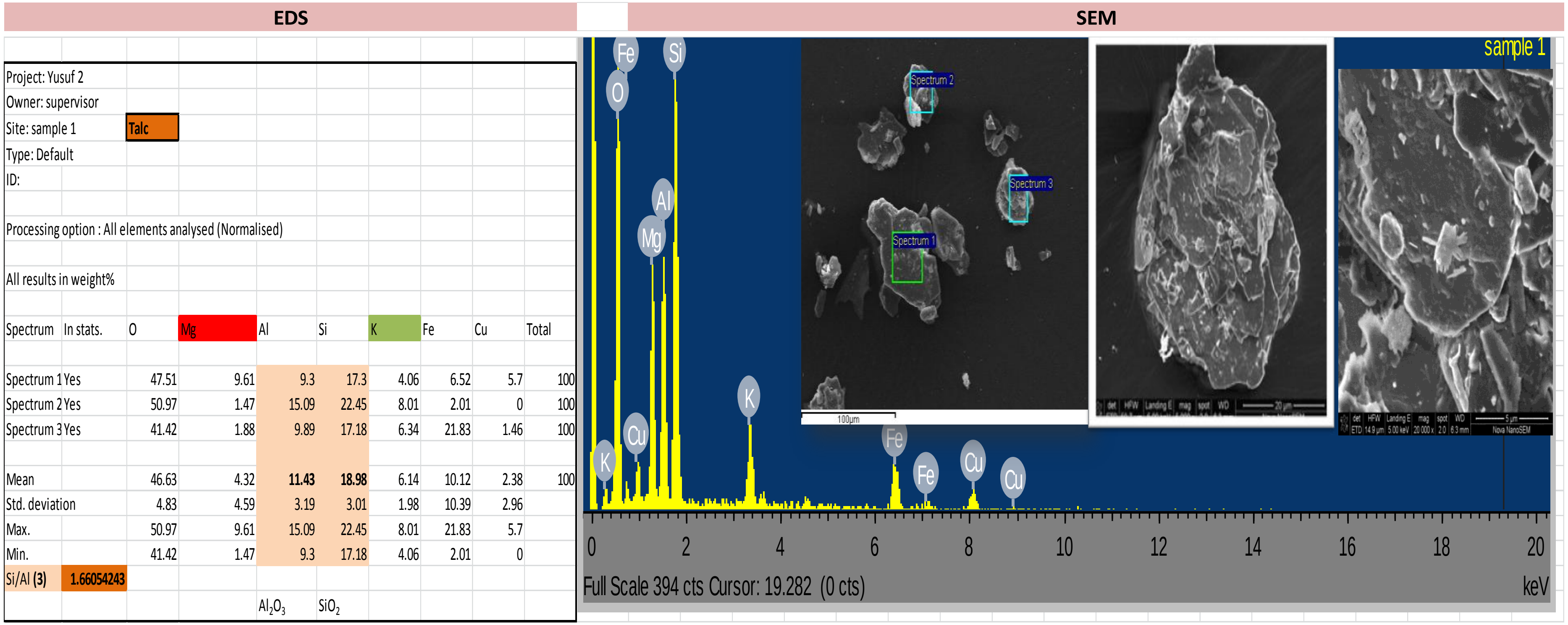
Objective 7 (Data results): Assess and improve the catalyst activity, stability and selectivity during the conversion.

Table 7.6: Assessment and improvement of catalyst activity, selectivity and stability toward ethanol conversion and hydrocarbon distribution in the product (Liquid and gas product)

	Rxn no.	Rxn.1	Rxn.16	Rxn.10		Rxn.17	Rxn.15	Rxn.21
	Synthesis method -->			**Acid-modified clays**		**Catalyst from clay**		
	Clay-based Catalyst -->	N.B (75-212 um)	B.B (<53 um)	B.B1M	B.B1M	ZeoClay	H-ZeoClay @ 350 C	H-ZeoClay @ 400 C
	Reaction time	6 hours reaction	6 hours reaction	2 hours reaction	6 hours	6 hours	6 hours (@ 350 C)	6 hours (@ 400 C)
	Ethanol conversion (%) ---->	**84.95**	**81.01**	**83.58**	**87.28**	**87.95**	**99.91**	**99.95**
Product distribution & selectivity (Conc.-selectivity / %)	**Hydrocarbon liquid fractions**	**RT (Component)** % Composition	**R.T (Component)** % Composition	**R.T (Component)** % Composition	R.T (Component) % Composition	**R.T (Component)** % Composition	**RT (Component)** % Composition	**RT (Component)** % Composition
		10.862 (BuOH) 3.52 %	10.84 (BuOH) 2.64 %	10.878 (BuOH) 0.56 %	10.883 (BuOH) 1.4 %	10.85 (BuOH) 2.0 %	??(BuOH)	??(BuOH)
		11.144 (??) 3.57 %	11.125 (??) 4.90 %	11.158 (??) 12.02 %	11.163 (??) 5.5 %	11.13 (??) 7.6 %	11.136	11.132 (??)
		11.482 (MeOH) 4.64 %	11.457 (MeOH) 2.64 %	11.498 (MeOH) 1.8 %	11.502 (MeOH) 3.74 %	11.466 (MetOH) 3 %	?? (MeOH)	?? (MeOH)
		11.674 (EtOH) 88.27 %	**11.65 (EtOH) 18.9 %**	**11.706 (EtOH) 16.42 %**	**11.709 (EtOH) 12.72 %**	**11.667 (EtOH) 12.05 %**	**11.69 (EtOH) 0.088 %**	**11.681 (EtOH) 0.048 %**
			n/a **Water 70.83 %**	**Water** (+impurities) **69.2 %**	**Water 76.21 %**	-	-	-
						-	12.129 (Benzene) 5.3 %	12.118 (Benzene)
						-	12.742 (Toluene) 7.89 %	12.716 (Toluene)
						13.946 (Diethyl ether) 0.4 %	13.935 (Diethyl ether) 6.06 %	-
						Water (+Other impurities) **74.97 %**	**Water (+Other impurities) 60.92 %**	**Water 68.61 %**
	Volume of liquid produced (ml)	≈ 14.25 ml	5.95 ml - 6ml	≈ 3.1-2 ml	≈14.25 ml	≈ 13 ml	≈ 8.9 ml (+0.1 ml loss)	≈ 4.5 ml
		R.T Area (%) Quality%	**R.T Area (%) Qlty%**	**R.T Area (%) Qlty%**	**R.T Area (%) Qlty%**	R.T Area (%)	**RT Area (%) Qlty**	**R.T Area (%)** Qlty
		1.935 33.04%	**1.935 37.716%**	**1.940 48.83%**	**1.940 38.46%**	1.934 28.69%	**1.922 18.07%**	**1.924 23.11%**
		Bicyclo[1.1.0]butane	Bicyclo[1.1.0]butane	2-Butene, (E) -	1-Propene, 2-methyl	Bicyclo [1.1.0]butane	1-Propene, 2-methyl- (42)	1-Butene
		1-Methylcyclopropene	1-Methylcyclopropene	2-Butene	2-Butene, (E) -	1,3-Butadiene	1-Butene (9)	1-Propene, 2-methyl-
	Hydrocarbon gas fractions	1,3-Butadiene	1,3-Butadiene	1-Butene	2-Propenal	1-Methylcyclopropene	2-Butene (Z)- (9)	1-Butene
		2.115 66.96%	**2.114 62.284%**	**2.115 47.09%**	**2.115 52.84%**	2.115 47.17%	**1.952 18.53%**	**1.948 22.34%**
		Ethyl ether	Ethyl ether	Ethyl ether	Ethyl ether	Ethyl ether	1-Propene, 2-methyl- (72)	1-Butene
		Ethyl ether	Ethyl ether	Ethyl ether	Ethyl ether	Ethyl ether	1-Butene (50)	1-Butene
		Ethyl ether	Ethyl ether	Ethyl ether	Ethylether	Ethyl ether	1-Butene (50)	2-Butene, (Z)-
				2.161 4.07%	**2.161 1.81%**		**2.040 16.67%**	**2.042 11.72%**
				2-Methyl-1-butene	2-Methyl-1-butene (86)		Butane, 2-methyl- (64)	Butane, 2-methyl-
				2-Butene, 2-methyl-	2- Pentene (86)		Butane, 2-methyl- (64)	Butane, 2-methyl-
				Cyclopropane, 1,2-dimethyl-, cis (90)	2-Butene, 2-methyl- (86)		Butane, 2-methyl- (45)	Butane, 2-methyl-
							2.093 11%	**2.094 10.74%**
							2-Methyl-1-butene (64)	Cyclopropane, 1,1 - dimethyl- (
							Cyclopropane, 1.1 - dimethyl- (64)	2-Pentene (Z)-
							2-Pentene (Z)- (64)	Cyclopropane, 1.2 - dimethyl-, trans (72)
					4.004 6.88%		**2.123 5.08%**	**2.124 5.35%**
					Ethane, 1,1-diethoxy- (9)		2-Pentene (Z)-	2-Pentene (E)-
					Ethane, 1,1-diethoxy- (9)		2-Pentene (Z)-	2-Butene, 2-methyl-
					Ethanamine, 2,2-diethoxy- (4)		2-Butene, 2-methyl-	2-Butene, 2-methyl-
						2.161 7.29%	**2.160 19.02%**	**2.161 20%**
	Average Total gas produced (ml/h)	12579.5	2597.8	4396.62	3335.81	2-Butene, 2-methyl-	2-Butene, 2-methyl-	2-Pentene (Z)-
						Cyclopropane, 1,2-dimethyl-, cis (90)	Cyclopropane, 1.2 - dimethyl-, cis (90)	2-Pentene
						2-Butene, 2-methyl-	2-Pentene (Z)-	Cyclopropane, 1,2 - dimethyl-, cis (90
							2.305 1.19%	**2.306 1.15%**
							Cyclopentene	Cyclopentene
							Cyclopentene	Cyclopentene
							Cyclopentene	Cyclopentene
							2.342 3.64%	**2.346 2.47%**
							Hexane, 2,3-dimethyl	Cyclopropane, 1,2-dimethyl-, tran (64)
							Cyclopropane, 1,2-dimethyl-, trans (43)	1-Heptene, 5-methyl
							Trans-3-Penten-2-ol	Butane, 2-cyclopropyl-
							2.411 1.18%	**2.735 1.1%**
							Pentane, 3-methyl-	Cyclopentane, methyl-
							Pentane, 3-methyl-	Cyclopentane, methyl-
							Pentane, 3-methyl-	Cyclopentane, methyl-
						2.944 3.23%	**2.734 1.75%**	**3.056 2.02%**
						Cyclopentene, 1-methyl- (8	Cyclopentane, methyl-	Benzene
						2,4-Hexadiene	Cyclopentane, methyl-	Benzene
						1,3-Pentadiene, 2-methyl-, (E) - (81)	Cyclopentane, methyl-	Benzene
						2.62 2.62%	**3.054 3.86%**	
						Benzene	Benzene (91)	
						Benzene	Benzene (91)	
						Benzene	Benzene (91)	
						3818.72	2273.92	1295.28

Appendix 2

7.5 EDS and corresponding SEM of non-modified clays (Figure 7.1 - 7.5)



EDS

Project: Yusuf 2
Owner: supervisor
Site: sample 1 Talc
Type: Default
ID:

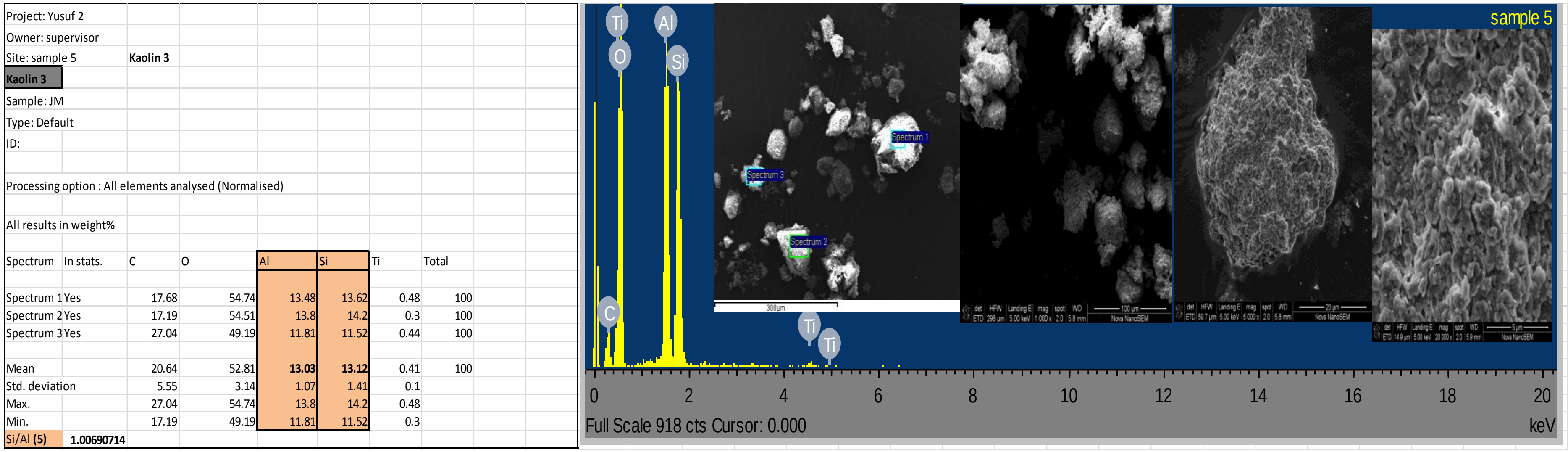
Processing option : All elements analysed (Normalised)

All results in weight%

Spectrum	In stats.	O	Mg	Al	Si	K	Fe	Cu	Total
Spectrum 1	Yes	47.51	9.61	9.3	17.3	4.06	6.52	5.7	100
Spectrum 2	Yes	50.97	1.47	15.09	22.45	8.01	2.01	0	100
Spectrum 3	Yes	41.42	1.88	9.89	17.18	6.34	21.83	1.46	100
Mean		46.63	4.32	**11.43**	**18.98**	6.14	10.12	2.38	100
Std. deviation		4.83	4.59	3.19	3.01	1.98	10.39	2.96	
Max.		50.97	9.61	15.09	22.45	8.01	21.83	5.7	
Min.		41.42	1.47	9.3	17.18	4.06	2.01	0	
Si/Al **(3)**	**1.66054243**								
				Al_2O_3	SiO_2				

SEM

Figure 7.1: EDS and corresponding SEM of non-modified Talc sample



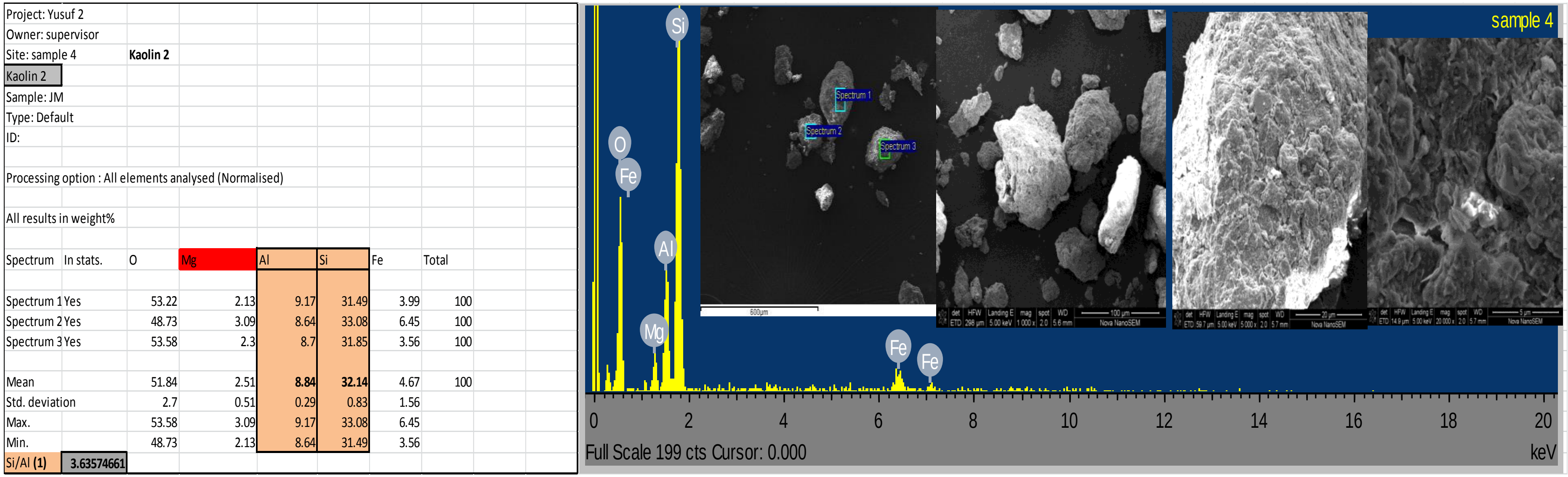
Project: Yusuf 2
Owner: supervisor
Site: sample 5 **Kaolin 3**
Kaolin 3
Sample: JM
Type: Default
ID:

Processing option : All elements analysed (Normalised)

All results in weight%

Spectrum	In stats.	C	O	Al	Si	Ti	Total
Spectrum 1	Yes	17.68	54.74	13.48	13.62	0.48	100
Spectrum 2	Yes	17.19	54.51	13.8	14.2	0.3	100
Spectrum 3	Yes	27.04	49.19	11.81	11.52	0.44	100
Mean		20.64	52.81	**13.03**	**13.12**	0.41	100
Std. deviation		5.55	3.14	1.07	1.41	0.1	
Max.		27.04	54.74	13.8	14.2	0.48	
Min.		17.19	49.19	11.81	11.52	0.3	
Si/Al (5)	**1.00690714**						

Figure 7.2: EDS and corresponding SEM of non-modified Kaolin (N.K3) clay catalyst



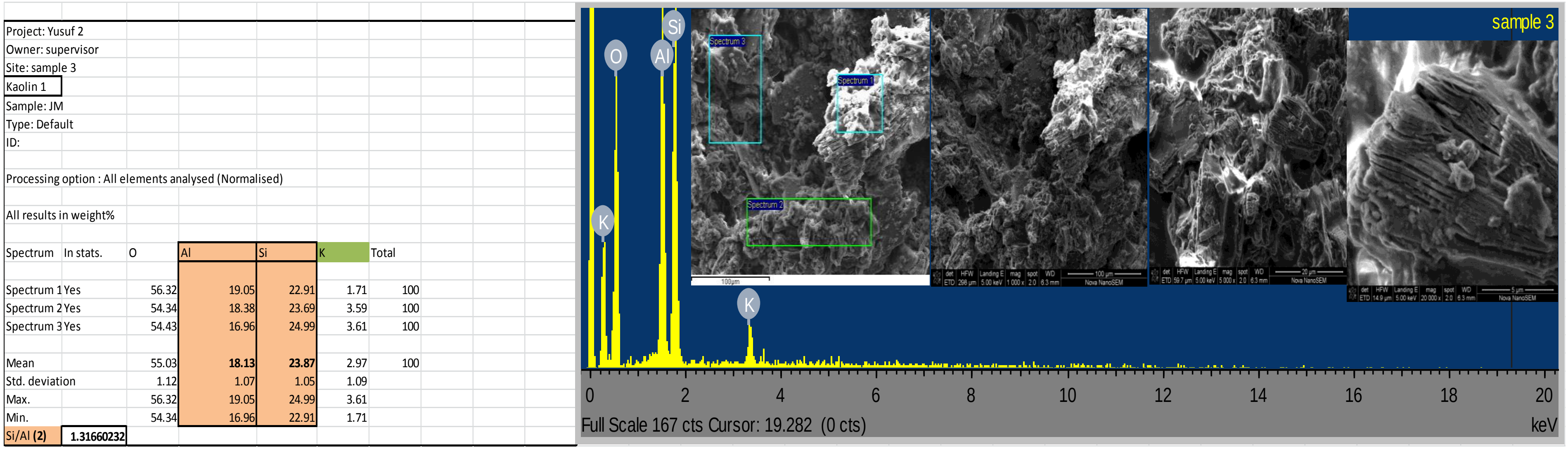
Project: Yusuf 2
Owner: supervisor
Site: sample 4 **Kaolin 2**
Kaolin 2
Sample: JM
Type: Default
ID:

Processing option : All elements analysed (Normalised)

All results in weight%

Spectrum	In stats.	O	Mg	Al	Si	Fe	Total
Spectrum 1	Yes	53.22	2.13	9.17	31.49	3.99	100
Spectrum 2	Yes	48.73	3.09	8.64	33.08	6.45	100
Spectrum 3	Yes	53.58	2.3	8.7	31.85	3.56	100
Mean		51.84	2.51	**8.84**	**32.14**	4.67	100
Std. deviation		2.7	0.51	0.29	0.83	1.56	
Max.		53.58	3.09	9.17	33.08	6.45	
Min.		48.73	2.13	8.64	31.49	3.56	
Si/Al (1)	**3.63574661**						

Figure 7.3: EDS and corresponding SEM of non-modified Kaolin clay (N.K2)



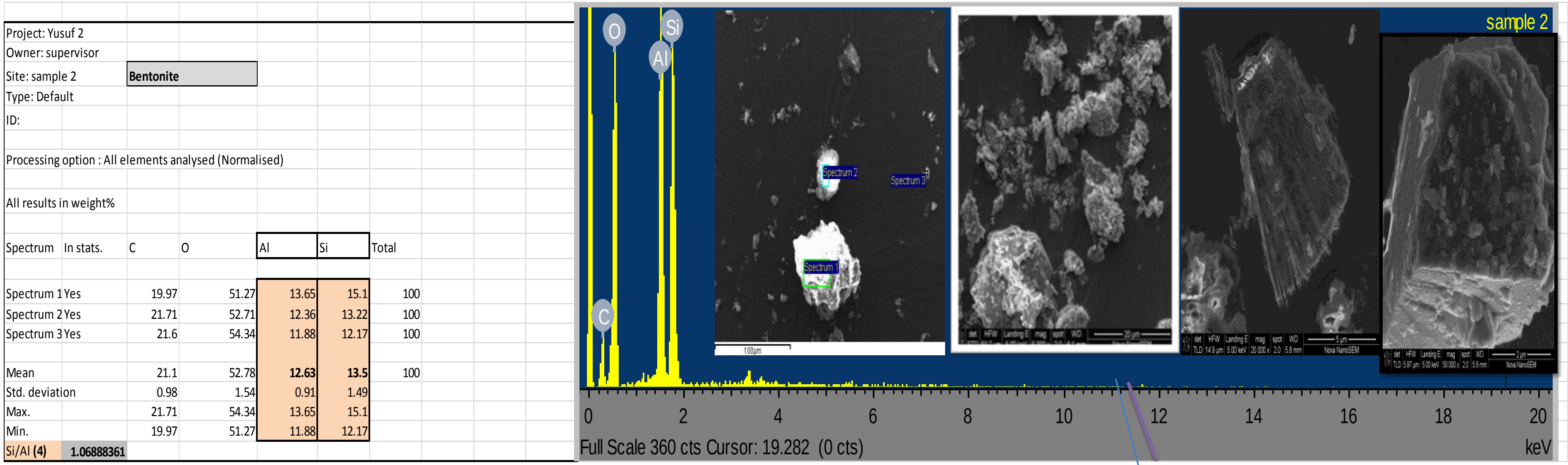
Project: Yusuf 2
Owner: supervisor
Site: sample 3
Kaolin 1
Sample: JM
Type: Default
ID:

Processing option : All elements analysed (Normalised)

All results in weight%

Spectrum	In stats.	O	Al	Si	K	Total
Spectrum 1	Yes	56.32	19.05	22.91	1.71	100
Spectrum 2	Yes	54.34	18.38	23.69	3.59	100
Spectrum 3	Yes	54.43	16.96	24.99	3.61	100
Mean		55.03	**18.13**	**23.87**	2.97	100
Std. deviation		1.12	1.07	1.05	1.09	
Max.		56.32	19.05	24.99	3.61	
Min.		54.34	16.96	22.91	1.71	
Si/Al (2)	**1.31660232**					

Figure 7. 4: EDS and corresponding SEM of non-modified Kaolin clay (N.K1)



Project: Yusuf 2
Owner: supervisor
Site: sample 2 Bentonite
Type: Default
ID:

Processing option : All elements analysed (Normalised)

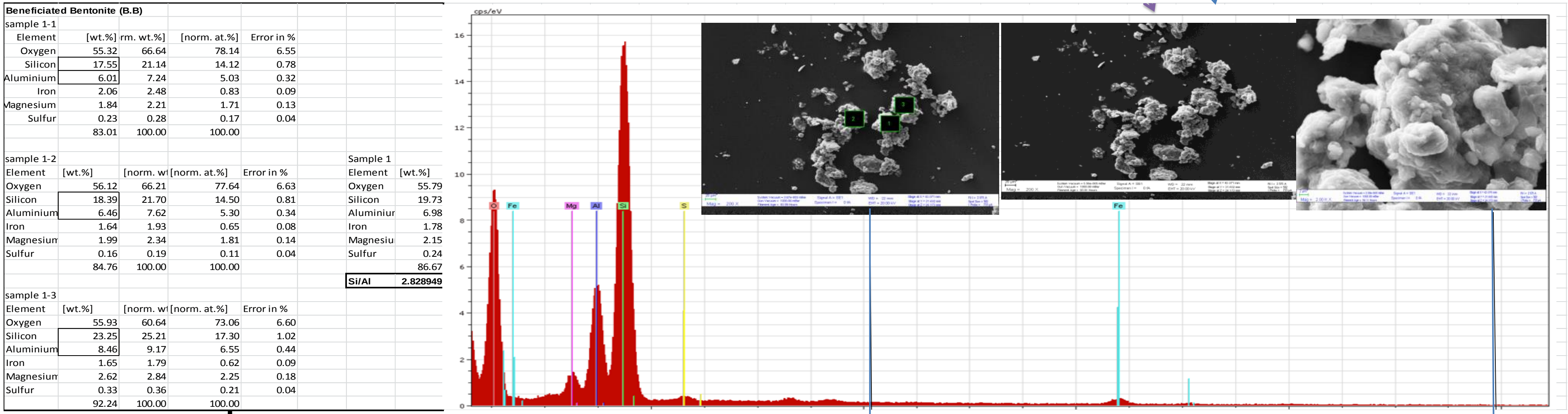
All results in weight%

Spectrum	In stats.	C	O	Al	Si	Total
Spectrum 1	Yes	19.97	51.27	13.65	15.1	100
Spectrum 2	Yes	21.71	52.71	12.36	13.22	100
Spectrum 3	Yes	21.6	54.34	11.88	12.17	100
Mean		21.1	52.78	**12.63**	**13.5**	100
Std. deviation		0.98	1.54	0.91	1.49	
Max.		21.71	54.34	13.65	15.1	
Min.		19.97	51.27	11.88	12.17	
Si/Al (4)	**1.06888361**					

Figure 7.5: EDS and corresponding SEM of non-modified Bentonite clay (N.B)

7.6 EDS and corresponding SEM of Beneficiated and acid-modified clay catalysts (Figure 7.6 - 7.9)

SEM



Beneficiated Bentonite (B.B)

sample 1-1

Element	[wt.%]	rm. wt.%]	[norm. at.%]	Error in %
Oxygen	55.32	66.64	78.14	6.55
Silicon	17.55	21.14	14.12	0.78
Aluminium	6.01	7.24	5.03	0.32
Iron	2.06	2.48	0.83	0.09
Magnesium	1.84	2.21	1.71	0.13
Sulfur	0.23	0.28	0.17	0.04
	83.01	100.00	100.00	

sample 1-2

Element	[wt.%]	[norm. wt	[norm. at.%]	Error in %
Oxygen	56.12	66.21	77.64	6.63
Silicon	18.39	21.70	14.50	0.81
Aluminium	6.46	7.62	5.30	0.34
Iron	1.64	1.93	0.65	0.08
Magnesium	1.99	2.34	1.81	0.14
Sulfur	0.16	0.19	0.11	0.04
	84.76	100.00	100.00	

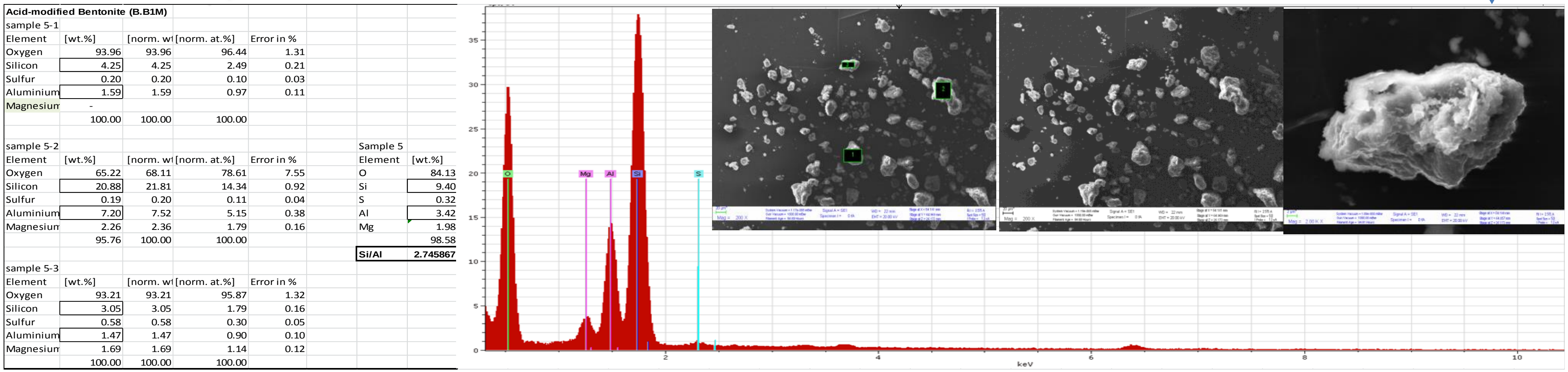
Sample 1

Element	[wt.%]
Oxygen	55.79
Silicon	19.73
Aluminiur	6.98
Iron	1.78
Magnesiu	2.15
Sulfur	0.24
	86.67
Si/Al	**2.828949**

sample 1-3

Element	[wt.%]	[norm. wt	[norm. at.%]	Error in %
Oxygen	55.93	60.64	73.06	6.60
Silicon	23.25	25.21	17.30	1.02
Aluminium	8.46	9.17	6.55	0.44
Iron	1.65	1.79	0.62	0.09
Magnesium	2.62	2.84	2.25	0.18
Sulfur	0.33	0.36	0.21	0.04
	92.24	100.00	100.00	

Figure 7. 6: EDS and corresponding SEM of beneficiated bentonite clay catalyst (B.B)



Acid-modified Bentonite (B.B1M)

sample 5-1

Element	[wt.%]	[norm. wt	[norm. at.%]	Error in %
Oxygen	93.96	93.96	96.44	1.31
Silicon	4.25	4.25	2.49	0.21
Sulfur	0.20	0.20	0.10	0.03
Aluminium	1.59	1.59	0.97	0.11
Magnesium	-			
	100.00	100.00	100.00	

sample 5-2

Element	[wt.%]	[norm. wt	[norm. at.%]	Error in %
Oxygen	65.22	68.11	78.61	7.55
Silicon	20.88	21.81	14.34	0.92
Sulfur	0.19	0.20	0.11	0.04
Aluminium	7.20	7.52	5.15	0.38
Magnesium	2.26	2.36	1.79	0.16
	95.76	100.00	100.00	

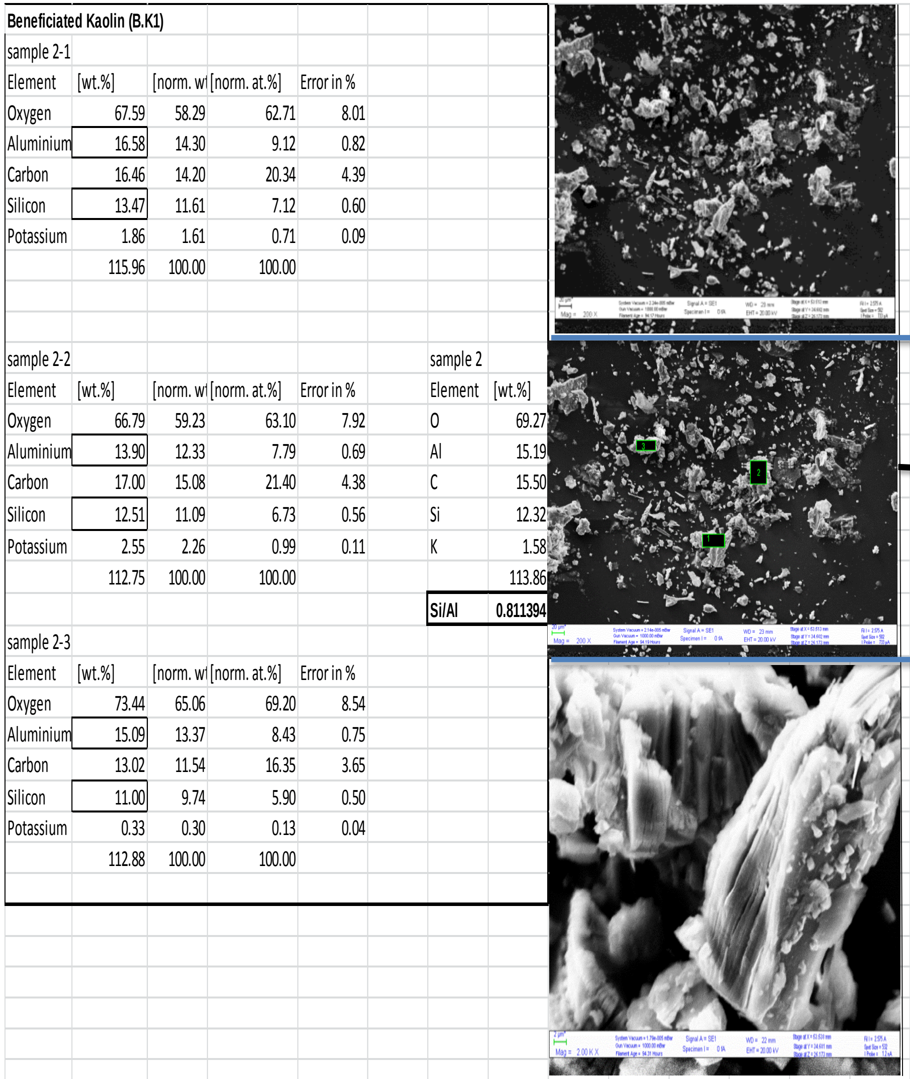
Sample 5

Element	[wt.%]
O	84.13
Si	9.40
S	0.32
Al	3.42
Mg	1.98
	98.58
Si/Al	**2.745867**

sample 5-3

Element	[wt.%]	[norm. wt	[norm. at.%]	Error in %
Oxygen	93.21	93.21	95.87	1.32
Silicon	3.05	3.05	1.79	0.16
Sulfur	0.58	0.58	0.30	0.05
Aluminium	1.47	1.47	0.90	0.10
Magnesium	1.69	1.69	1.14	0.12
	100.00	100.00	100.00	

Figure 7.7: EDS and corresponding SEM of acid-modified bentonite clay (B.B1M)



Beneficiated Kaolin (B.K1)

sample 2-1

Element	[wt.%]	[norm. wt	[norm. at.%]	Error in %
Oxygen	67.59	58.29	62.71	8.01
Aluminium	16.58	14.30	9.12	0.82
Carbon	16.46	14.20	20.34	4.39
Silicon	13.47	11.61	7.12	0.60
Potassium	1.86	1.61	0.71	0.09
	115.96	100.00	100.00	

sample 2-2

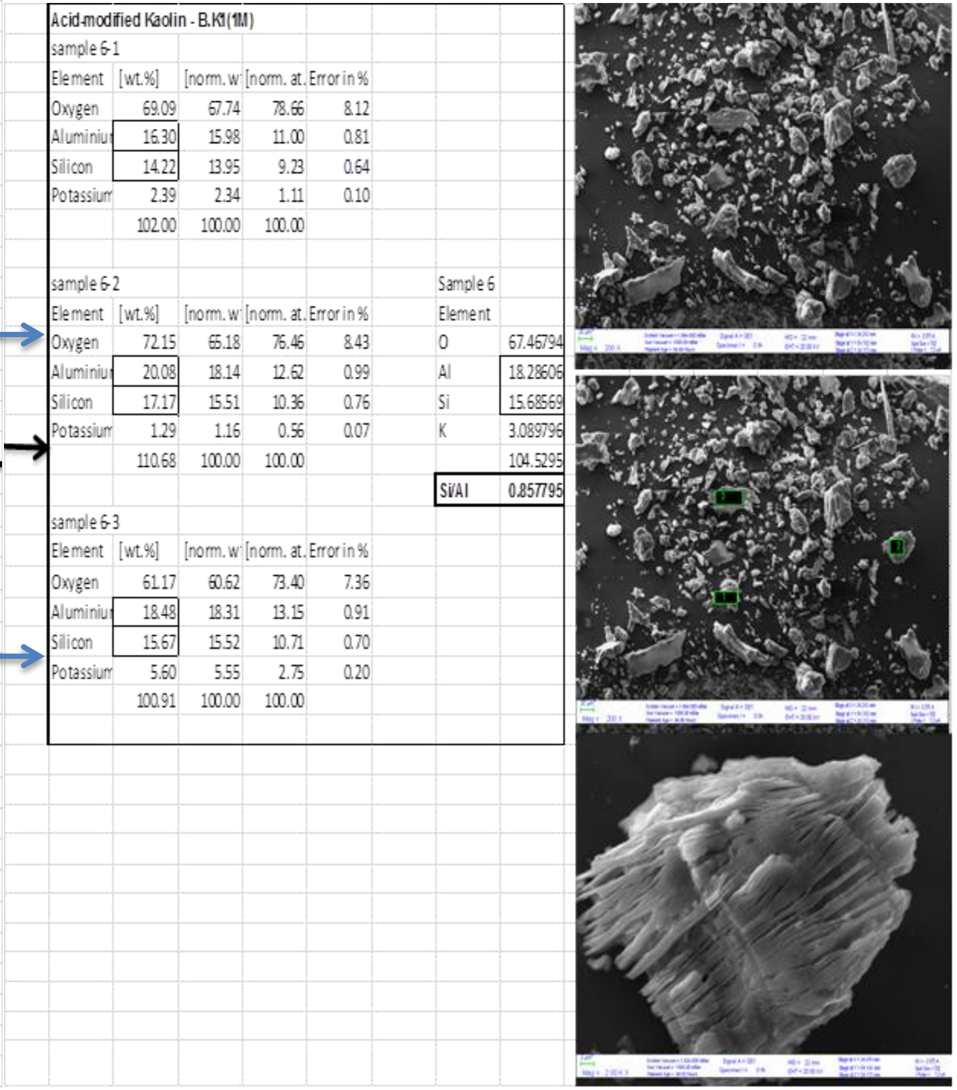
Element	[wt.%]	[norm. wt	[norm. at.%]	Error in %
Oxygen	66.79	59.23	63.10	7.92
Aluminium	13.90	12.33	7.79	0.69
Carbon	17.00	15.08	21.40	4.38
Silicon	12.51	11.09	6.73	0.56
Potassium	2.55	2.26	0.99	0.11
	112.75	100.00	100.00	

sample 2

Element	[wt.%]
O	69.27
Al	15.19
C	15.50
Si	12.32
K	1.58
	113.86
Si/Al	**0.811394**

sample 2-3

Element	[wt.%]	[norm. wt	[norm. at.%]	Error in %
Oxygen	73.44	65.06	69.20	8.54
Aluminium	15.09	13.37	8.43	0.75
Carbon	13.02	11.54	16.35	3.65
Silicon	11.00	9.74	5.90	0.50
Potassium	0.33	0.30	0.13	0.04
	112.88	100.00	100.00	



Acid-modified Kaolin - B.K1(1M)

sample 6-1

Element	[wt.%]	[norm. w	[norm. at.	Error in %
Oxygen	69.09	67.74	78.66	8.12
Aluminiu	16.30	15.98	11.00	0.81
Silicon	14.22	13.95	9.23	0.64
Potassiu	2.39	2.34	1.11	0.10
	102.00	100.00	100.00	

sample 6-2

Element	[wt.%]	[norm. w	[norm. at.	Error in %
Oxygen	72.15	65.18	76.46	8.43
Aluminiu	20.08	18.14	12.62	0.99
Silicon	17.17	15.51	10.36	0.76
Potassiu	1.29	1.16	0.56	0.07
	110.68	100.00	100.00	

Sample 6

Element	
O	67.46794
Al	18.28606
Si	15.68569
K	3.089796
	104.5295
Si/Al	**0.857795**

sample 6-3

Element	[wt.%]	[norm. w	[norm. at.	Error in %
Oxygen	61.17	60.62	73.40	7.36
Aluminiu	18.48	18.31	13.15	0.91
Silicon	15.67	15.52	10.71	0.70
Potassiu	5.60	5.55	2.75	0.20
	100.91	100.00	100.00	

Figure 7. 8 (Left): EDS and corresponding SEM of Beneficiated Kaolin clay (B.K1)

Figure 7. 9 (Right): EDS and Corresponding SEM of acid-modified Kaolin clay (B.K1(1M))

7.7 EDS/SEM of the produced clay-based catalysts (Figure 7.10-7.19)

Sample: J 1 **ZeoClay**
Type: Default
ID:

Processing option : All elements analysed (Normalised)

All results in weight%

Spectrum	In stats.	O	Na	Al	Si	K	Total
Spectrum 1	Yes	54.63	6.99	2.21	31.33	0.35	100
Spectrum 2	Yes	53.37	3.73	1.08	34.79	3.03	100
Spectrum 3	Yes	53.69	3.48	1.33	39.5	0	100
Mean		53.89	4.73	1.54	35.21	1.13	100
Std. deviation		0.65	1.96	1.69	4.1	1.66	
Max.		54.63	6.99	6.7	39.5	3.03	
Min.		53.37	3.48	3.33	31.33	0	
Si/Al	**22.864**						

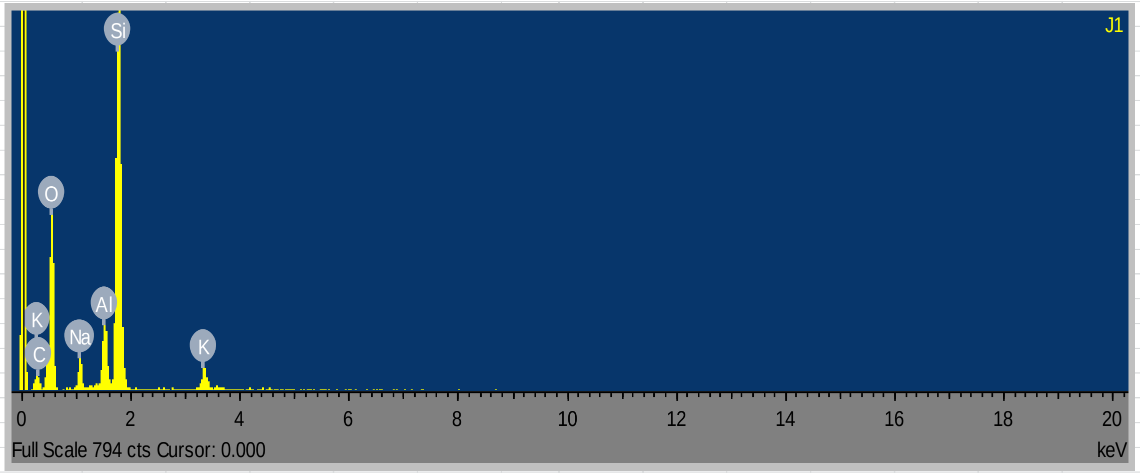


Figure 7.10: EDS and corresponding SEM of non-protonated clay-based Zeolite sample (Zeoclay)

Reference
pg.85-86

Sample: J 2 **H-ZeoClay**
Type: Default
ID:

Processing option : All elements analysed (Normalised)

All results in weight%

Spectrum	In stats.	O	Al	Si	Total
J2	Yes	57.91	1.67	39.21	100
Spectrum 2	Yes	50.86	1.49	44.1	100
Spectrum 3	Yes	53.77	2.06	37.28	100
Mean		54.18	1.74	40.2	100
Std. deviation		3.55	3.08	3.51	
Max.		57.91	8.95	44.1	
Min.		50.86	2.87	37.28	
Si/Al	**23.103**				

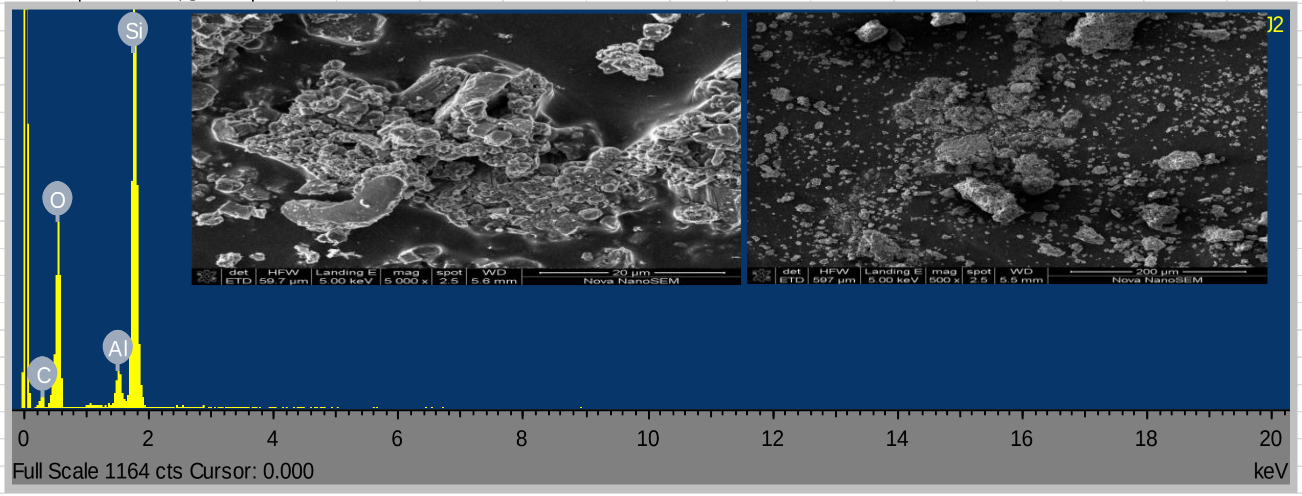


Figure 7.11: EDS and corresponding SEM of produced clay-based zeolite sample (H-ZeoClay)

Reference

pg.86

Sample: J 5	**H-ZeoCOM**				
Type: Default					
ID:					
Processing option : All elements analysed (Normalised)					
All results in weight%					
Spectrum	In stats.	O	Al	Si	Total
Spectrum 1	Yes	54.02	1.47	61.51	100
Spectrum 2	Yes	58.68	1.27	56.79	100
Spectrum 3	Yes	53.63	1.13	59.24	100
Mean		55.44	1.29	59.18	100
Std. deviation		2.81	0.17	2.81	
Max.		58.68	1.47	45.24	
Min.		53.63	1.13	40.04	
Si/Al	**45.876**				

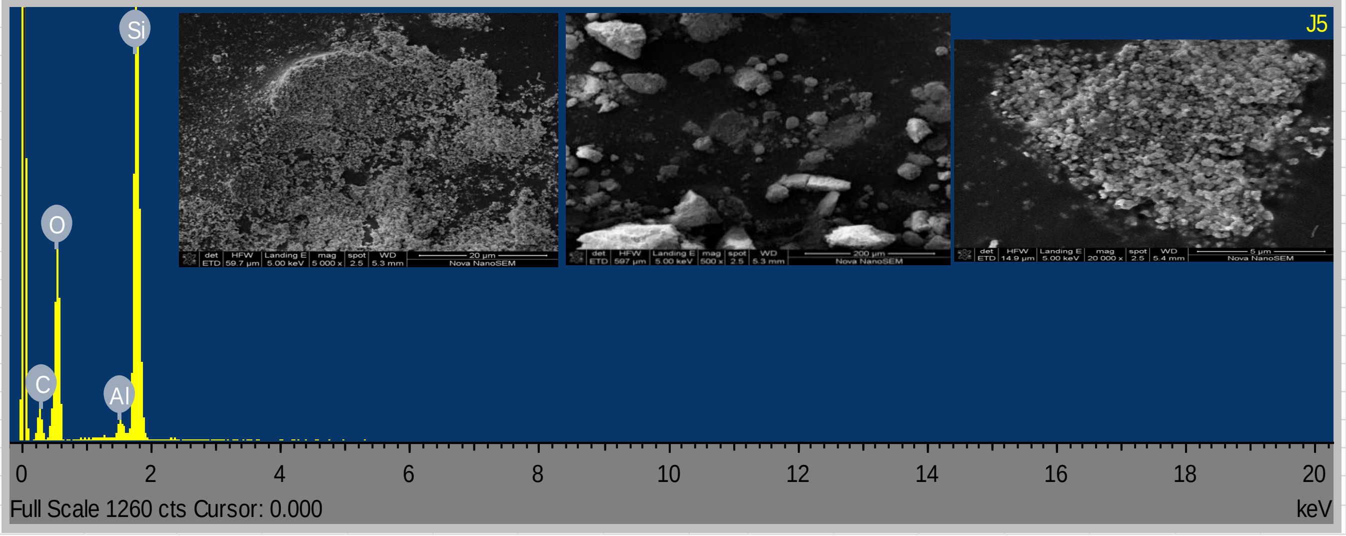


Figure 7. 12: EDS and corresponding SEM of commercial zeolite sample (H-ZeoCOM)

Type: Default							
ID:							
Processing option : All elements analysed (Normalised)							
All results in weight%							
Spectrum	In stats.	O	Na	Al	Si	K	Total
Spectrum 1	Yes	53.58	1.41	1.73	36.27	0.36	100
Spectrum 2	Yes	45.23	0.61	1.88	50.36	0	100
Spectrum 3	Yes	54.43	7.56	1.78	29.08	0.29	100
Mean		51.08	3.19	1.8	38.57	0.22	100
Std. deviation		5.09	3.8	2.72	10.82	0.19	
Max.		54.43	7.56	8.64	50.36	0.36	
Min.		45.23	0.61	3.81	29.08	0	
Si/Al	**21.43**						

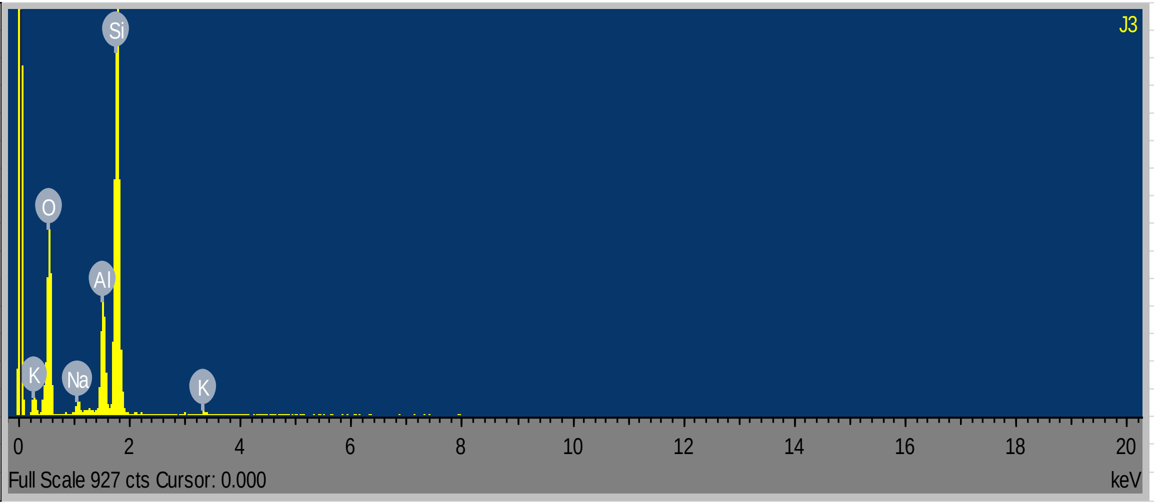


Figure 7.13: EDS of H-ZeoClay sample (After 6 hour reaction at 350 °C)

Sample: J 4	**H-ZeoClay (400 ºC) - After reaction**					
Type: Default						
ID:						
Processing option : All elements analysed (Normalised)						
All results in weight%						
Spectrum	In stats.	O	Na	Al	Si	Total
Spectrum 1	Yes	55.08	0	1.586	40.2	100
Spectrum 2	Yes	53.42	2.26	1.28	39.04	100
Spectrum 3	Yes	55.05	0	1.89	42.06	100
Mean		54.52	0.75	1.59	40.43	100
Std. deviation		0.95	1.3	1.25	1.52	
Max.		55.08	2.26	5.28	42.06	
Min.		53.42	0	2.89	39.04	
Si/Al	**25.428**					

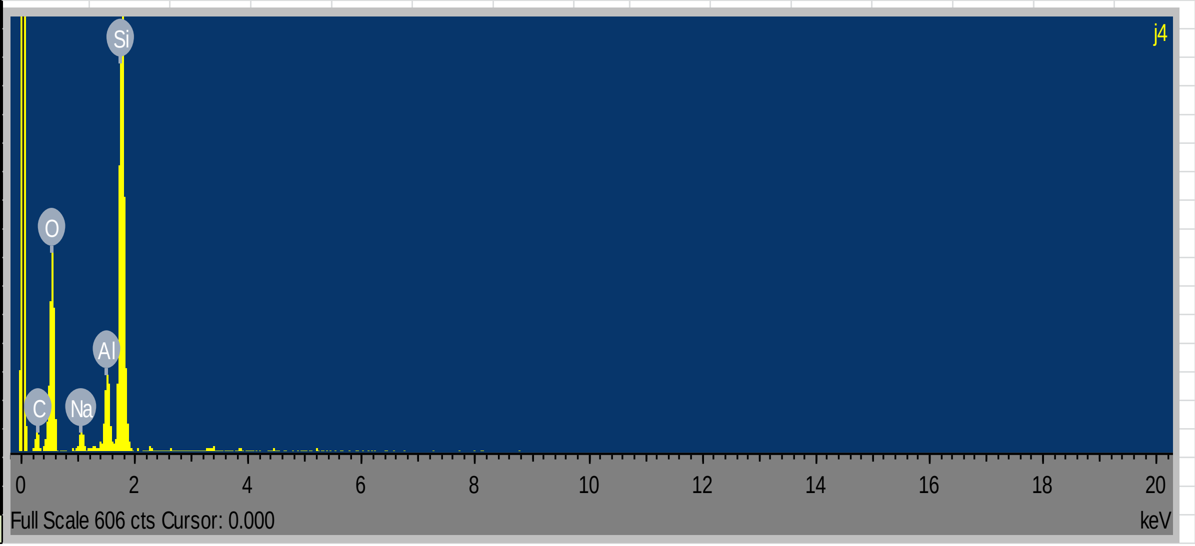


Figure 7.14: EDS of H-ZeoClay sample (After 6 hour reaction of 400 ºC)

Sample: J 6	**H-ZeoCOM – After reaction**				
Type: Default					
ID:					
Processing option : All elements analysed (Normalised)					
All results in weight%					
Spectrum	In stats.	O	Al	Si	Total
Spectrum 1	Yes	58.03	1.54	40.43	100
Spectrum 2	Yes	47.29	1.47	51.24	100
Spectrum 3	Yes	51.25	1.52	47.22	100
Mean		52.19	1.51	46.3	100
Std. deviation		5.43	0.04	5.46	
Max.		58.03	1.54	51.24	
Min.		47.29	1.47	40.43	
Si/Al	**30.662**				

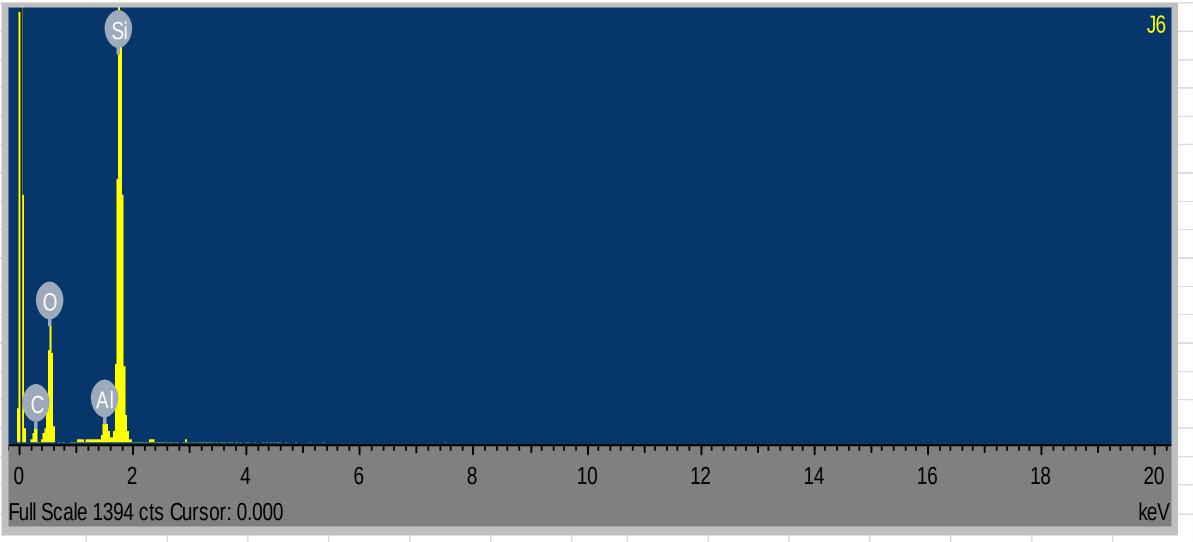


Figure 7. 15: EDS of H-ZeoCOM sample (After reaction of 350 ^{o}C)

Sample: J 7	**H-ZeoClay (Ni)**						**Reference**
Type: Default							pg.87-90
ID:							
Processing option : All elements analysed (Normalised)							
All results in weight%							
Spectrum	In stats.	O	Al	Si	Ni	Total	
Spectrum 1	Yes	56.03	1.02	36.73	5.31	100	
Spectrum 2	Yes	38.32	1.06	23.96	34.96	100	
Spectrum 3	Yes	34.32	1.05	23.61	39.12	100	
Mean		42.89	1.044	28.1	26.46	100	
Std. deviation		11.55	0.55	7.48	18.43		
Max.		56.03	2.95	36.73	39.12		
Min.		34.32	1.92	23.61	5.31		
Si/Al	**26.916**						

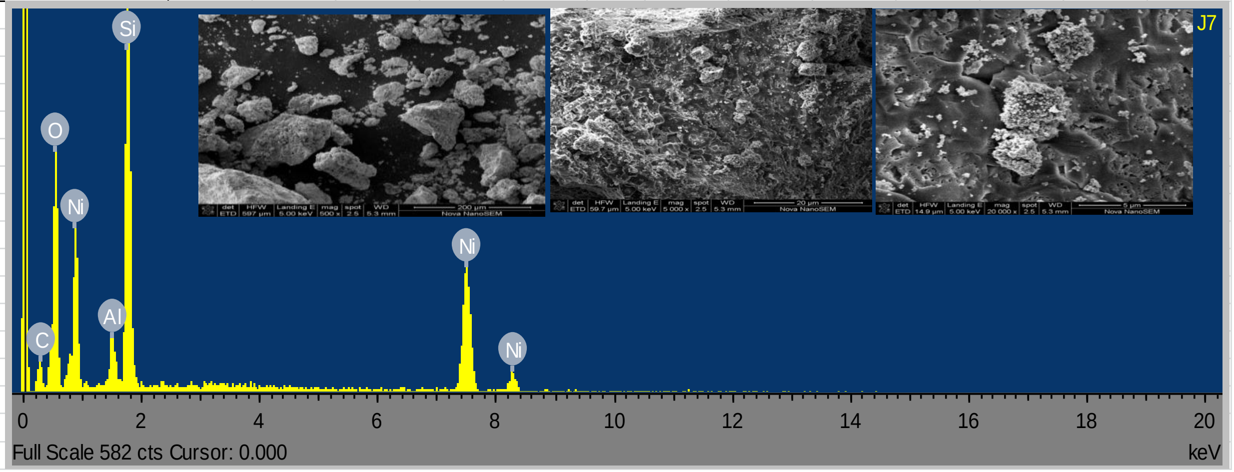


Figure 7. 16: EDS and corresponding SEM of H-ZeoCOM (Ni) sample

Sample: J 8	**H-ZeoClay (Co)**							**Reference**
Type: Default								pg.87-90
ID:								
Processing option : All elements analysed (Normalised)								
All results in weight%				1.4633333				
Spectrum	In stats.	O	Na	Al	Si	Fe	Total	
Spectrum 1	Yes	50.16	5.4	1.47	28.86	8.67	100	
Spectrum 2	Yes	48.32	4.7	1.51	29.29	9.86	100	
Spectrum 3	Yes	49.18	0.49	1.41	33.29	13.4	100	
Mean		49.22	3.53	1.46	30.48	10.64	100	
Std. deviation		0.92	2.66	2.2	2.44	2.46		
Max.		50.16	5.4	7.82	33.29	13.4		
Min.		48.32	0.49	3.64	28.86	8.67		
Si/Al	**20.877**							

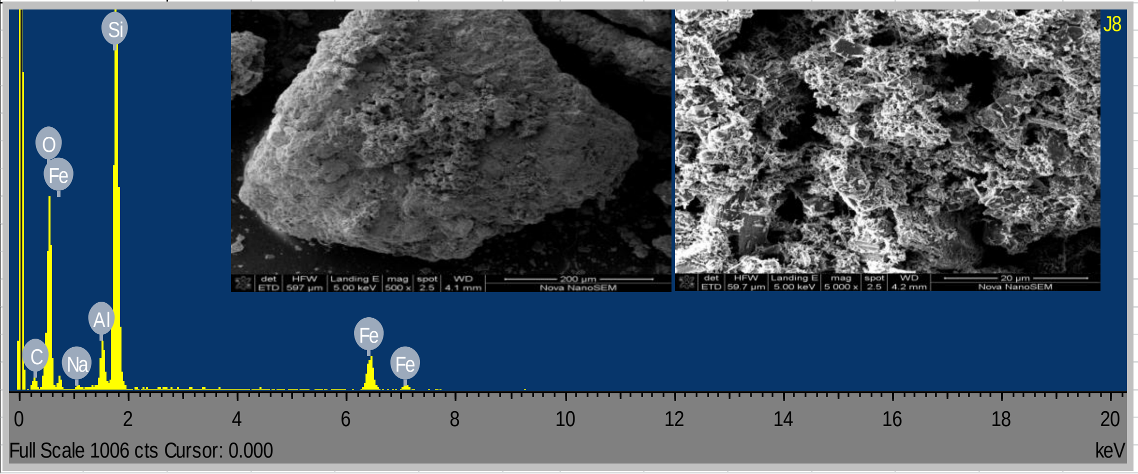


Figure 7.17: EDS and corresponding SEM of H-ZeoCOM (Co) sample

Sample: J 9	**H-ZeoClay (Fe)**						
Type: Default							
ID:							
Processing option : All elements analysed (Normalised)							
All results in weight%				1.052	1.053333		
Spectrum	In stats.	O	Na	Al	Si	Co	Total
Spectrum 1	Yes	37.24	0	1.1	21	39.21	100
Spectrum 2	Yes	46.81	3.78	1.02	19.15	23.85	100
Spectrum 3	Yes	45.58	0.66	1.04	27.01	23.24	100
Mean		43.21	1.48	1.052	22.39	28.76	100
Std. deviation		5.21	2.02	2.01	4.11	9.05	
Max.		46.81	3.78	6.41	27.01	39.21	
Min.		37.24	0	2.55	19.15	23.24	
Si/Al	**21.28**						

Reference

pg.87-90

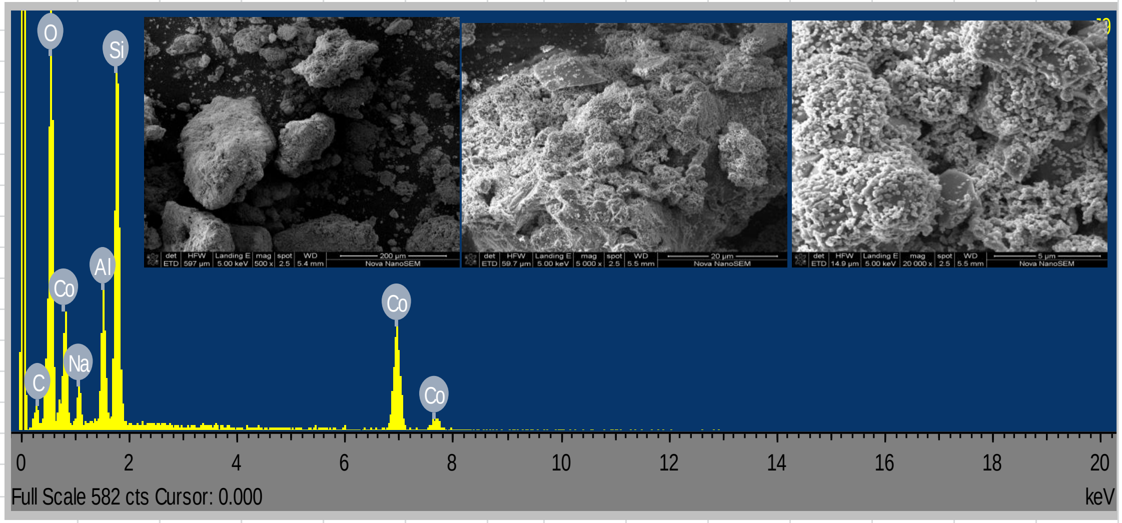


Figure 7. 18: EDS and corresponding SEM of H-ZeoCOM (Fe) sample

Sample: J 10	**B.B1M – After reaction**								
Type: Default									
ID:									
Processing option : All elements analysed (Normalised)									
All results in weight%									
Spectrum	In stats.	O	Na	Al	Si	S	K	Ca	Total
Spectrum 1	Yes	50.23	0	6.06	42.55	0	0	1.15	100
Spectrum 2	Yes	51.21	2.31	9.1	31.2	0	6.19	0	100
Spectrum 3	Yes	60.63	0	3.74	23.52	6.43	0	5.68	100
Mean		54.03	0.77	6.3	32.43	2.14	2.06	2.28	100
Std. deviation		5.74	1.33	2.69	9.57	3.71	3.57	3	
Max.		60.63	2.31	9.1	42.55	6.43	6.19	5.68	
Min.		50.23	0	3.74	23.52	0	0	0	
Si/Al	**5.15**								

Reference

pg.77-79

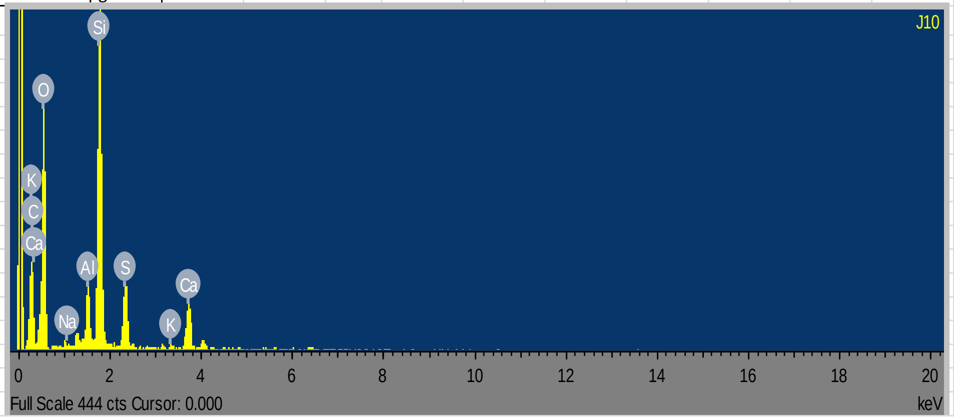


Figure 7. 19: EDS of B.B1M sample (After reaction of 350 ºC)

7.8 XRD patterns and corresponding SEM of the non-modified clay samples (Figure 7.20 -7.25) – Reference (pg.79-80; pg. 133)

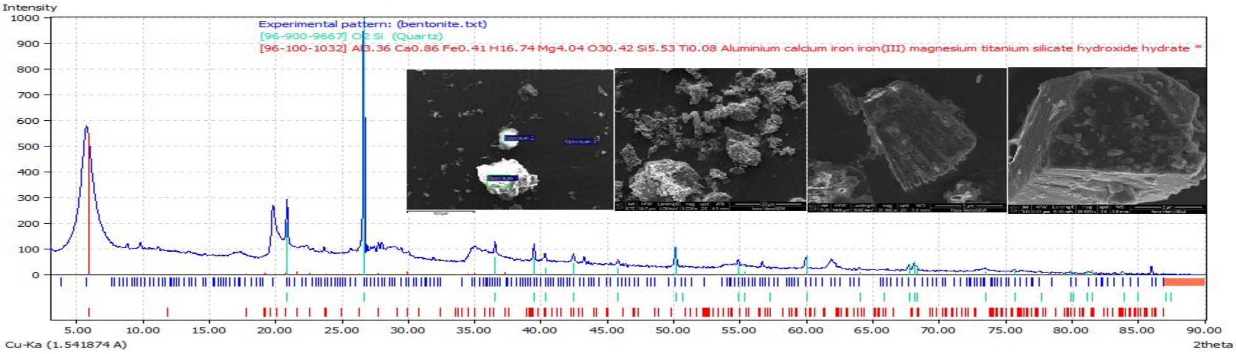


Figure 7. 20: XRD pattern and respective SEM micrographs of N.B catalyst

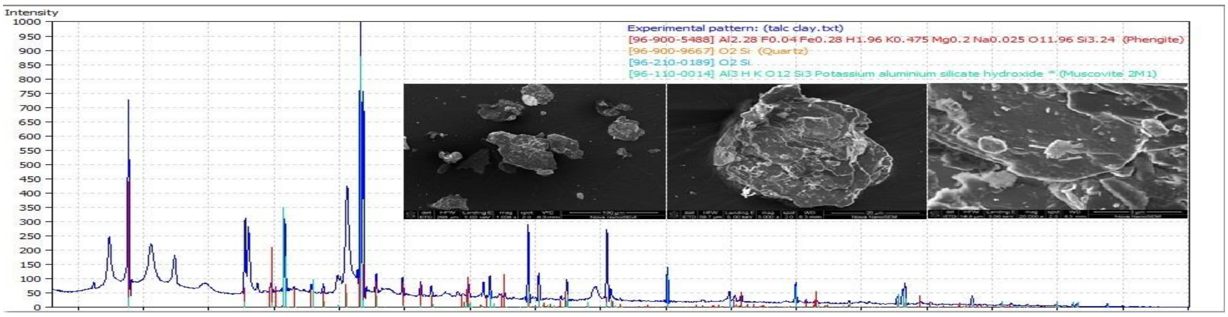


Figure 7. 21: XRD pattern and respective SEM micrographs of N.T catalyst

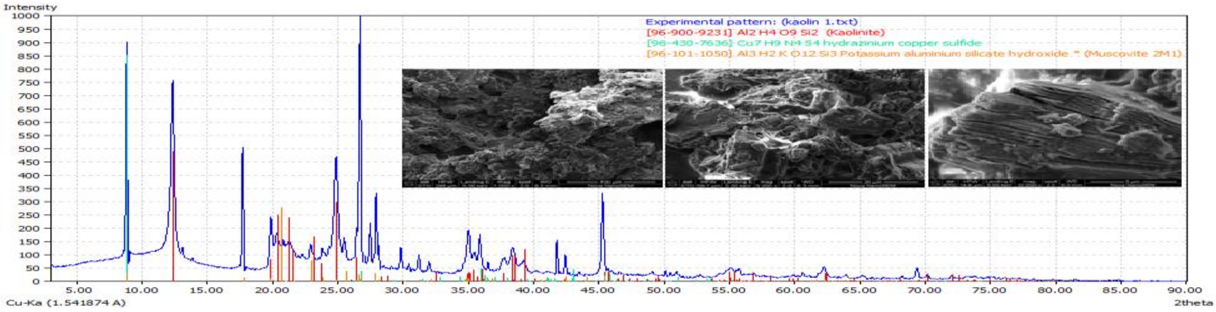


Figure 7.22: XRD pattern and respective SEM micrographs of N.K1 catalyst

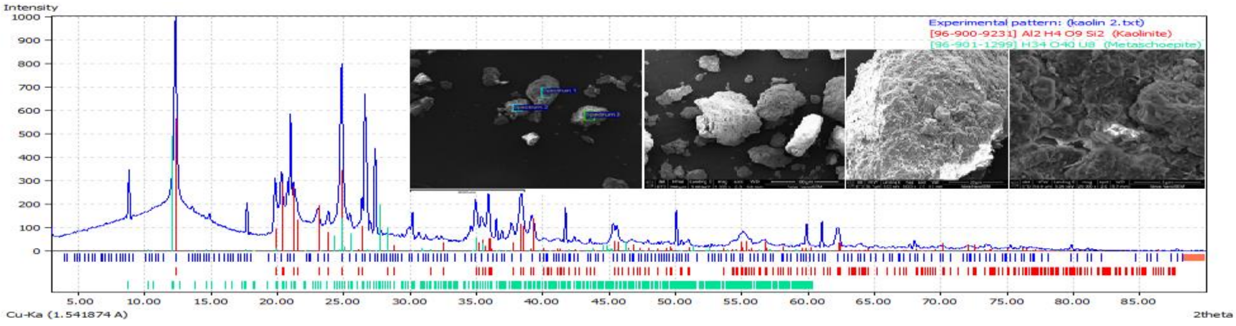


Figure 7.23: XRD pattern and respective SEM micrographs of N.K2 catalyst

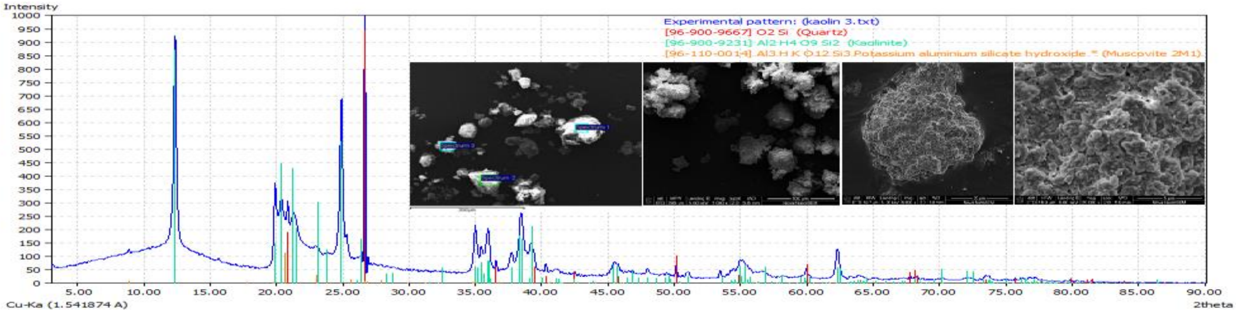


Figure 7.24: XRD pattern and respective SEM micrographs of N.K3 catalyst

Reference
pg.90-92

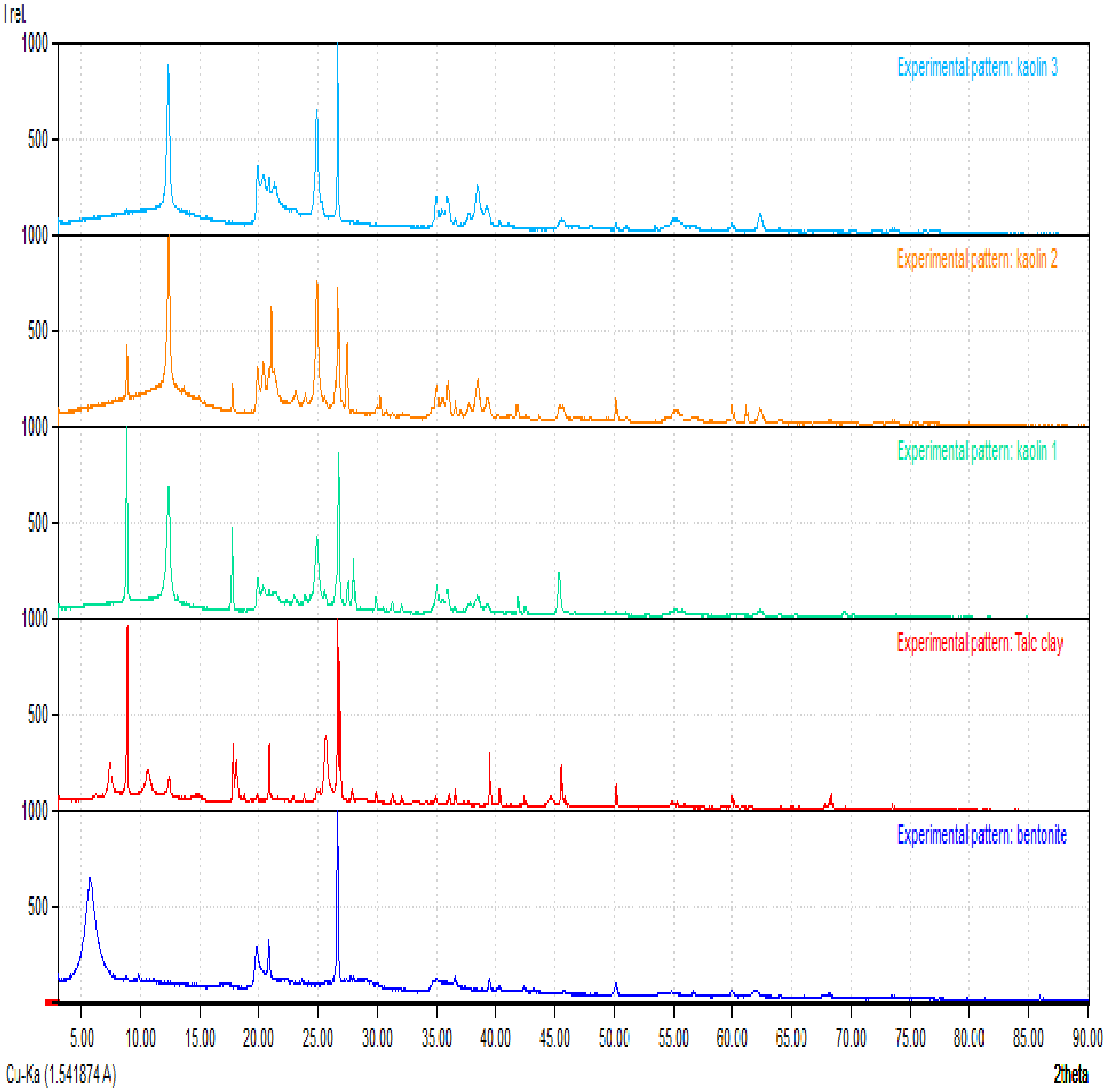


Figure 7.25: XRD patterns of non-modified clay catalysts (combined)

7.9 XRD patterns for clay modification samples starting from N.B, B.B and B.B1M

(Figure 7.26 - 7.28) - Reference (pg.92-94)

Reference
pg.92-94

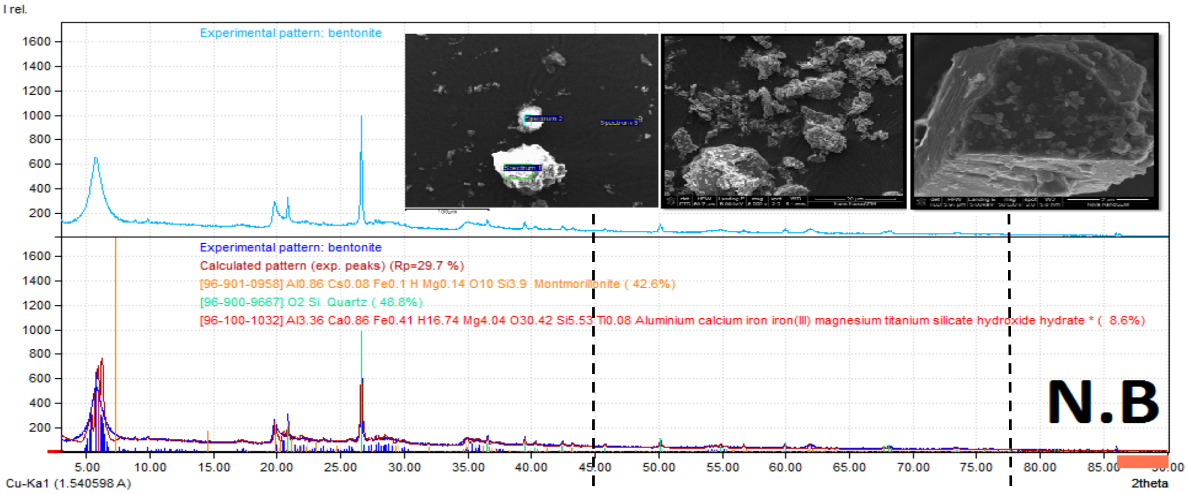


Figure 7. 26: XRD pattern and respective SEM image of N.B clay catalyst

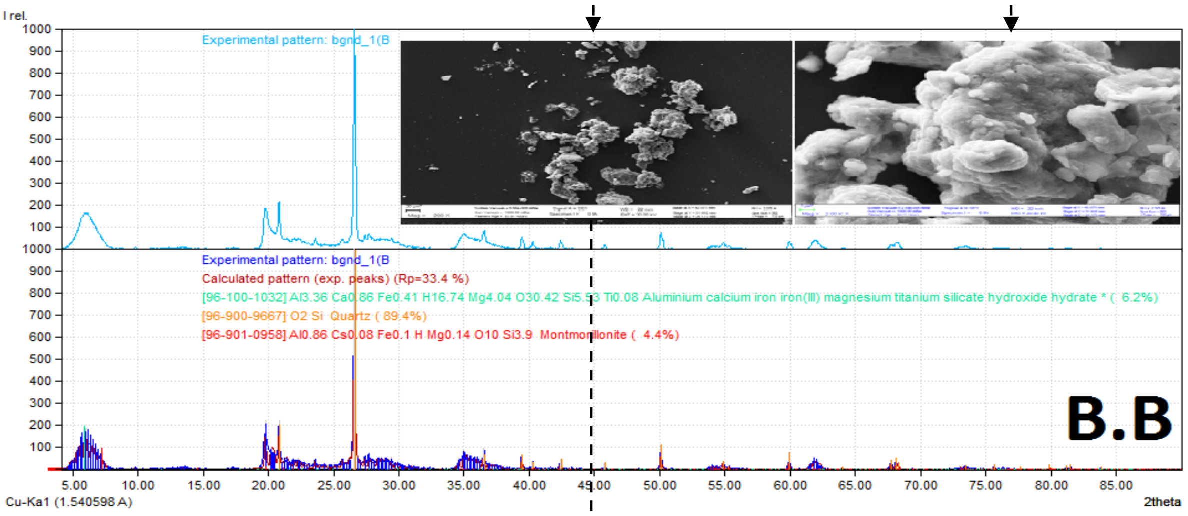


Figure 7. 27: XRD pattern and respective SEM image of B.B clay catalyst

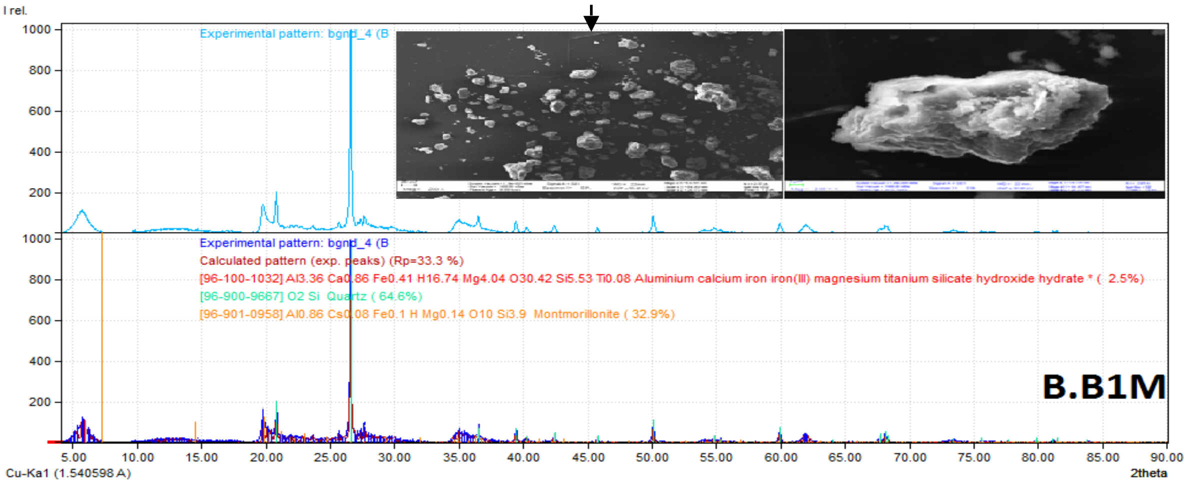


Figure 7. 28: XRD pattern and respective SEM image of B.B1M clay catalyst

7.10 Additional Figures relative to this work

Referenced

pg. 77

Table 7.8: Elemental composition in the oxide form of the various (non-modified) clay samples (Department of Geology, UCT XRF results).

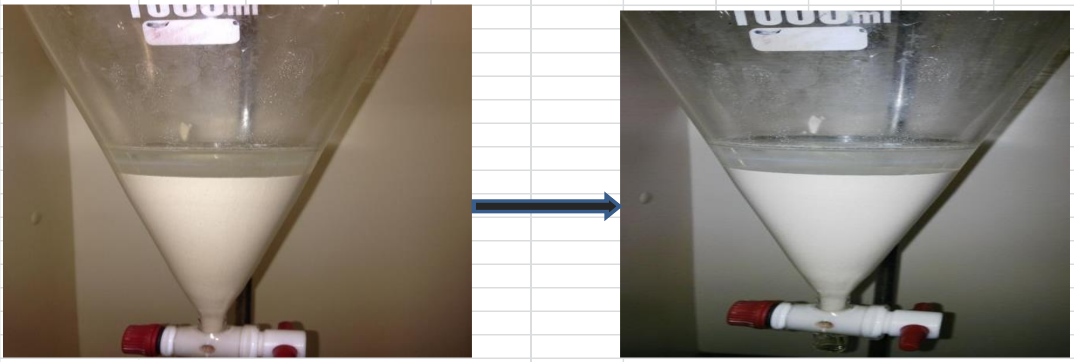
Major element		NB	BB(1M)	NK1	BK1	BK1(1M)	NK2	BK2(1M)
SiO2	wt.%	57.64	61.40	49.86	47.06	48.26	54.04	48.39
Al2O3	wt.%	13.86	12.36	32.92	35.15	34.67	29.95	33.81
TiO2	wt.%	0.16	0.17	0.06	0.02	0.02	0.35	1.52
Fe2O3	wt.%	**2.52**	**1.82**	**0.24**	**0.18**	**0.13**	0.46	0.57
MnO	wt.%	0.05	0.02	0.02	0.02	0.00	0.01	0.01
MgO	wt.%	3.26	2.13	0.32	0.26	0.22	0.15	0.06
CaO	wt.%	1.12	0.51	0.11	0.11	0.00	0.07	0.00
Na2O	wt.%	1.41	0.47	0.46	0.36	0.36	0.28	0.15
K2O	wt.%	0.75	0.66	4.72	2.59	2.65	4.02	0.36
P2O5	wt.%	0.03	0.01	b.d.	0.01	b.d.	0.03	0.07
SO3	wt.%	0.06	0.18	b.d.	b.d.	b.d.	b.d.	b.d.
Cr2O3	wt.%	b.d.	0.02	b.d.	b.d.	b.d.	b.d.	0.01
NiO	wt.%	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
H2O-	wt.%	12.24	13.16	0.86	1.17	1.36	0.47	1.20
LOI	wt.%	6.05	6.19	9.08	11.10	10.67	9.05	12.18
Sum	wt.%	99.16	99.12	98.68	98.04	98.36	98.86	98.32
SiO2/AL2O3		4.157566	4.968758	1.514344	1.338659	1.392303	1.804383	1.430982
		2	1	4	7	6	3	5
		NB		NK1			NK2	
SiO2/AL2O3		4.16		1.51			1.80	
Average SiO2/AL2O3		**2.49**						

Referenced

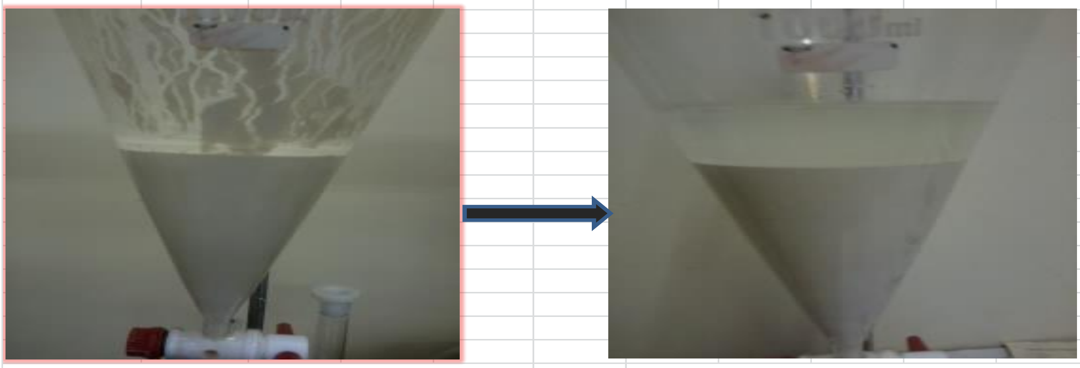
pg.83

Figure 7. 29: Non-modified natural (Raw) bentonite before and after crushing and milling (Prior Catalytic reaction and beneficiation)

Referenced
pg.83



Kaolin 2 (N.K2) Kaolin 2 (N.K2)



Kaolin 1 (N.K1) Kaolin 1 (N.K1)

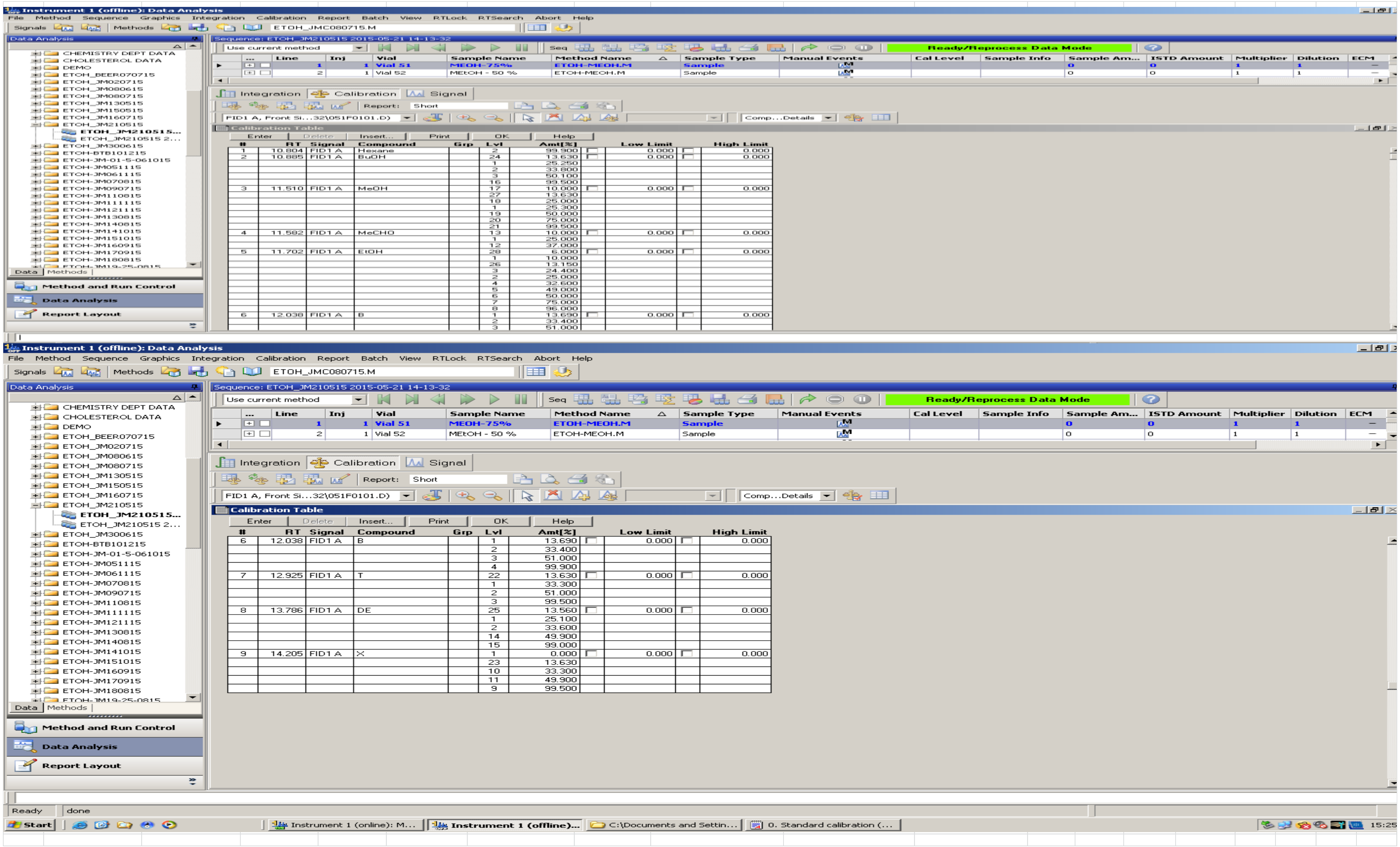
Figure 7. 30: Kaolin clay before and after settling during beneficiation

Appendix 3

7.11 GC analyses of liquid and gaseous product

GC analyses test using an auto sampler GC-FID equipped with a Polar Capillary column (Model - HP88, 7890B GC system). Sofware (GC)

7.11.1 Retention time and concentrations calibration of liquid standards



Sequence: ETOH_JM210515 2015-05-21 14-13-32

Method: ETOH_JMC080715.M

Line	Inj	Vial	Sample Name	Method Name	Sample Type	Manual Events	Cal Level	Sample Info	Sample Am...	ISTD Amount	Multiplier	Dilution
1	1	Vial 51	MEOH-75%	ETOH-MEOH.M	Sample				0	0	1	1
2	1	Vial 52	MEtOH - 50 %	ETOH-MEOH.M	Sample				0	0	1	1

Report: Short

FID1 A, Front Si...32\051F0101.D)

Calibration Table

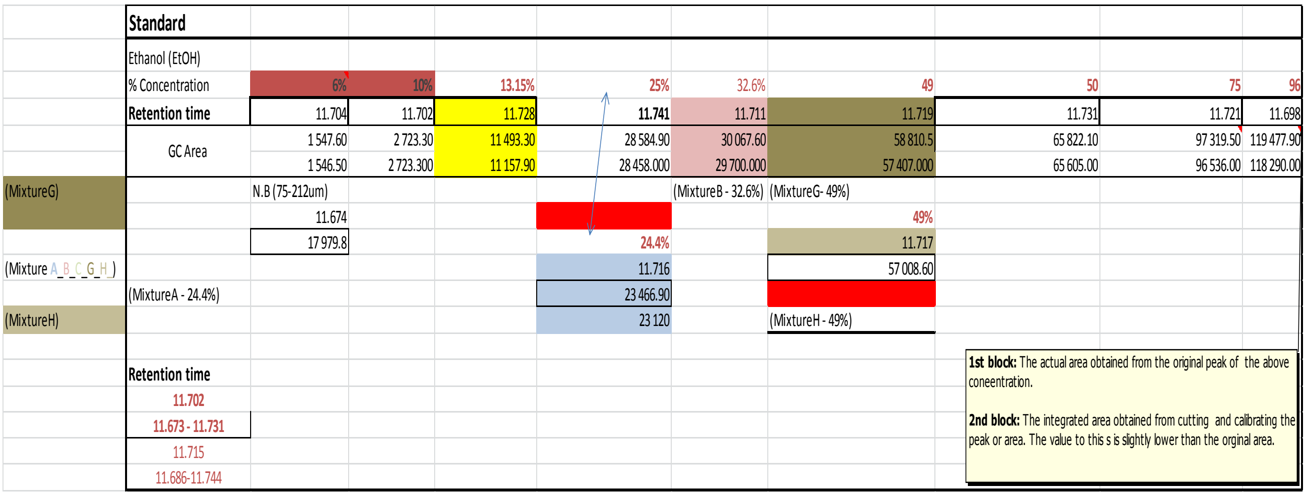
#	RT	Signal	Compound	Grp	Lvl	Amt[%]		Low Limit		High Limit
1	10.804	FID1 A	Hexane		2	99.900	☐	0.000	☐	0.000
2	10.885	FID1 A	BuOH		24	13.630	☐	0.000	☐	0.000
					1	25.250				
					2	33.800				
					3	50.100				
					16	99.500				
3	11.510	FID1 A	MeOH		17	10.000	☐	0.000	☐	0.000
					27	13.630				
					18	25.000				
					1	25.300				
					19	50.000				
					20	75.000				
					21	99.500				
4	11.582	FID1 A	MeCHO		13	10.000	☐	0.000	☐	0.000
					1	25.000				
					12	37.000				
5	11.702	FID1 A	EtOH		28	6.000	☐	0.000	☐	0.000
					1	10.000				
					26	13.150				
					3	24.400				
					2	25.000				
					4	32.600				
					5	49.000				
					6	50.000				
					7	75.000				
					8	96.000				
6	12.038	FID1 A	B		1	13.690	☐	0.000	☐	0.000
					2	33.400				
					3	51.000				

#	RT	Signal	Compound	Grp	Lvl	Amt[%]		Low Limit		High Limit
6	12.038	FID1 A	B		1	13.690	☐	0.000	☐	0.000
					2	33.400				
					3	51.000				
					4	99.900				
7	12.925	FID1 A	T		22	13.630	☐	0.000	☐	0.000
					1	33.300				
					2	51.000				
					3	99.500				
8	13.786	FID1 A	DE		25	13.560	☐	0.000	☐	0.000
					1	25.100				
					2	33.600				
					14	49.900				
					15	99.000				
9	14.205	FID1 A	X		1	0.000	☐	0.000	☐	0.000
					23	13.630				
					10	33.300				
					11	49.900				
					9	99.500				

Figure 7. 31: GC Standard Calibration

7.11.2 Retention time and GC area for liquid Standards (Pure solvent) at different concentrations (Table 7.9 - 7.17)

Table 7. 9: Retention time and GC area for ethanol standard at various concentrations

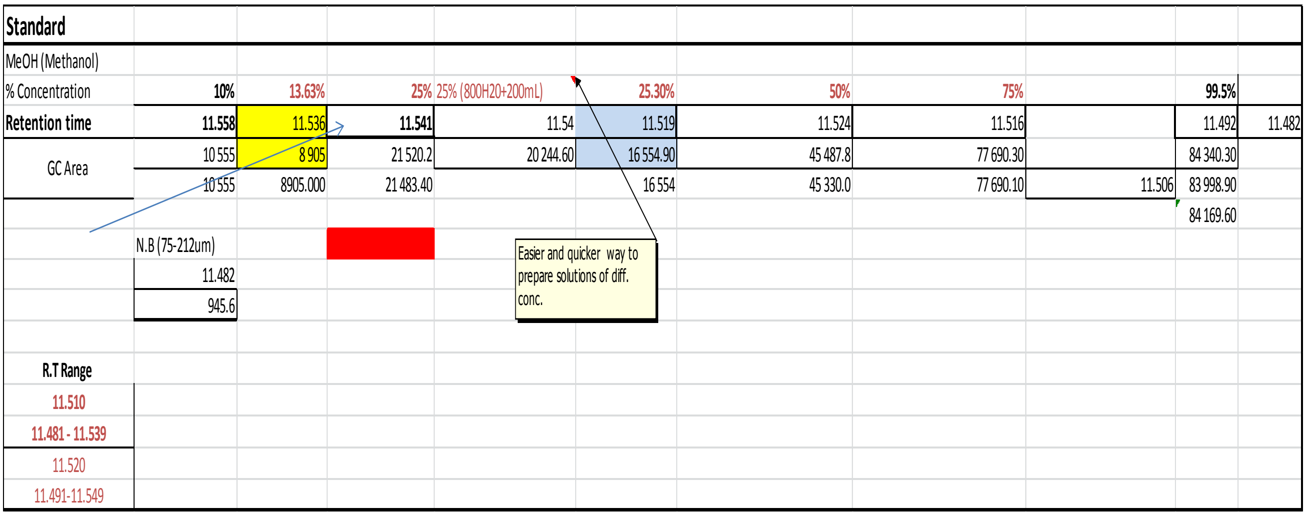


	Standard									
	Ethanol (EtOH)									
	% Concentration	6%	10%	13.15%	25%	32.6%	49	50	75	96
	Retention time	11.704	11.702	11.728	**11.741**	11.711	11.719	11.731	11.721	11.698
	GC Area	1 547.60	2 723.30	11 493.30	28 584.90	30 067.60	58 810.5	65 822.10	97 319.50	119 477.90
		1 546.50	2 723.300	11 157.90	28 458.000	29 700.000	57 407.000	65 605.00	96 536.00	118 290.00
(MixtureG)		N.B (75-212um)				(MixtureB - 32.6%)	(MixtureG- 49%)			
		11.674			🟥		49%			
		17 979.8			24.4%		11.717			
(Mixture A_B_C_G_H_)					11.716		57 008.60			
	(MixtureA - 24.4%)				23 466.90		🟥			
(MixtureH)					23 120		(MixtureH - 49%)			
	Retention time									
	11.702									
	11.673 - 11.731									
	11.715									
	11.686-11.744									

1st block: The actual area obtained from the original peak of the above coneentration.

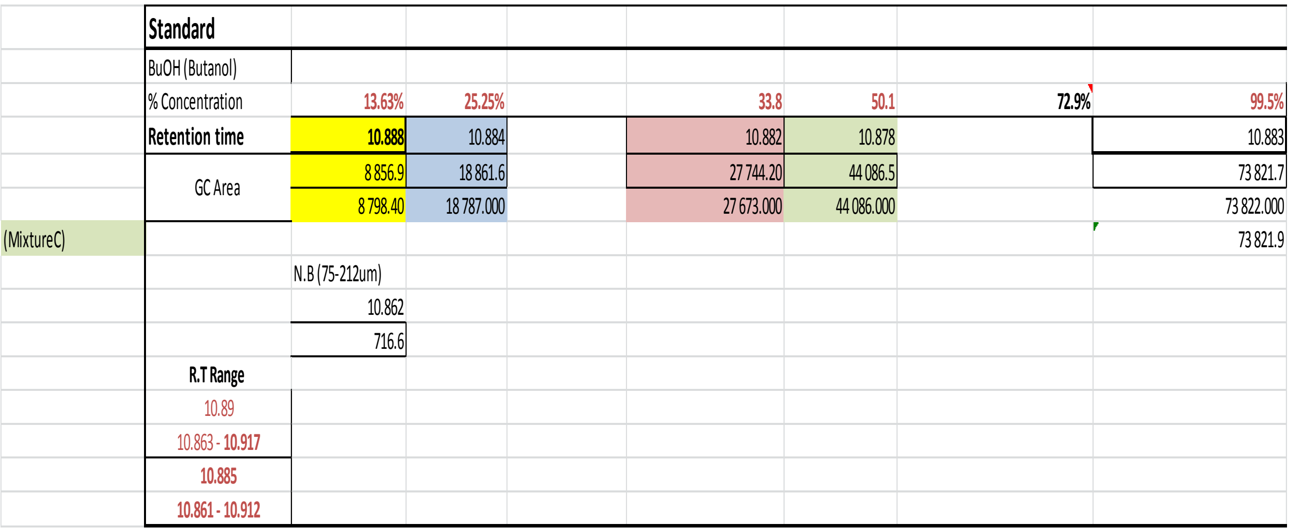
2nd block: The integrated area obtained from cutting and calibrating the peak or area. The value to this s is slightly lower than the orginal area.

Table 7. 10: Retention time and GC area for methanol standard at various concentrations



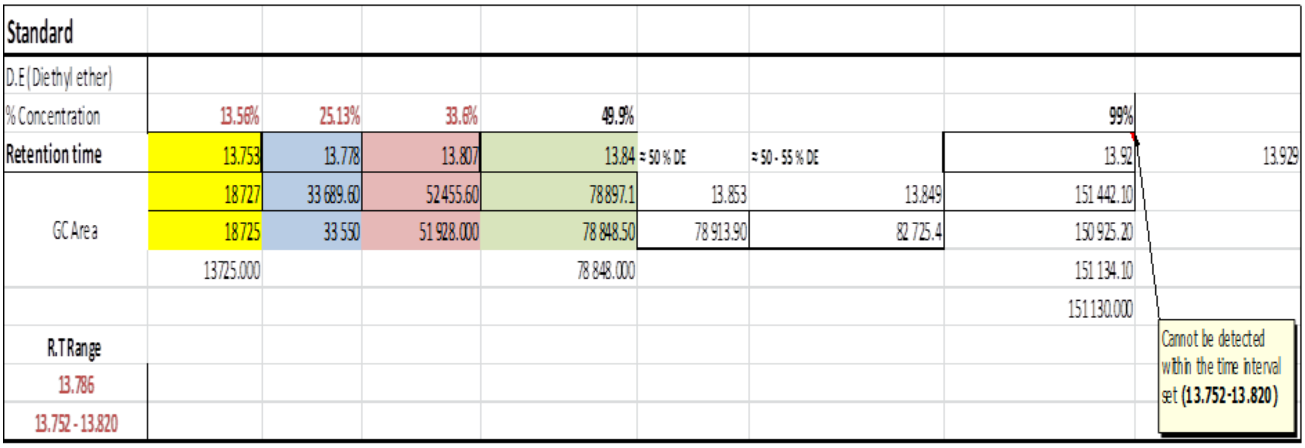
Standard										
MeOH (Methanol)										
% Concentration	**10%**	13.63%	25%	25% (800H20+200mL)	25.30%	50%	75%		**99.5%**	
Retention time	**11.558**	11.536	**11.541**	11.54	11.519	11.524	11.516		11.492	11.482
GC Area	10 555	8 905	21 520.2	20 244.60	16 554.90	45 487.8	77 690.30		84 340.30	
	10 555	8905.000	21 483.40		16 554	45 330.0	77 690.10	11.506	83 998.90	
									84 169.60	
	N.B (75-212um)		🟥	Easier and quicker way to prepare solutions of diff. conc.						
	11.482									
	945.6									
R.T Range										
11.510										
11.481 - 11.539										
11.520										
11.491-11.549										

Table 7. 11: Retention time and GC area for butanol standard at various concentrations



	Standard							
	BuOH (Butanol)							
	% Concentration	13.63%	25.25%		33.8	50.1	**72.9%**	99.5%
	Retention time	**10.888**	10.884		10.882	10.878		10.883
	GC Area	8 856.9	18 861.6		27 744.20	44 086.5		73 821.7
		8 798.40	18 787.000		27 673.000	44 086.000		73 822.000
(MixtureC)								73 821.9
		N.B (75-212um)						
		10.862						
		716.6						
	R.T Range							
	10.89							
	10.863 - **10.917**							
	10.885							
	10.861 - 10.912							

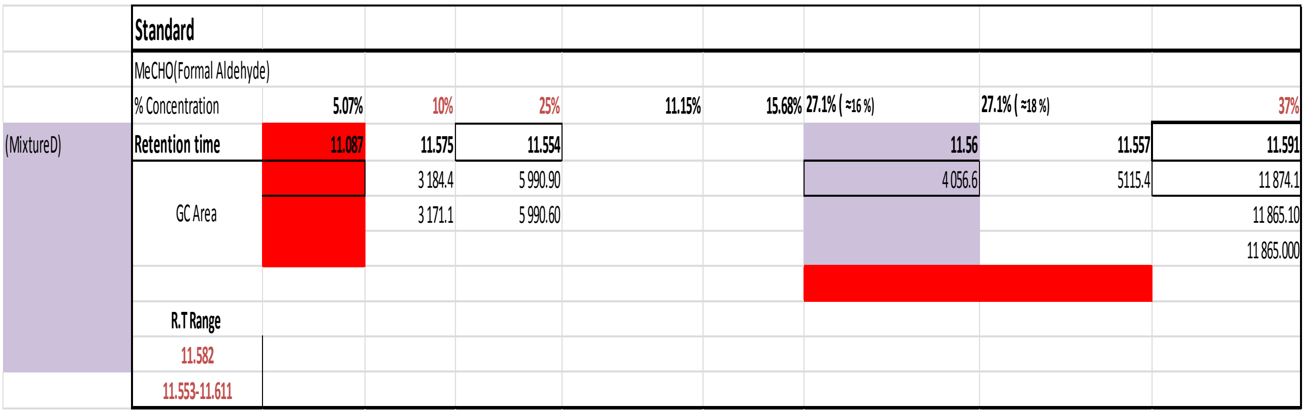
Table 7. 12: Retention time and GC area for Diethyl ether standard at various concentrations



Standard								
D.E (Diethyl ether)								
% Concentration	13.56%	25.13%	33.6%	49.9%			99%	
Retention time	13.753	13.778	13.807	13.84	≈ 50 % DE	≈ 50 - 55 % DE	13.92	13.929
GC Area	18727	33 689.60	52455.60	78897.1	13.853	13.849	151 442.10	
	18725	33 550	51 928.000	78 848.50	78 913.90	82 725.4	150 925.20	
	13725.000			78 848.000			151 134.10	
							151130.000	
R.T Range								
13.786								
13.752 - 13.820								

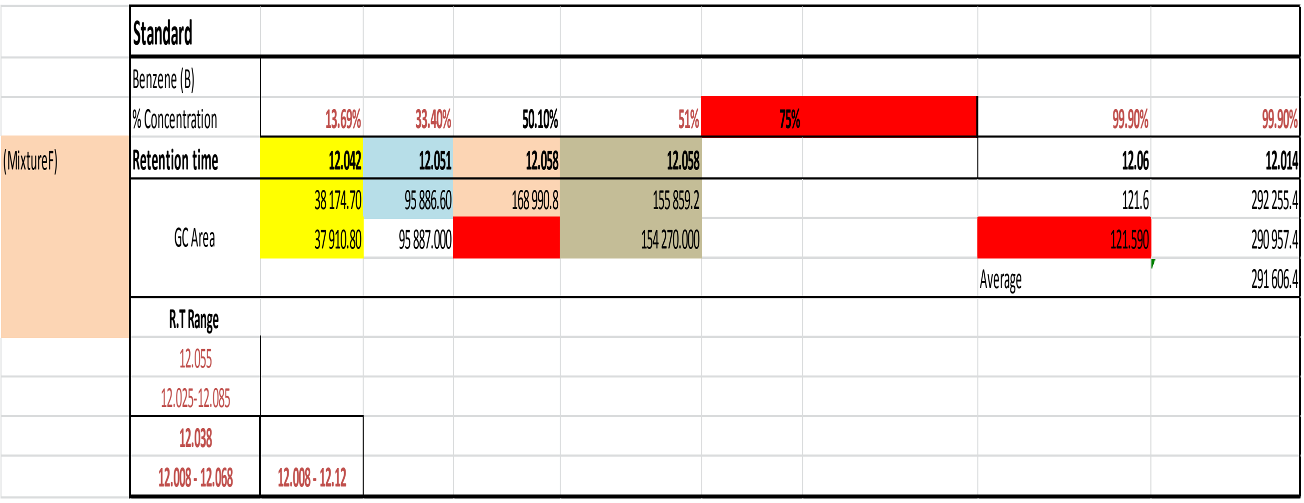
Cannot be detected within the time interval set **(13.752-13.820)**

Table 7.13: Retention time and GC area for Formal aldehyde standard at various concentrations



	Standard								
	MeCHO(Formal Aldehyde)								
	% Concentration	5.07%	10%	25%	11.15%	15.68%	27.1% (≈16 %)	27.1% (≈18 %)	37%
(MixtureD)	**Retention time**	11.087	11.575	11.554			11.56	11.557	11.591
	GC Area		3 184.4	5 990.90			4 056.6	5115.4	11 874.1
			3 171.1	5 990.60					11 865.10
									11 865.000
	R.T Range								
	11.582								
	11.553-11.611								

Table 7. 14: Retention time and GC area for Benzene standard at various concentrations



	Standard								
	Benzene (B)								
	% Concentration	13.69%	33.40%	50.10%	51%	75%		99.90%	99.90%
(MixtureF)	**Retention time**	12.042	12.051	12.058	12.058			12.06	12.014
	GC Area	38 174.70	95 886.60	168 990.8	155 859.2			121.6	292 255.4
		37 910.80	95 887.000		154 270.000			121.590	290 957.4
								Average	291 606.4
	R.T Range								
	12.055								
	12.025-12.085								
	12.038								
	12.008 - 12.068	12.008 - 12.12							

Table 7.15: Retention time and GC area for Toluene standard at various concentrations

Standard					
Toluene (T)					
% Concentration	*13.63%*	*33.3%*	*51%*	*99.5%*	
Retention time	12.907	12.922	12.947	12.931	
GC Area	28 568.70	97 639	166 322.7	279 107.3	
	28 291.60	*98 478.000*	166 320.0	278 072.4	
				278 070	
R.T Range					
12.925					
12.893-12.957			?		

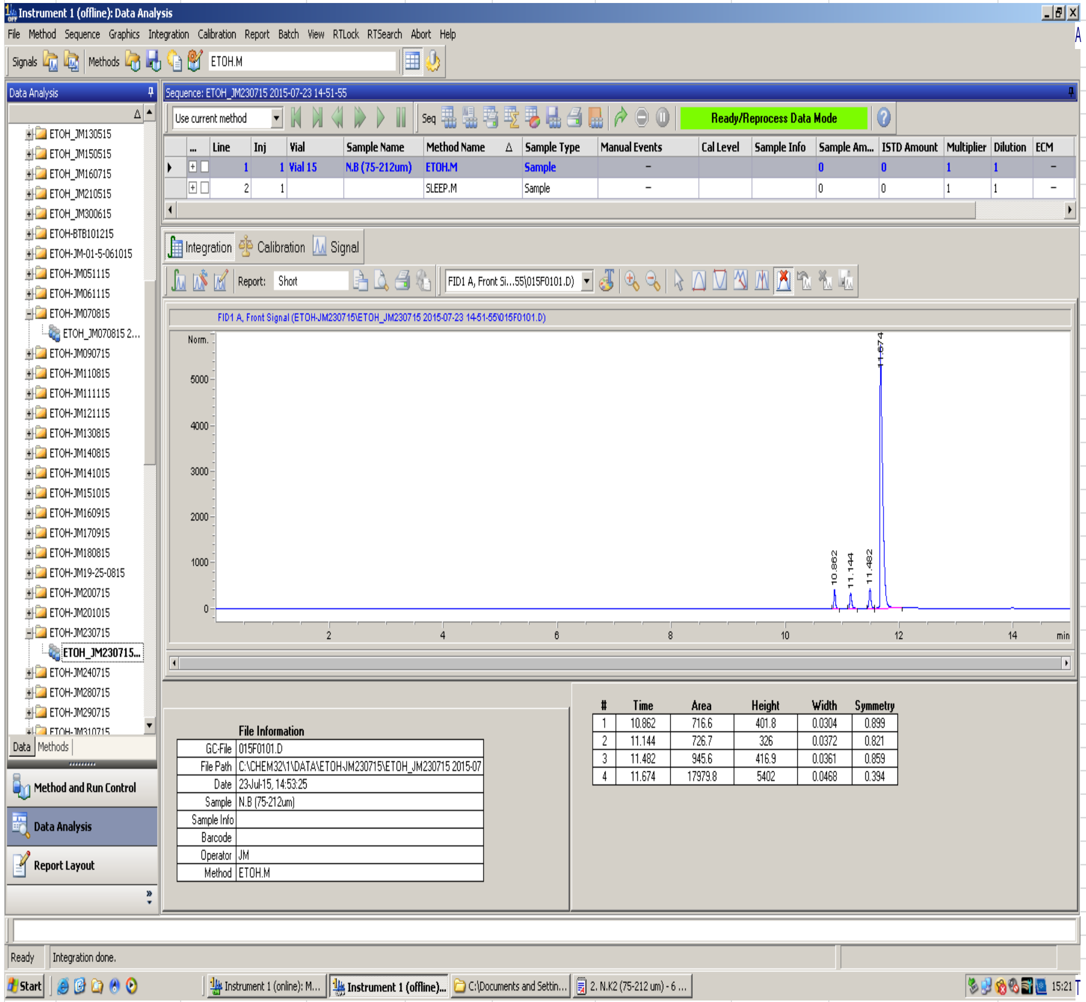
Table 7. 16: Retention time and GC area for Xylene standard at various concentrations

Standard								
Xylene(X)								
% Concentration	13.63%		33.3%		**49.9%**		72-75 %	**99.5%**
Retention time	14.17	14.171	14.222	14.226	14.276	14.281		14.353
GC Area	16 998		42 388.2		63 548.7			135 186
	16 540.10		41 879.4		62 457.9			134 769.3
							Average	134 977.7
R.T Range								
14.205								
14.169 - 14.241								

Table 7.17: Retention time and GC area for Hexane standard at various concentrations

Standard				
Hexane				
% Concentration	99.9%			
Retention time	10.805			
	138 656.1			
10.804	138 550.80			
10.777 - 10.831	138 550.000			

7.11.3 GC Chromatogram of liquid and gaseous product obtained by various clay-based catalysts (Figure 7.32 - 7.41)



...	Line	Inj	Vial	Sample Name	Method Name	Sample Type	Manual Events	Cal Level	Sample Info	Sample Am...	ISTD Amount	Multiplier	Dilution	ECM
+ ☐	1	1	Vial 15	N.B (75-212um)	ETOH.M	Sample	–			0	0	1	1	–
+ ☐	2	1			SLEEP.M	Sample	–			0	0	1	1	–

File Information

GC-File	015F0101.D
File Path	C:\CHEM32\1\DATA\ETOH-JM230715\ETOH_JM230715 2015-07
Date	23-Jul-15, 14:53:25
Sample	N.B (75-212um)
Sample Info	
Barcode	
Operator	JM
Method	ETOH.M

#	Time	Area	Height	Width	Symmetry
1	10.862	716.6	401.8	0.0304	0.899
2	11.144	726.7	326	0.0372	0.821
3	11.482	945.6	416.9	0.0361	0.859
4	11.674	17979.8	5402	0.0468	0.394

Ready
Integration done.

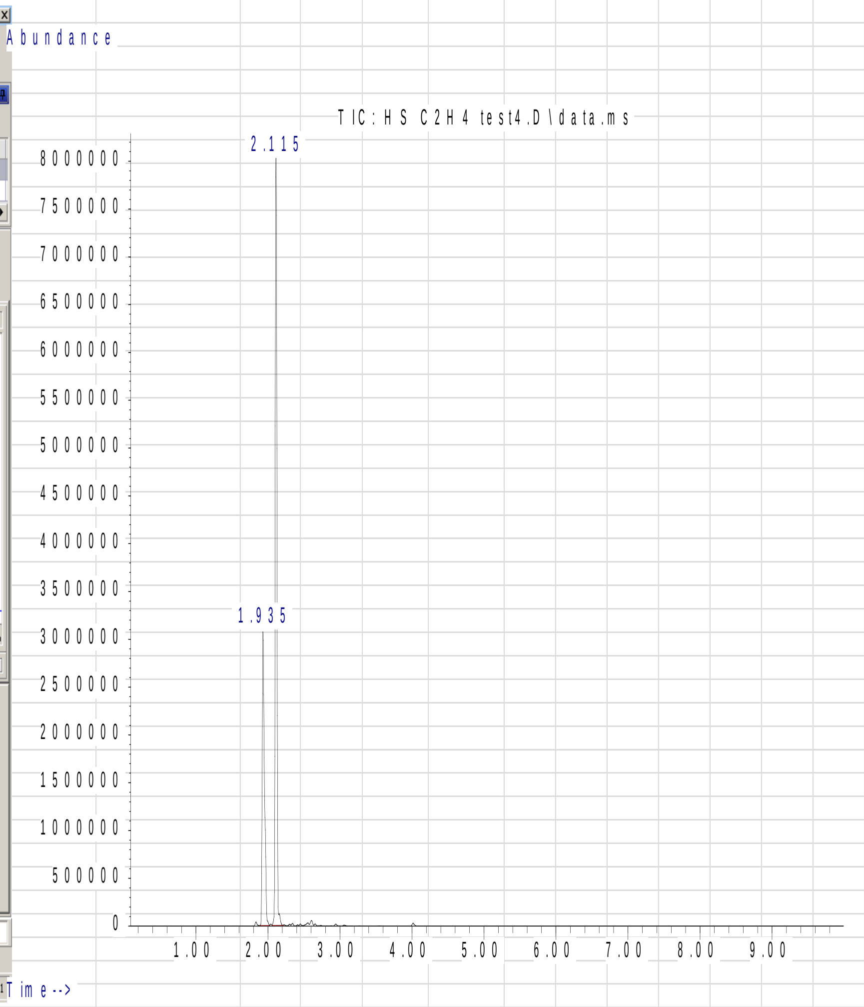
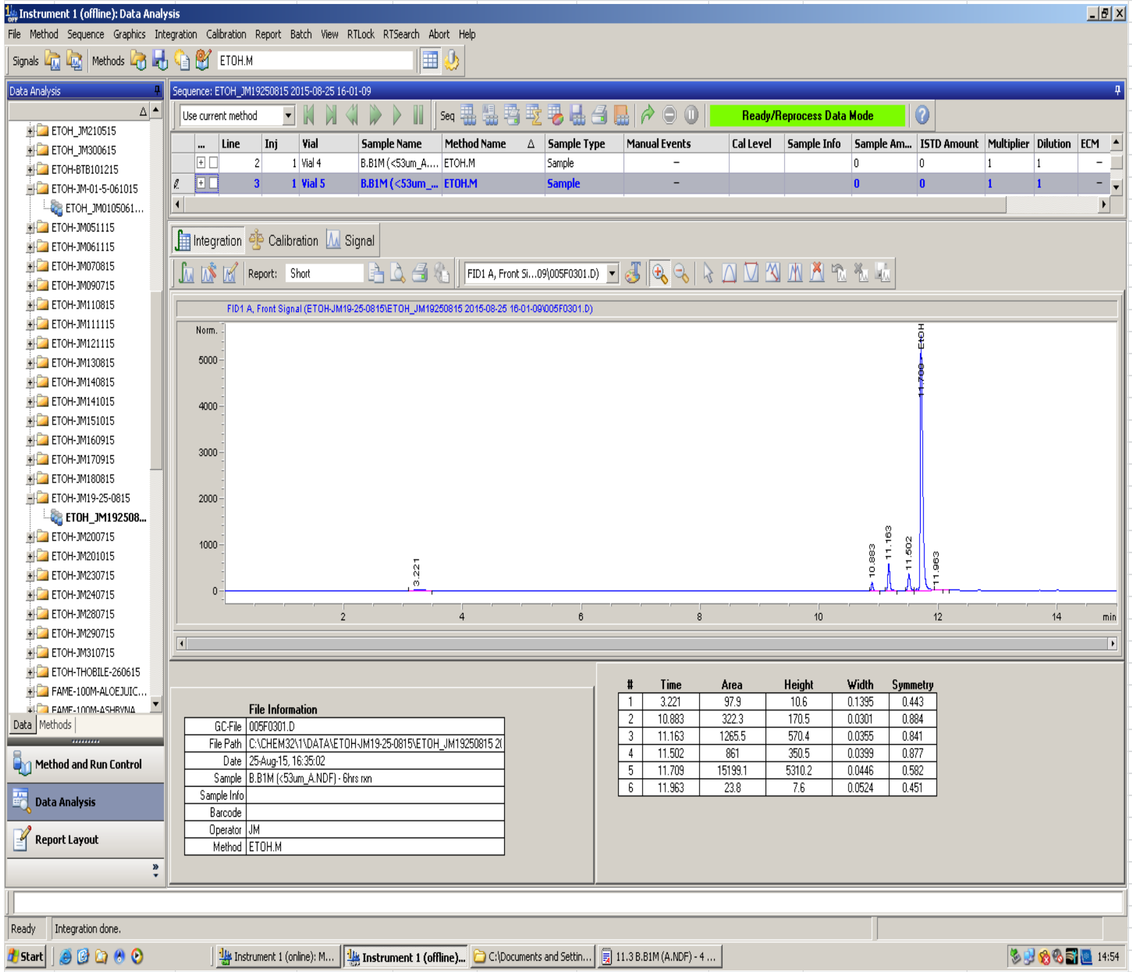


Figure 7. 32: GC Chromatogram of liquid product obtained by Natural Non-modified Bentonite catalyst (N.B)

Figure 7.33 (Right above): GC Chromatograms of gas product obtained by Non-modified Bentonite clay catalyst (N.B)

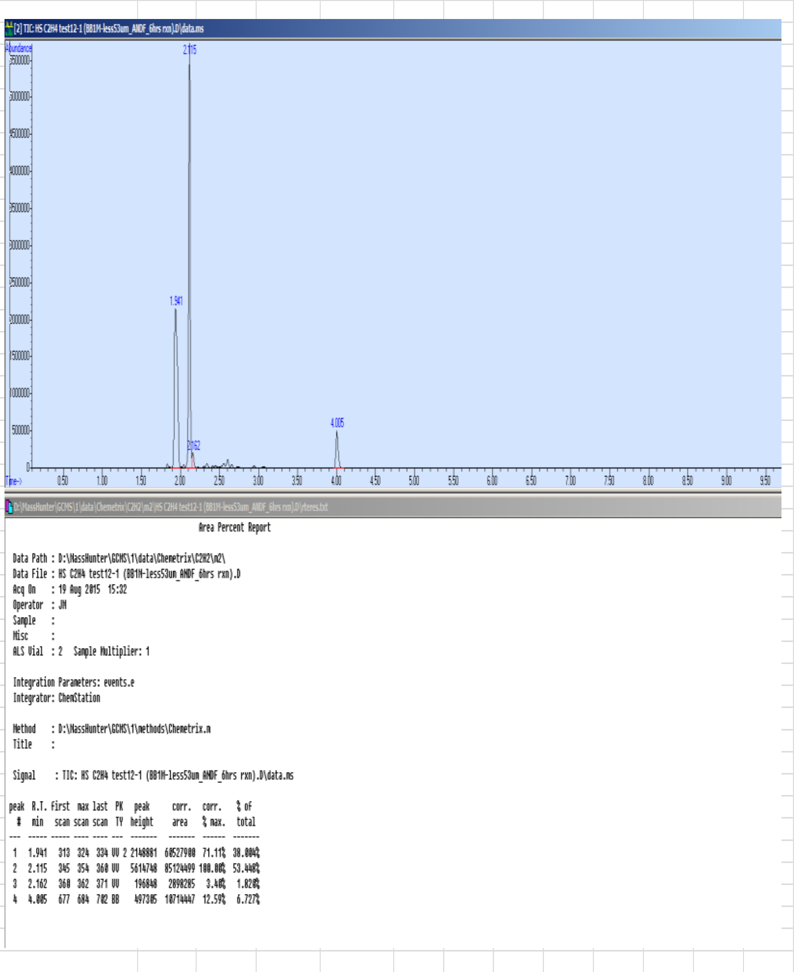


...	Line	Inj	Vial	Sample Name	Method Name	Sample Type	Manual Events	Cal Level	Sample Info	Sample Am...	ISTD Amount	Multiplier	Dilution	ECM
☐	2	1	Vial 4	B.B1M (<53um_A....	ETOH.M	Sample	–			0	0	1	1	–
☐	3	1	Vial 5	B.B1M (<53um_...	ETOH.M	Sample	–			0	0	1	1	–

File Information

GC-File	005F0301.D
File Path	C:\CHEM32\1\DATA\ETOH-JM19-25-0815\ETOH_JM19250815 2(
Date	25-Aug-15, 16:35:02
Sample	B.B1M (<53um_A.NDF) - 6hrs rxn
Sample Info	
Barcode	
Operator	JM
Method	ETOH.M

#	Time	Area	Height	Width	Symmetry
1	3.221	97.9	10.6	0.1395	0.443
2	10.883	322.3	170.5	0.0301	0.884
3	11.163	1265.5	570.4	0.0355	0.841
4	11.502	861	350.5	0.0399	0.877
5	11.709	15199.1	5310.2	0.0446	0.582
6	11.963	23.8	7.6	0.0524	0.451



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                              Area Percent Report

 Data Path : D:\MassHunter\GCMS\1\data\Chemetrix\C2H2\m2\
 Data File : HS C2H4 test12-1 (BB1M-less53um_ANDF_6hrs rxn).D
 Acq On    : 19 Aug 2015  15:32
 Operator  : JM
 Sample    :
 Misc      :
 ALS Vial  : 2   Sample Multiplier: 1

 Integration Parameters: events.e
 Integrator: ChemStation

 Method    : D:\MassHunter\GCMS\1\methods\Chemetrix.m
 Title     :

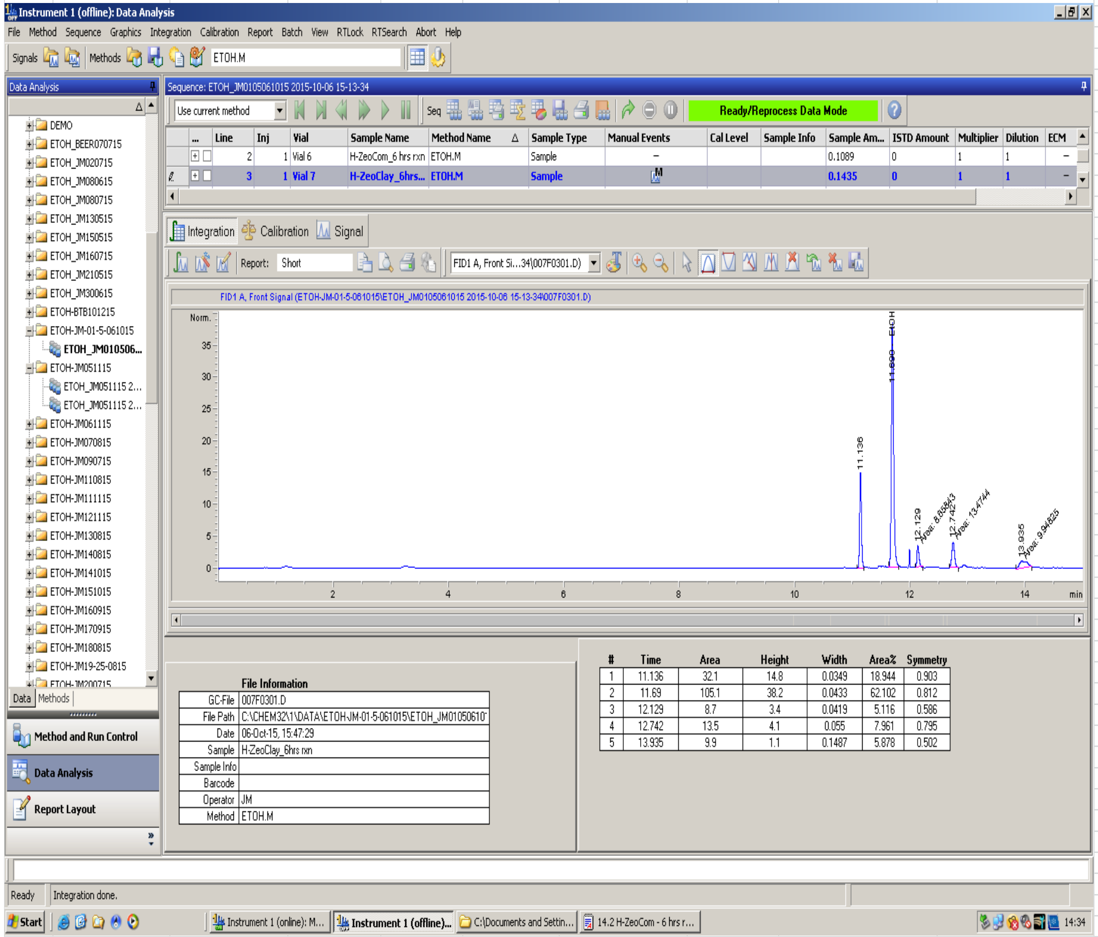
 Signal     : TIC: HS C2H4 test12-1 (BB1M-less53um_ANDF_6hrs rxn).D\data.ms

peak  R.T. first  max last  PK   peak      corr.   corr.    % of
  #   min   scan scan scan  TY  height     area   % max.   total
---  ----- ----- ---- ---- ---  -------   ------- ------  -------

 1   1.941   313  324  334 VV 2 2148881  60527980  71.11%  38.004%
 2   2.115   345  354  360 VV   5614748  85124499 100.00%  53.448%
 3   2.162   360  362  371 VV    196848   2898285   3.40%   1.820%
 4   4.005   677  684  702 BB    497305  10714447  12.59%   6.727%
```

Figure 7. 34 (Left): GC Chromatograms of liquid product obtained by acid-modified bentonite clay catalyst (B.B1M)

Figure 7.35 (Right above): GC Chromatograms of gas product obtained by acid-modified bentonite clay catalyst (B.B1M)

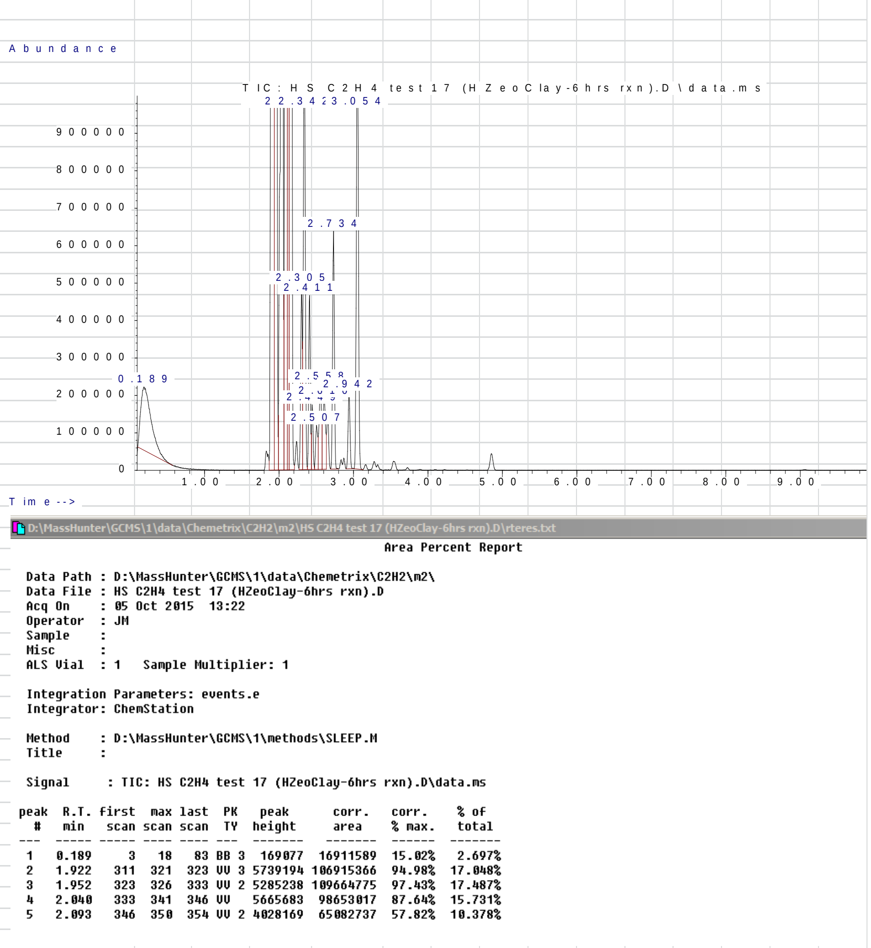


...	Line	Inj	Vial	Sample Name	Method Name	Sample Type	Manual Events	Cal Level	Sample Info	Sample Am...	ISTD Amount	Multiplier	Dilution	ECM
+ ☐	2	1	Vial 6	H-ZeoCom_6 hrs rxn	ETOH.M	Sample	–			0.1089	0	1	1	–
+ ☐	3	1	Vial 7	H-ZeoClay_6hrs...	ETOH.M	Sample	M			0.1435	0	1	1	–

File Information

GC-File	007F0301.D
File Path	C:\CHEM32\1\DATA\ETOH-JM-01-5-061015\ETOH_JM01050610
Date	06-Oct-15, 15:47:29
Sample	H-ZeoClay_6hrs rxn
Sample Info	
Barcode	
Operator	JM
Method	ETOH.M

#	Time	Area	Height	Width	Area%	Symmetry
1	11.136	32.1	14.8	0.0349	18.944	0.903
2	11.69	105.1	38.2	0.0433	62.102	0.812
3	12.129	8.7	3.4	0.0419	5.116	0.586
4	12.742	13.5	4.1	0.055	7.961	0.795
5	13.935	9.9	1.1	0.1487	5.878	0.502



```
                              Area Percent Report

  Data Path : D:\MassHunter\GCMS\1\data\Chemetrix\C2H2\m2\
  Data File : HS C2H4 test 17 (HZeoClay-6hrs rxn).D
  Acq On    : 05 Oct 2015  13:22
  Operator  : JM
  Sample    :
  Misc      :
  ALS Vial  : 1   Sample Multiplier: 1

  Integration Parameters: events.e
  Integrator: ChemStation

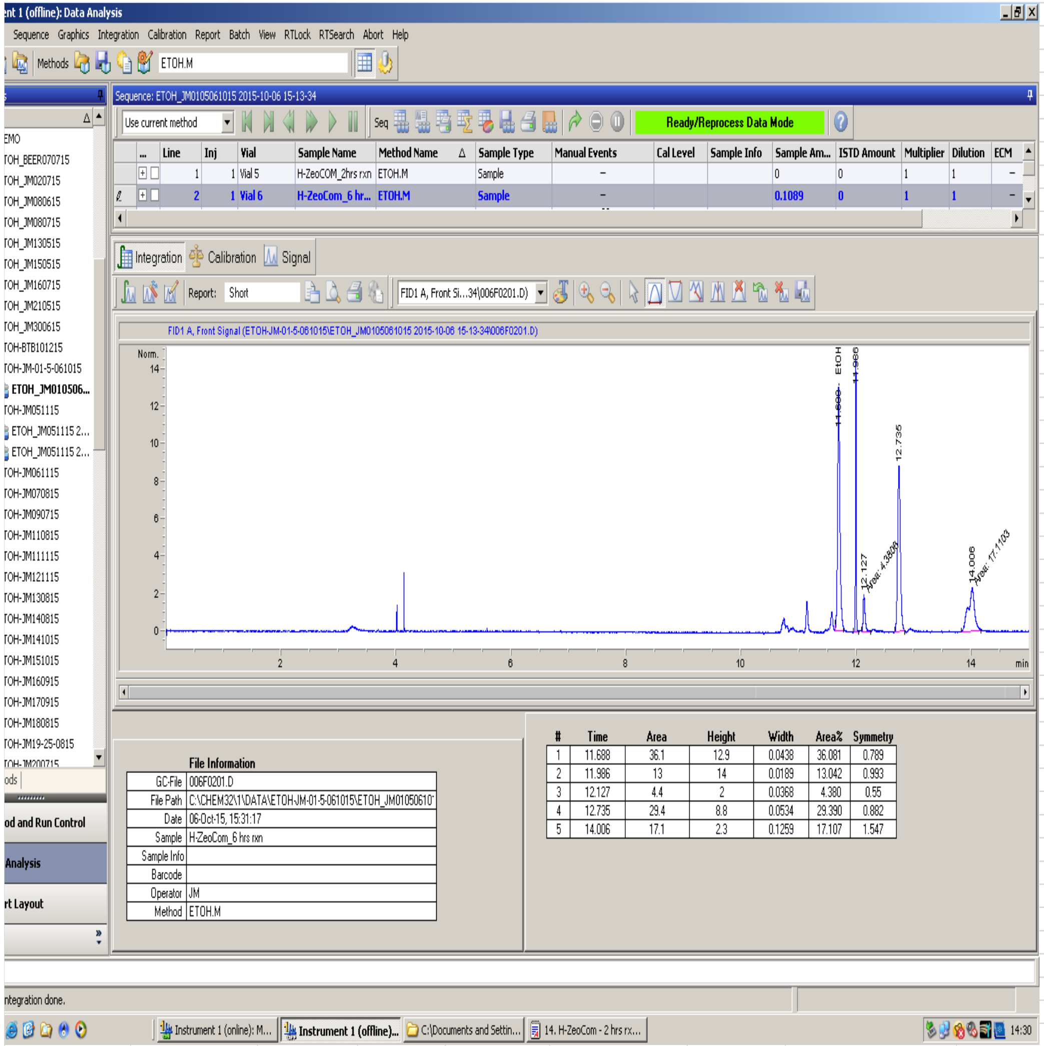
  Method    : D:\MassHunter\GCMS\1\methods\SLEEP.M
  Title     :

  Signal     : TIC: HS C2H4 test 17 (HZeoClay-6hrs rxn).D\data.ms

 peak  R.T. first  max last  PK   peak      corr.    corr.    % of
  #    min   scan scan scan  TY  height     area    % max.   total
 ---  ----- ----- ---- ---- --- -------   -------  ------  -------
  1   0.189     3   18   83 BB 3  169077  16911589  15.02%   2.697%
  2   1.922   311  321  323 VV 3 5739194 106915366  94.98%  17.048%
  3   1.952   323  326  333 VV 2 5285238 109664775  97.43%  17.487%
  4   2.040   333  341  346 VV   5665683  98653017  87.64%  15.731%
  5   2.093   346  350  354 VV 2 4028169  65082737  57.82%  10.378%
```

Figure 7. 36: GC Chromatogram of liquid product obtained by the produced clay-based zeolite catalyst (H-ZeoClay).

Figure 7. 37 (Right above): GC Chromatogram of gas product obtained by the produced clay-based zeolite catalyst (H-ZeoClay)

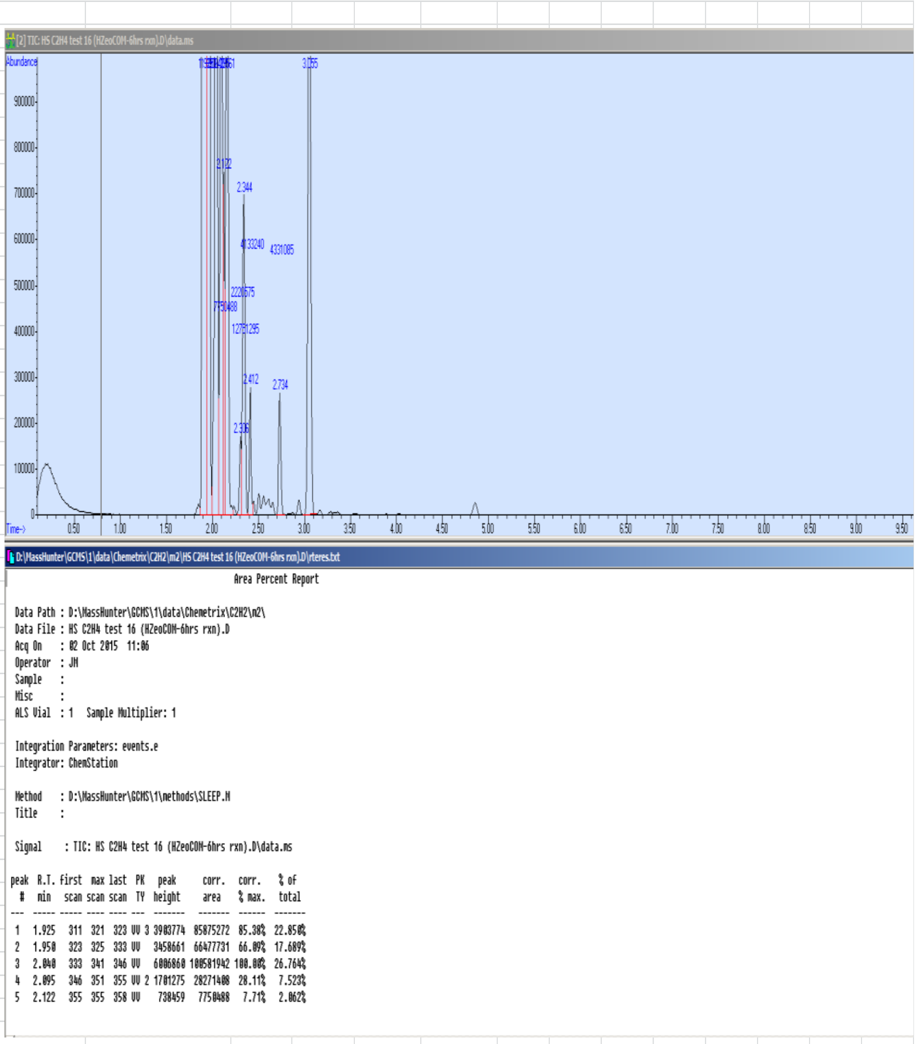


	...	Line	Inj	Vial	Sample Name	Method Name	Sample Type	Manual Events	Cal Level	Sample Info	Sample Am...	ISTD Amount	Multiplier	Dilution	ECM
	⊞ ☐	1	1	Vial 5	H-ZeoCOM_2hrs rxn	ETOH.M	Sample	–			0	0	1	1	–
	⊞ ☐	2	1	Vial 6	H-ZeoCom_6 hr...	ETOH.M	Sample	–			0.1089	0	1	1	–

File Information

GC-File	006F0201.D
File Path	C:\CHEM32\1\DATA\ETOH-JM-01-5-061015\ETOH_JM01050610
Date	06-Oct-15, 15:31:17
Sample	H-ZeoCom_6 hrs rxn
Sample Info	
Barcode	
Operator	JM
Method	ETOH.M

#	Time	Area	Height	Width	Area%	Symmetry
1	11.688	36.1	12.9	0.0438	36.081	0.789
2	11.986	13	14	0.0189	13.042	0.993
3	12.127	4.4	2	0.0368	4.380	0.55
4	12.735	29.4	8.8	0.0534	29.390	0.882
5	14.006	17.1	2.3	0.1259	17.107	1.547



```
                              Area Percent Report

 Data Path : D:\MassHunter\GCMS\1\data\Chemetrix\C2H2\m2\
 Data File : HS C2H4 test 16 (HZeoCOM-6hrs rxn).D
 Acq On    : 02 Oct 2015  11:06
 Operator  : JM
 Sample    :
 Misc      :
 ALS Vial  : 1   Sample Multiplier: 1

 Integration Parameters: events.e
 Integrator: ChemStation

 Method    : D:\MassHunter\GCMS\1\methods\SLEEP.M
 Title     :

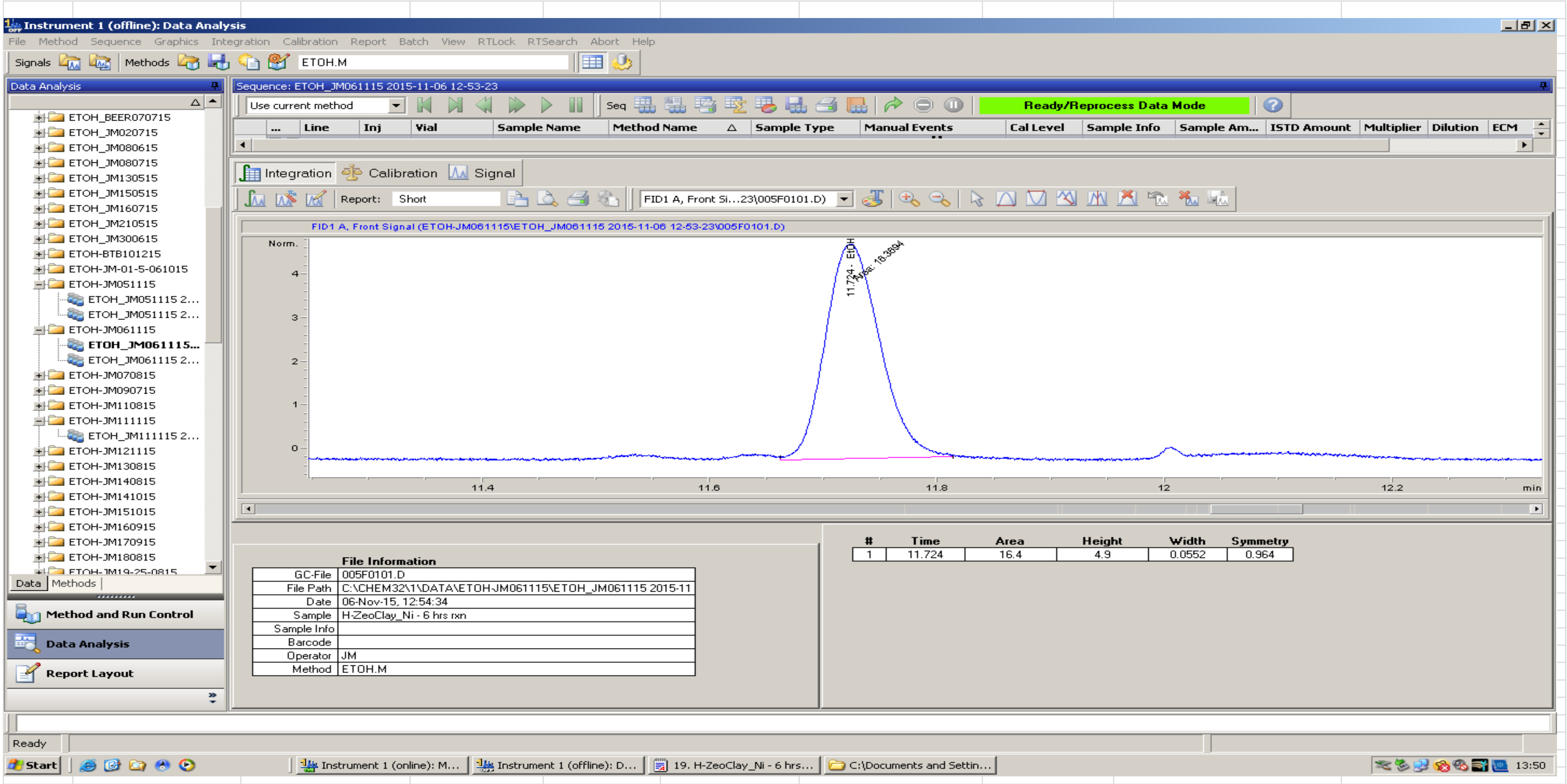
 Signal     : TIC: HS C2H4 test 16 (HZeoCOM-6hrs rxn).D\data.ms

peak  R.T. first  max last  PK   peak      corr.   corr.    % of
 #    min   scan scan scan  TY  height     area   % max.   total
---  ----- ----- ---- ---- ---  -------   ------- ------  -------

 1   1.925   311  321  323 VV 3 3903774  85875272  85.38%  22.850%
 2   1.950   323  325  333 VV    3458661  66477731  66.09%  17.689%
 3   2.040   333  341  346 VV    6006860 100581942 100.00%  26.764%
 4   2.095   346  351  355 VV 2 1701275  28271408  28.11%   7.523%
 5   2.122   355  355  358 VV     738459   7750488   7.71%   2.062%
```

Figure 7. 38: GC Chromatogram of liquid product obtained by the commercial zeolite catalyst (H-ZeoCOM)

Figure 7. 39 (Right above): GC Chromatogram of gas product obtained by the commercial zeolite catalyst (H-ZeoCOM).



#	Time	Area	Height	Width	Symmetry
1	11.724	16.4	4.9	0.0552	0.964

File Information

GC-File	005F0101.D
File Path	C:\CHEM32\1\DATA\ETOH-JM061115\ETOH_JM061115 2015-11
Date	06-Nov-15, 12:54:34
Sample	H-ZeoClay_Ni - 6 hrs rxn
Sample Info	
Barcode	
Operator	JM
Method	ETOH.M

Figure 7. 40: GC Chromatogram of liquid product obtained by the Nickel (Ni)-impregnated clay-based catalyst (H-Zeoclay+Ni).

Figure 7. 41: GC Chromatogram of liquid product obtained by the Nickel (Ni)-impregnated clay-based catalyst (H-Zeoclay+Ni)

Appendix 4

7.12 The resultant activity of clay-based catalysts on bioethanol conversion

Reference
(pg. 104 - 111)

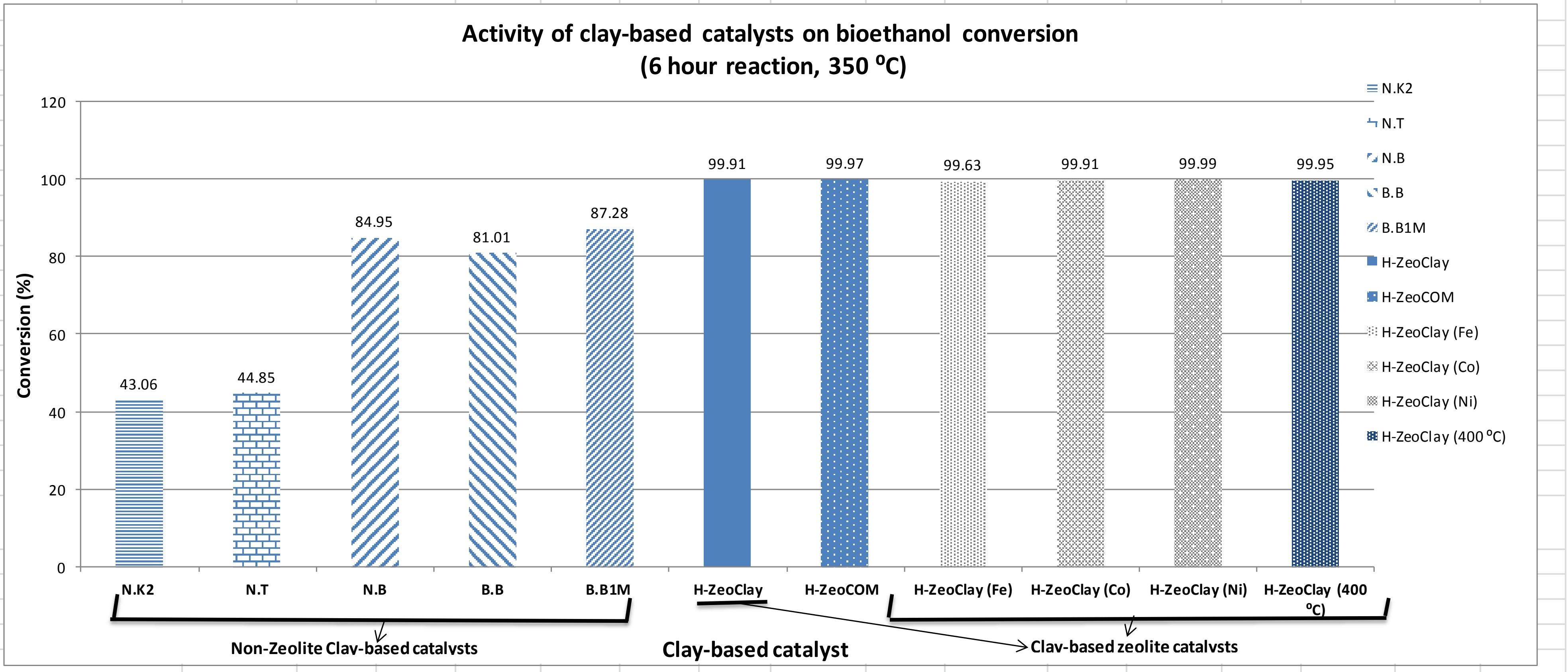


Figure 7.42: Activity of clay-based catalysts on bioethanol conversion

7.12.1 Effect of reaction time for gaseous olefins and paraffin selectivity by non-zeolite clay-based catalysts (Table 7.18)

Reference
Figure 4.32 (pg. 116)

Table 7.18: Effect of reaction time for gaseous olefins and parrafins selectivity by non-zeolite clay-based catalysts

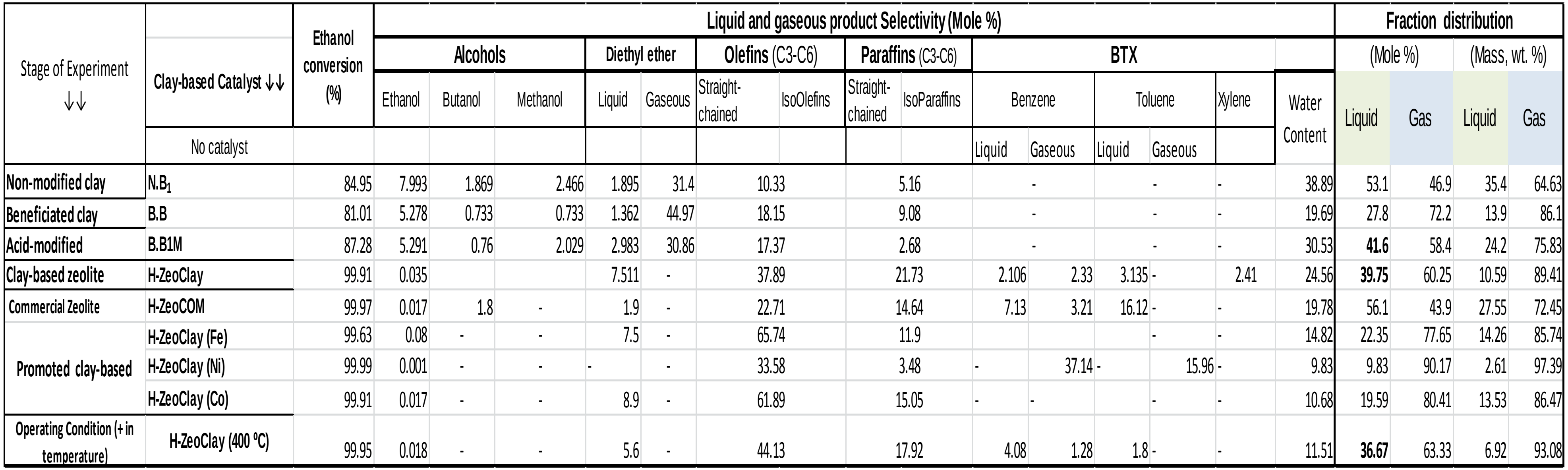
	Gaseous hydrocarbons selectivity (%)					
Clay-based Catalyst	**Paraffins ($C_3 – C_6$)**	**Olefins ($C_3 – C_6$)**	**Diethyl ether**	**Others**		
N.B (2hrs)	**15.82**	**33.19**	50.99	-		
N.B (6hrs)	11.01	22.03	**66.96**	-		
				1-Propanamine,N1-methyl-2-methoxy		
B.B (2hrs)	**19.11**	**27.27**	51.61	2.997		
B.B (6hrs)	12.57	25.144	62.28			
B.B1M (2hrs)	1.36	**51.54**	47.09			
B.B1M (6hrs)	0	25.64	52.84	12.82		
B.B1M (4hrs)	**5.57**	38.56	51.41	1.07		

7.13 Product distribution and selectivity of hydrocarbons by clay-based catalysts (In mole and mass %)

Referenced

pg. 126-127

Table 4.7: Product Selectivity and distribution of hydrocarbons from bioethanol conversion by clay-based catalysts



Stage of Experiment ↓↓	Clay-based Catalyst ↓↓	Ethanol conversion (%)	Liquid and gaseous product Selectivity (Mole %)															Fraction distribution			
			Alcohols			**Diethyl ether**		**Olefins** (C3-C6)		**Paraffins** (C3-C6)		**BTX**						(Mole %)		(Mass, wt. %)	
			Ethanol	Butanol	Methanol	Liquid	Gaseous	Straight-chained	IsoOlefins	Straight-chained	IsoParaffins	Benzene		Toluene		Xylene	Water Content	Liquid	Gas	Liquid	Gas
	No catalyst											Liquid	Gaseous	Liquid	Gaseous						
Non-modified clay	**N.B$_1$**	84.95	7.993	1.869	2.466	1.895	31.4	10.33		5.16		-		-		-	38.89	53.1	46.9	35.4	64.63
Beneficiated clay	**B.B**	81.01	5.278	0.733	0.733	1.362	44.97	18.15		9.08		-		-		-	19.69	27.8	72.2	13.9	86.1
Acid-modified	**B.B1M**	87.28	5.291	0.76	2.029	2.983	30.86	17.37		2.68		-		-		-	30.53	**41.6**	58.4	24.2	75.83
Clay-based zeolite	**H-ZeoClay**	99.91	0.035			7.511	-	37.89		21.73		2.106	2.33	3.135	-	2.41	24.56	**39.75**	60.25	10.59	89.41
Commercial Zeolite	**H-ZeoCOM**	99.97	0.017	1.8	-	1.9	-	22.71		14.64		7.13	3.21	16.12	-	-	19.78	56.1	43.9	27.55	72.45
Promoted clay-based	**H-ZeoClay (Fe)**	99.63	0.08	-	-	7.5	-	65.74		11.9				-		-	14.82	22.35	77.65	14.26	85.74
	H-ZeoClay (Ni)	99.99	0.001	-	-	-	-	33.58		3.48		-	37.14	-	15.96	-	9.83	9.83	90.17	2.61	97.39
	H-ZeoClay (Co)	99.91	0.017	-	-	8.9	-	61.89		15.05		-	-	-		-	10.68	19.59	80.41	13.53	86.47
Operating Condition (+ in temperature)	**H-ZeoClay (400 °C)**	99.95	0.018	-	-	5.6	-	44.13		17.92		4.08	1.28	1.8	-	-	11.51	**36.67**	63.33	6.92	93.08

Reference
pg. 114-115

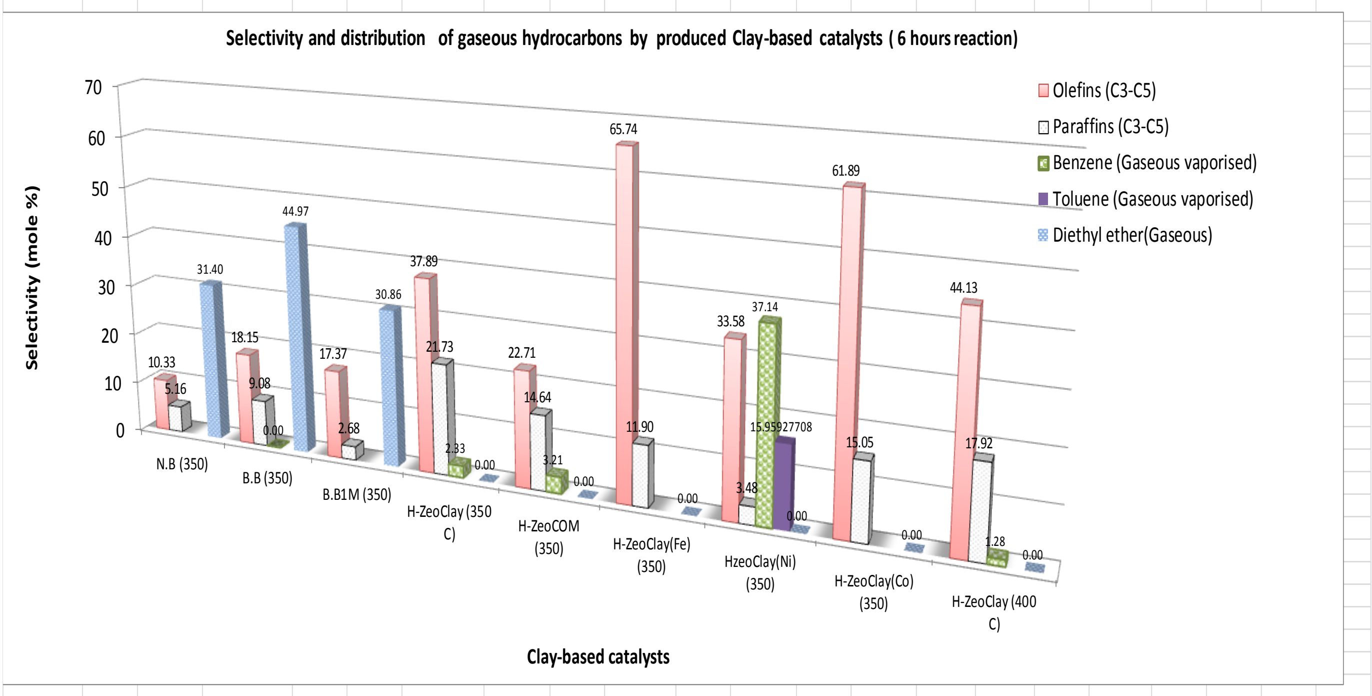


Figure 4.30 (a): Gaseous hydrocarbons selectivity by produced clay-based catalysts (mol. % Selectivity)

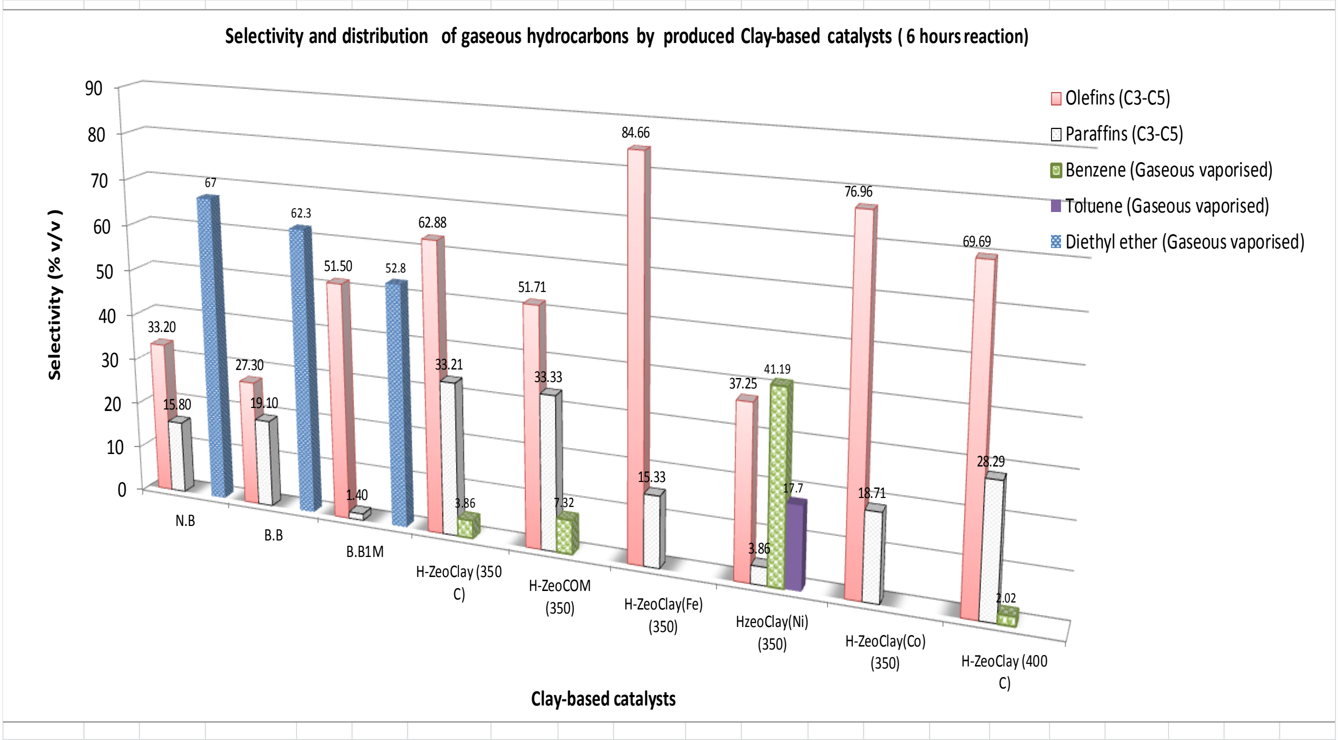


Figure 4.30 (Pg.110): Gaseous hydrocarbons selectivity by produced clay-based catalysts (v/v % selectivity)