

**n-HEPTANE HYDROISOMERIZATION OVER
BIFUNCTIONAL ZEOLITE CATALYSTS**

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ABSTRACT

Isomerization is an industrially important process which involves converting less desirable n-alkanes into more desirable iso-alkanes. Increased iso-alkanes are preferred in gasoline to increase the octane number and to help meet the demand for more efficient automotive engines. Bifunctional catalysts containing noble metals such as Pt on USY zeolites has been widely used in the petroleum refining for the isomerization process.

This research was carried out to study the n-heptane hydroisomerization over bifunctional monometallic (Ni or Pt) and bimetallic (Pt-Ni) catalysts supported on a commercial CBV-712 zeolite. Catalysts were prepared by ion exchange and competitive ion exchange in order to determine any positive catalytic effect of Pt and Ni over 1% Pt-USY. Five metal-loaded CBV-712 USY zeolite catalysts, with varying levels of both metals (Pt and Ni), were first characterized with ICP-OES, XRD, SEM and TEM. After in-situ activation, all catalysts were tested for the hydroisomerization of n-heptane co-fed with hydrogen. The liquid and gas products were analyzed using GC-FID and GC-MS, and the coke content on the catalyst was determined using TGA.

For short times-on-stream, the Pt-Ni catalysts were more active than the Pt catalysts as described in the literature. However, the bi-metallic catalysts deactivated to different degrees dependent on the method of ion exchange used.

In addition, the results tended to indicate that after longer periods-on-stream, the bimetallic tended to behave similar to the 1 wt% Pt only. However, the 1 wt% Pt 2 wt% Ni remained more active and appeared stable even up to 6000 minutes-on-stream. This is the first time these results are reported in the literature.

Another finding in this dissertation indicates the control of pH throughout the ion exchange procedure is essential as the resultant metal cluster size impacts on the catalytic performance and stability.

DECLARATION

No portion of the work referred to in the dissertation has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning

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LIST OF ABBREVIATIONS

ARC	Atlantic Refining Company
CB	Chemically Bonded
EFAL	Extra Framework Aluminum
ESEM	Environmental Scanning Electron Microscopy
EDAX	Energy Dispersive X-ray
FAU	Faujasite
FCC	Fluid Catalytic Cracking
FE	Field Emission
FBR	Fixed Bed Reactor
FID	Flame Ionization Detector
GC	Gas Chromatography or Gas Chromatograph
HPLC	High Performance Liquid Chromatography
HPC	Houdry Process Corporation
HC	Hydrocarbon
ICP	Inductively Coupled Plasma
IZA	International Zeolite Association
MS	Mass Spectrometer
MSD	Mass Selective Detector
MFC	Mass Flow Controller
OES	Optical Emission Spectroscopy
PONA	Paraffins, Olefins, Naphthenes, Aromatics
PBUs	Primary Building Units
RON	Research Octane Number
RF	Response Factor
SBUs	Secondary Building Units
SA	Sodium Aluminate
SD	Standard Deviation

SGE	Scientific Glass Engineering
TGA	Thermogravimetric Analysis
TEM	Transmission Electron Microscopy
USY	Ultra Stable Zeolite Y
WHSV	Weighted Hourly Space Velocity
XRD	X-ray Diffraction
ZSM	Zeolite Socony Mobile

CHAPTER ONE

INTRODUCTION

1.1. Introduction

The petroleum refining industry treats the distillates after crude oil distillation to produce a variety of valuable refined products. These include liquefied petroleum gas, gasoline, kerosene, diesel fuel and feedstock for downstream processes and other industries.

The increasing demand for more efficient automotive motors and strict environmental legislation has called for more regulation on not only toxic additives such as lead but decreasing the emission of toxic compounds such as sulfur-containing aromatics components. This therefore requires development of new catalysts and petroleum refining processes to produce high quality fuels such as gasoline with improved octane number. Since hydroisomerization of normal alkanes/ paraffin over platinum supported on acid catalysts is a well-known effective process to improve the octane number, it is therefore the subject of this dissertation [1].

Catalysts are usually used in petroleum industries to ensure that refining processes occur at reduced operating conditions and to obtain the desired products. Therefore, choice of the catalyst is an important step [2].

Zeolites based catalysts have been widely used in petroleum refining industry such as hydrocracking, and isomerization because of their unique porous properties. For example, ultra-stable zeolite Y is the key catalytic element in the FCC process since their introduction 40 years ago [3] for the enhancements in octane number of gasoline and in the production of cleaner fuels with high performance properties [4].

Zeolites are microporous crystalline aluminosilicates with a three dimensional structure. The structure is created by linking Al and Si atoms with oxygen atoms. For every Al atom in the framework there is a negative charge which has to be compensated a cation. In as-synthesized zeolites, this is often balanced by sodium and subsequently ammonium ions. By exchanging these ions with other ions such as metals, the property of the zeolite can be altered [5, 6].

Acid zeolite catalyst crack hydrocarbons and isomerization occurs. For selective hydrocarbon transformations including hydroisomerization, a metal function for hydrogenation/dehydrogenation purposes is required. Bifunctional catalysts containing noble metals like Pt and Pd on acidic supports like zeolites to boost the octane number of gasoline. A variety of metals like Cu, Ni, Pd, Sn and Zn have already been used as promoter with Pt/zeolite catalysts for the isomerization of n-alkanes [7, 8].

All catalysts go through a mechanical, physical and/ or chemical change, Therefore, loss in activity, often selectivity and other catalytic properties, might occur which is known as catalyst deactivation. Catalyst deactivation has economic impact in the practice of industrial chemical processes. Deactivation occurs from poisoning such as coke deposition on the active site which causes pore blockage which can prevent the access of reactants to active sites [2].

1.2. Objective

The objectives of this work are as follows:

- Synthesis and characterization of zeolite Y catalyst followed by comparison with a commercial zeolite Y.
- NH_4 ion exchange of the synthesized zeolite Y followed by comparison with a commercial CBV-712 USY.
- Investigation of the behavior of mono- and bi- metallic zeolite catalysts for hydroisomerization applications for the purpose of enhancing the RON of gasoline.

- Study of the deactivation mechanism of the zeolite catalysts using the relevant characterization analytical techniques.
- Hydroisomerization of n-C₇ over catalysts prepared during this dissertation namely Pt USY and Pt/Ni USY.

CHAPTER TWO

LITERATURE REVIEW

2.1. Introduction to Zeolites

Zeolites are microporous crystalline aluminosilicates minerals containing exchangeable group IA and group IIA cations such as sodium, potassium, magnesium, and calcium, which are broadly present in nature and were identified over 250 years ago [5]. They were discovered by the Swedish mineralogist Axel Fredrick Crönstedt in 1756, who observed that a natural occurring mineral, nowadays known as stilbite, lost large amounts of steam upon heating and he named the material ‘zeolite’, which comes from the Greek words zeo, which means ‘to boil’ and lithos, which means ‘stone’ [9]. Zeolites have the following general chemical formula: $M_{2/n}O \cdot Al_2O_3 \cdot ySiO_2 \cdot wH_2O$, where y ranges from 2 to 10, n is the cation valence number, and w represents the number of water molecules contained within the voids of zeolites. Whilst many types of zeolites occur naturally as minerals, but others can be synthesized and are made commercially for specific uses [10].

Zeolites are unique when compared to other crystalline inorganic oxide-materials due to their distinct properties, which include: -

- Zeolites are microporous materials with uniform pore dimensions that vary between 3-15 Å [11].
- They have ion exchange properties and possess high thermal stability [12].
- Zeolites act as sieves on a molecular scale as they adsorb only molecules that fit inside their pores, preventing molecules that are too large from entering [3].

2.1.1. Zeolite structure

The structures of zeolites were first determined in 1930 by Taylor and Pauling [6], with each structure consisting of silicon (Si^{4+}) and aluminum (Al^{3+}) cations that surrounded by four oxygen anions (O^{2-}) representing the primary-building units. Each oxygen atom connects two cations and contains water and/or other molecules within pores. This results in a three-dimensional macromolecular framework, with a net neutral SiO_2 and negatively charged AlO_2^- tetrahedra. The negative charges results from the valence differences between the silicon and aluminum cations, and are positioned on one of the oxygen anions connected to the aluminum cation. The negative charge is normally balanced by extra non-framework cations such as sodium (Na^+), which is present during the synthesis of the zeolite. However, for catalyst applications, Na^+ is replaced with NH_4^+ which during the heating process, generating protons (H^+) that form a bond with the negatively charged oxygen anions of the zeolite [13, 14, 15].

The framework structure contains channels, and cages with dimensions ranging from 0.2 to 1 nm, and interconnected voids occupied by cations and water molecules. The cations are mobile and exchangeable [16, 17], with the primary building units (PBUs) linked together to form secondary building units (SBUs), as shown in Figure 2-1. These secondary building units can be linked to form cages or channels within the structure, linking of the cages and channels to create a wide range of zeolites with different structures [13].

The International Zeolite Association (IZA) database indicates that the number of structural types of special microporous frameworks increased rapidly from 27 in 1970 to around 174 by 2007 [18] with many more being identified each year. Each framework type is allocated a three letter code, with the codes are derived from the name of the materials type, e.g. FAU for the mineral Faujasite, X and Y or from the company linked to its preparation as in the case for ZSM-5 (Zeolite Socony Mobile) [6].

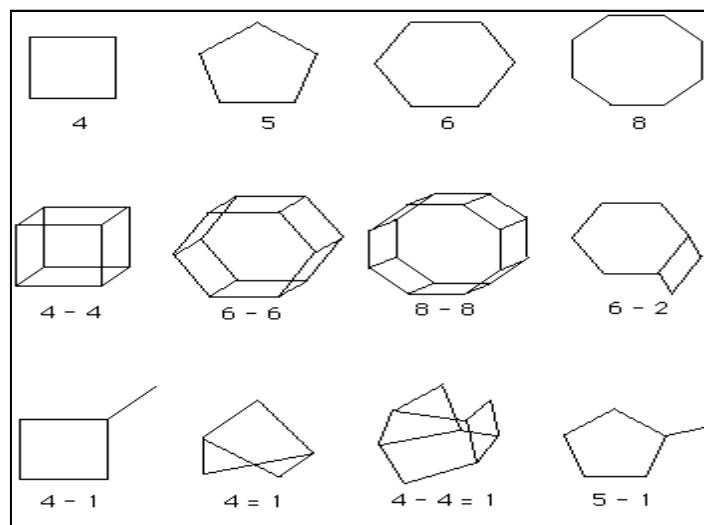


Figure 2-1: The secondary-building units (SBUs) found in a zeolite structure [19].

A description of a zeolite structure begins with the framework type in terms of the size of the pore openings and dimensions of the channel system, as shown in Figure 2-2. Pore openings are characterized by the size of the ring that defines the pore, with an 8-ring having a diameter of 4.1 Å considered as a small pore opening; a 10-ring having a diameter of 5.5 Å and termed a medium pore size. Finally, a 12- ring with a diameter of 7.4 Å is a large pore size [20].

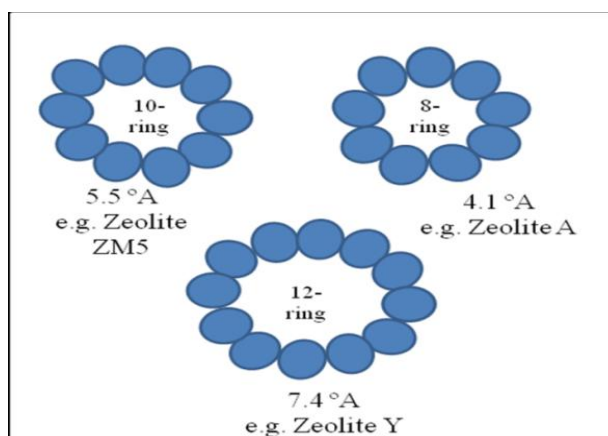


Figure 2-2: Classification of zeolite based on the pore size (redrawn) [3].

2.1.2. Zeolite framework type

As stated previously, many types of zeolite framework catalysts are available such as FAU and MFI (Figure 2-3). However, this review will focus on the zeolite FAU (zeolite Y).

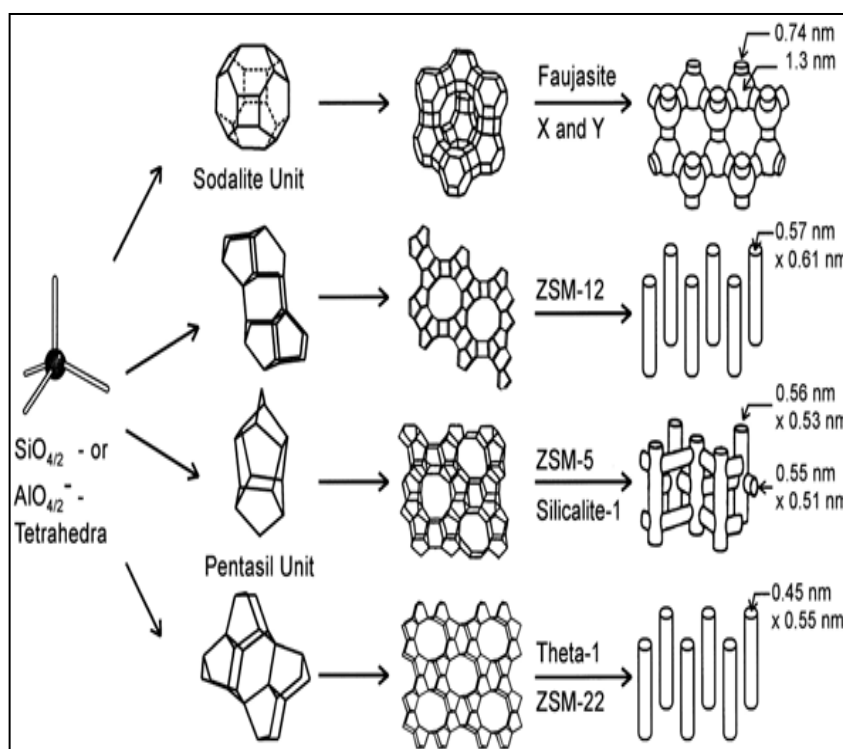


Figure 2-3: Structure of four selected zeolites (Faujasite, ZSM-12, ZSM-5, Theta-1) and their micropore systems and dimensions [16].

2.1.3. Zeolite Y- Faujasite (FAU)

The FAU framework type is also characterized by sodalite cages with cubic symmetry [6, 21]. It has three dimensions with large cavities in the structure that are interconnected by 12 membered ring channels which represent the 12 cations (Si^{4+} and Al^{3+}) and 12 anions (O^{2-}) in the ring. The size of the pore is around 0.7 nm [6]. Both the X and Y zeolites have the FAU framework structure and the same building units, however, they have different Si/Al ratio.

2.1.3.1. Zeolite Y

Zeolite Y shown in Figure 2-4 is a high silica Faujasite zeolite with a typical $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 1.5 - 3 [6]. It has a pore diameter of 7.4 Å and its crystal size is within the range of 0.2 - 0.5 µm. Zeolite Y is used as a catalyst in petroleum refineries because it has:

- High thermal stability (up to 1066 K)
- High concentration of active acid sites
- Three-dimensional structure
- Large void volume of ~ 50%
- High selectivity [6, 21].

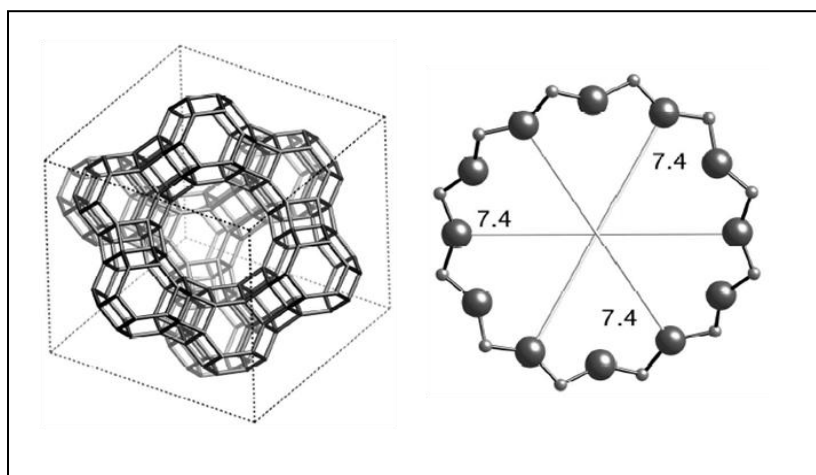


Figure 2-4: Pore diameter in Å and a three-dimensional view of zeolite Y framework [22].

2.1.4. Zeolite properties

In addition to the properties stated above, cation exchange, acidity, and shape selectivity are the most important properties of a zeolite.

2.1.4.1. Cation exchange

As stated previously, the presence of aluminum in the framework gives the zeolites a net negative charge equal to the number of aluminum atoms present, with the negative charge balanced by the presence of the extra-framework cations such as Na, Ca and K. Since the cations are mobile, ion exchange is used to replace these with other cationic species, enabling changes in the catalytic properties of the structure. For catalytic applications, it is essential to decrease the content of alkali metal to less than 1 percent by weight by ion exchange with ammonium salt solution [6, 11, 16]. By preparing the ammonium form of the zeolite and then calcining it between 573 -773 K it is possible to produce the proton form of Y(H-Y(FAU)) and release NH_3 , with this method becoming the method of choice when preparing an acid Y catalyst [11, 21].

2.1.4.2. Acidity

Among the most important properties of zeolites with respect to their use as catalysts is their surface acidity. In order to describe the acidity of zeolites, it is necessary to clearly identify the nature of acid sites, specifically the Brønsted and Lewis acidity. Brønsted acidity refers to proton donor acidity, while Lewis acidity corresponds to electron pair acceptors with both Brønsted and Lewis sites occurring in zeolites. The Brønsted acidity of zeolites is generally attributed to the bridging hydroxyl (Si-(OH)-Al) groups formed after ion exchange and which are extremely acidic, as shown in Figure 2-5. The concentration of Brønsted sites is proportional to the number of framework Al atoms per unit cell. Therefore, as Al in the zeolite framework structure increases so does the ion exchange capacity. On the other hand, Lewis acid sites can be related either to aluminum species in extra framework positions such as AlO^+ or partly linked to the framework. It should be noted that the concentration of Lewis sites decreases with acid leaching but increases on calcination and steaming treatments [14, 16, 23, 24].

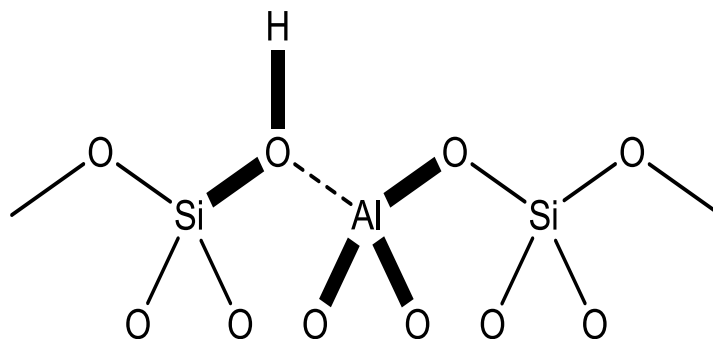


Figure 2-5: Illustration of the formation of the hydroxyl bridge responsible for Brønsted acidity (re-drawn) [25].

2.1.4.3. Shape selectivity

Shape-selectivity is one of the unique properties possessed by zeolites and it can be classified in to three types as shown below, depending on whether pore size limits the access of the reacting molecule, or the exit of the product molecule, or the formation of certain transition states as shown in Figure 2-6.

- 1- Reactant selectivity:** Small reactant molecules pass into the zeolite pores and react, whilst large molecules are prevented from entering the pores due to size constraints. For example, in most shape selective acid catalysis, normal paraffin can enter the pore, reach the active sites and therefore can react but branched ones which sometimes do not react at all.
- 2- Product selectivity:** Small product molecules exit the pore, and larger product molecules remain within the pore structure. They are either converted to small molecules or eventually deactivate the catalyst by blocking the pores. For example, a mixture of all three isomers of xylene is formed in the cavities but only the para form is able to leave the active sites and diffuse out through the channel.
- 3- Transition state selectivity:** During the transition state, the pore shape and crystal size of the zeolites force the transition-state molecules to form products that can pass through them, and consequently leave the

crystalline structure. This means that certain reactions are prohibited as the transition state is too large for the cavities of the zeolites. For example, acid-catalyzed transalkylation of dialkylbenzenes. In this reaction, one of the alkyl groups is moved from one molecule to another. This is a bimolecular reaction involving a diphenyl methane transition state. This means that a reaction is restricted more by its mechanism than by diffusion limitations [1, 16, 26].

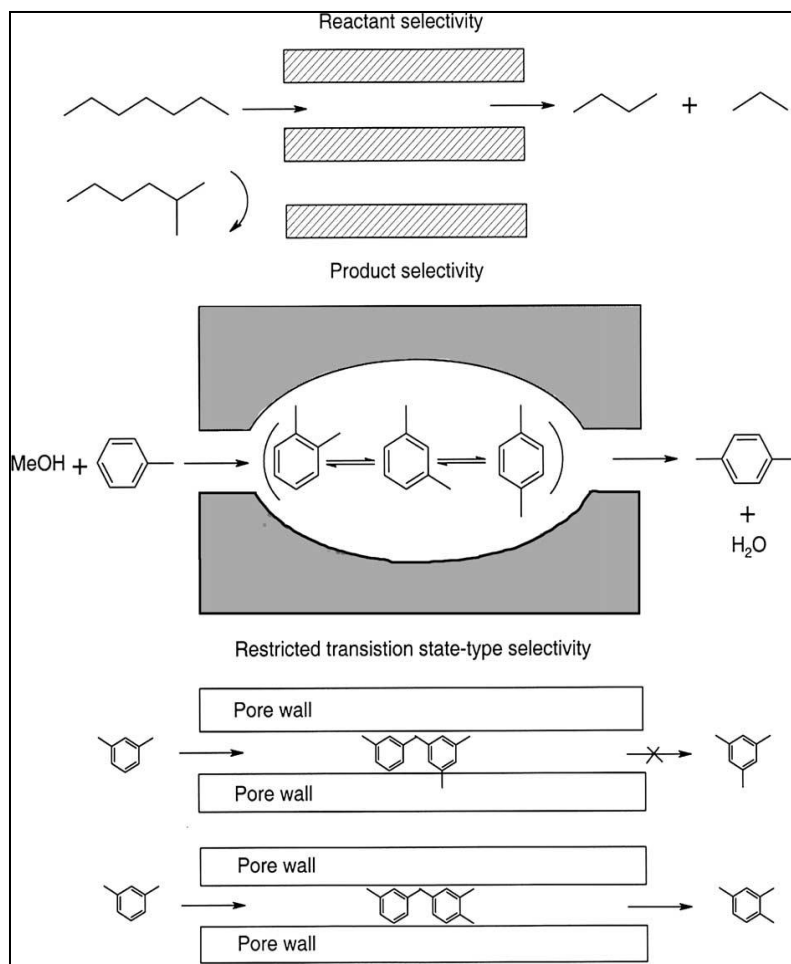


Figure 2-6: Schematic representation of the three types of shape-selectivity [27].

2.1.5. Applications of zeolites

Catalyst technology is the basis of the chemical and petroleum industries. It has played a major role in the economic development, with two of the largest

2.1.6. Zeolite synthesis

Compared with natural zeolites, synthesized zeolites have many advantages including high purity, uniform pore size and enhanced ion exchange abilities [6]. According to the literature, the first work to synthesize zeolite Y was in 1930 by Richard Barrer who used high pressure and temperature to aid the synthesis with this attempt followed by the first commercial application of zeolite Y in the petroleum industry. In addition, Barrer produced the first synthetic zeolite that did not have a natural counterpart in 1948 [6, 21, 30]. Zeolites are usually synthesized from low cost silica and alumina source in an alkaline phase under hydrothermal conditions [21].

In zeolite synthesis, temperature, chemical composition, and hydro-oxide (OH) concentration are the major parameters affecting the process (Table 2-1). For example, increasing the pH in the process leads to accelerated crystallization and minimization of the zeolite crystallization time. Different cations can be used in the synthesis process leading to the formation of different zeolite types [14].

Table 2-1: Chemical sources and their functions in zeolite synthesis [31].

Sources	Functions
SiO ₂	Primary building unit of the framework
AlO ₂ ⁻	Source of framework charge
OH ⁻	Mineralizer, guest molecule
Alkali cation, template	Concentration of AlO ₂ ⁻
Water	Solvent

2.1.7. Post-synthesis modifications

The Si/Al ratio of framework zeolites is an important factor that influences the zeolite properties such as ion-exchange capability, thermal stability, concentration, and strength of acid sites, and the catalytic activity and selectivity. Commonly, zeolites with a high Si/Al ratio (or low aluminum content) are

preferred, particularly when used as catalysts. However, the Si/Al ratio of the zeolite framework prepared by direct synthesis, such as direct hydrothermal crystallization is limited. For example, Faujasite zeolites cannot be directly synthesized with Si/Al ratios higher than 2.5 and it is therefore of the utmost importance to find methods to improve the Si/Al ratio by post-synthesis modification of zeolite frameworks by chemical reactions such as acid leaching and steaming [20].

2.1.7.1. Acid leaching

One method of changing the Si/Al ratio is by creating the acid form of zeolite Y using a direct ion exchange with a dilute mineral acid such as HCl. Since zeolites are sensitive to the pH of the solution and the critical pH value for zeolite Y is between 2.5 and 3. This may result in framework aluminum extraction followed by either structural collapse or framework destruction. As a result, acid leaching is a less favoured method [11, 21].

In the 1960's, it was known that the structure of Faujasite-type zeolites collapsed entirely with strong acid treatment. However, Lee and Rees discovered that the crystal of Y zeolite is not significantly affected if the amount of HCl applied in aqueous solutions does not exceed a certain concentration, i.e. 10 mmol/g Na-Y. This means that a dealumination / acid leaching process can be used to remove around 56% of the framework aluminum without significant lattice damage and complete removal of sodium cations, provided the acid leaching is applied carefully [16, 25]. In 1964, Barrer and Makki performed an elimination of aluminum from a zeolite framework, where they extracted aluminum from clinoptilolite by refluxing with HCl. They showed that depending on the acid concentration; almost 100% of the framework aluminum could be extracted. However, the thermo stability of the products decreased stepwise at dealumination levels higher than 65% [30].

2.1.7.2. Steaming

In this process, Al atoms are removed while the zeolites retain their crystallinity, as the vacancies created in the lattice by steaming are generally filled by Si migration. The result of this substitution in zeolite Y is a decrease in unit-cell size since the atomic radius of Si is smaller than that of Al [32]. Adding additional Si to a zeolite has also been shown to give structure stability and one example is the use of hexafluorosilicate ((NH₄)₂F₆Si) [33]. High temperature steaming or hydrothermal treatment involves calcining zeolites either in the hydrogen or ammonium forms. This typically results in the replacement of aluminum in the zeolite framework by silicon, which increases the Si/Al ratio of the framework. However, the removed aluminum atoms remain within the zeolite as extra framework aluminum species (EFAL) such as Al³⁺, AlO⁺, Al(OH)²⁺, Al(OH)₂⁺, AlO(OH) and Al(OH)₃ which can lead to an improved acidity through the formation of Lewis acid sites [1,34, 35]. The formation of EFAL species arises from the migration of aluminum from the framework into the external surface of crystals [13].

2.2. Introduction to Hydroisomerization

2.2.1. Introduction

Awareness and concern about the environment has been growing over the last few decades with increased pollution [36]. Against this background, the oil refinery industry has had to meet the growing fuel demands and fuel quality for the combustion engine. The combustion efficiency and knock resistance of a fuel is referred to as the Research Octane Number (RON). Since modern engines require fuels with a RON of between 92 and 100 [37] which cannot be obtained by the distillation of petroleum fractions, as a result the octane number must be increased. In the past, this was achieved using lead compounds (e.g. tetraethyl lead). However, these lead compounds are prohibited, as they are toxic and poison exhaust gas catalytic converters. Another approach to promote the RON is to add benzene and other aromatics. However, the legislation on the acceptable levels of

these compounds in fuel is also becoming stricter. Therefore, a catalytic solution is currently being sought to raise the octane rating of gasoline is by the use of isomerization of normal straight chain-alkanes (which have a relatively low octane number) into branched alkanes which have higher octane numbers [1].

2.2.2. Historical development

Originally, molybdenum-on-alumina catalysts were used to perform isomerization of normal alkanes, thus enhancing the octane number of gasoline. However, large amounts of coke are formed causing catalyst deactivation. In order to diminish the coke formation, hydrogen was introduced under conditions of high pressure and temperature. However the stability of the catalysts remained insufficient. In the 1950s, the Atlantic Refining Company (ARC) and Houdry Process Corporation (HPC) developed a process in which platinum loaded with alumina or silica alumina was used as a catalyst. Catalyst lifetime was significantly increasing the ability of platinum to suppress deactivation by catalyzing the hydrogenation of the coke precursor. A major weakness of these processes, however, is that due to the relatively low acid strength of alumina, meaning that comparatively elevated operational temperatures are essential, when higher temperatures have an unfavourable effect on the RON of the product. In the early 1960s, United Oil Products and BP introduced another process, which operates at a much lower temperature, below 200 °C. This approach was achieved by loading platinum-over-alumina catalysts whose acidity was strongly improved by treating the surface with hydrogen chloride. Since chloride alumina catalysts are sensitive to impurities, this requires careful preparation, and water must be removed to maintain the catalytic activity. In the 1960s, Shell developed zeolite catalysts for a hydroisomerization process. The main advantage of platinum-on-chlorinated alumina catalysts is that they have a great deal of resistance to feed impurities such as water. Moreover, zeolite catalysts do not require the continuous addition of chlorinating agents, and can operate at lower temperatures; which as previously mentioned as it is important for the RON of the product [1, 38].

2.2.3. Mechanisms of hydroisomerization

As stated previously in Section 2.1.5, the isomerization of light alkanes is an important process in oil refining. Hydrocracking and hydroisomerization require a metal function for hydrogenation and dehydrogenation purposes. Thus, the industrial process of n-paraffin hydroisomerization requires the presence of bifunctional catalysts, which means that two types of sites should be present in the catalyst. The main function for the metallic sites is to dehydrogenate the feed alkanes and to hydrogenate of isomer alkanes such as Pt as a noble metal. In contrast the acid sites (zeolite) function is to crack or to isomerize. In bifunctional catalysts, the balance between metal and acid functions has an effect on product selectivity and help to reduce unwanted side reactions [7, 39, 40].

In brief, the hydroisomerization process is divided in to the following reactions steps and Figure 2-8 shows a schematic representation of Weisz' bifunctional mechanism:

- 1- Adsorption of the reactant on the zeolite
- 2- Dehydrogenation of the reactant on the noble metal clusters of the catalyst
- 3- Isomerization on the acid site
- 4- Hydrogenation of the products on the noble metal clusters
- 5- Desorption of the products from the zeolite [1]

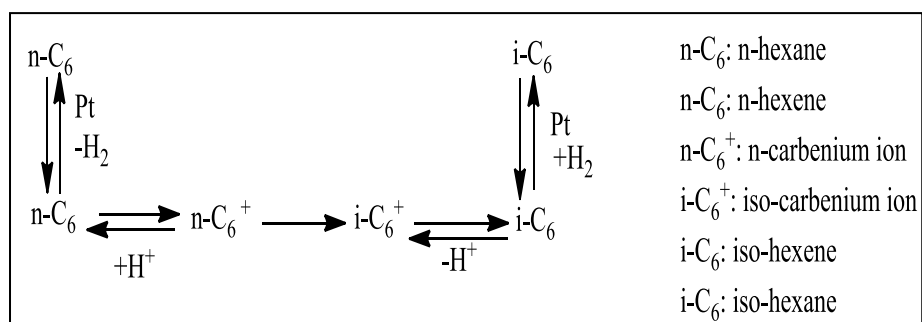


Figure 2-8: Schematic representation of Weisz' bifunctional mechanism [1].

In this process, the normal alkane such as n-hexane and n-heptane are isomerized to their branched through the monomolecular mechanism.

During this mechanism, the dehydrogenation of normal alkane in to its alkene takes on the noble metal. The alkene then transport from the metal site to an acidic site. A protonation of the resultant alkene then takes place on the acid site, converting the alkene to an alkylcarbenium ion intermediate. The resulting alkylcarbenium ion then goes through either a structural rearrangement. This is followed by migration and hydrogenation on a metal site to produce isomers of the initial alkane which have higher RON, or a beta-scission followed by hydrogenation on a metal site to form cracked products [1, 39].

Bifunctional zeolite catalysts reveal high activity in the hydroisomerization of alkanes. During the isomerization process, the zeolite gives the acid site, while a metal provides the hydrogenation/dehydrogenation capability as mentioned earlier. Hydrogenation and dehydrogenation reactions are rapid over these bifunctional catalysts, and the rearrangements of the hydrocarbon intermediates over the acid sites make up the rate-determining steps. Many metals can be used for this purpose such as Pt or Pd loaded Y, which have a high activity and selectivity for hydroisomerization of n-alkanes because of their high resistance against the deactivation by coke [7, 41].

Figure 2-9 demonstrates an example of heptane isomerization via a mechanism involving dimerization cracking (Figure 2-9a). The reaction mechanism involves an addition of an alkene to an adsorbed tertiary alkylcarbenium ion, followed by type A isomerization and type A β -scission. After β -scission, the initial tertiary alkylcarbenium ion is regenerated and can enter a new catalytic cycle. The conventional monomolecular isomerization of heptene to 2-methylhexene occurs via type B rearrangement (Figure 2-9b). The bimolecular isomerization mechanism involves faster alkylcarbenium ion reactions compared to the monomolecular one. Indeed, type A isomerization and type A β -scission are faster than type B isomerization [42].

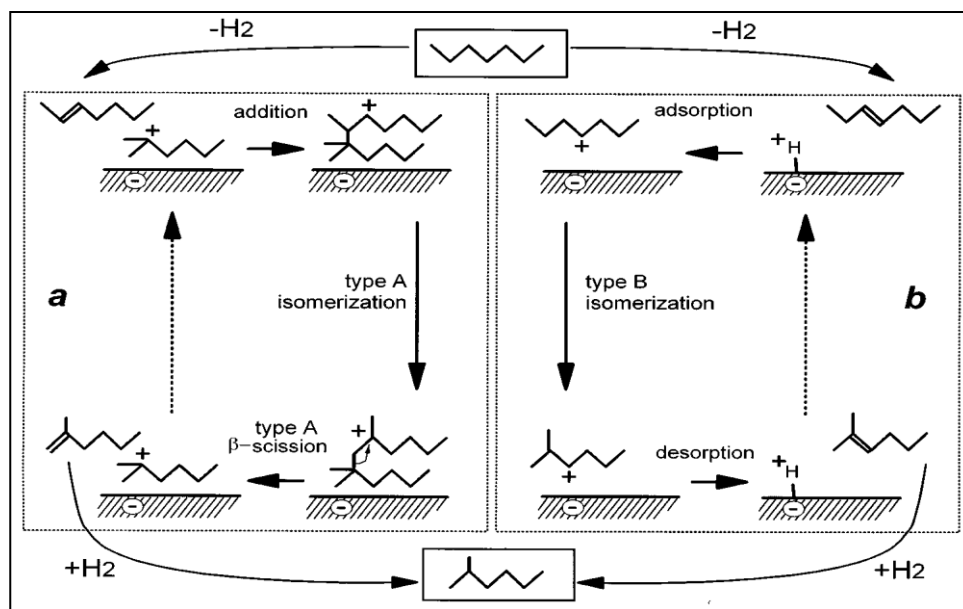


Figure 2-9: Bimolecular isomerization (a) against the conventional monomolecular isomerization mechanism (b) of heptane into 2-methylhexane on a bifunctional catalyst [42].

Hydroisomerization is a reaction which is thermodynamically controlled. For example, the octane number will decrease at a higher temperature. Hence, developing a more active catalyst to conduct this reaction at a lower temperature is required [38]. The bimetallic catalysts presented a higher activity in the isomerization of *n*-hexane/ *n*-heptane when compared to the mono metallic ones [40, 43, 44]. Additionally, it has been reported that the property of the first dispersed metal such as Pt is influenced by the addition of the second metal due to formation of metallic clusters [43, 44, 45]. A range of metals have been introduced as a second metals such as Cu, Ge, Zn and Ni which have been used as promoter with Pt/zeolite catalysts for the isomerization [8, 46].

In this dissertation Ni will be introduced as a second metal following in from work by Vazquez et al, who studied *n*-heptane isomerization and cracking over Ni-Mo/H-Y [47]. According to the literature, the behavior of bimetallic catalysts can be explained based on the following factors: as the nickel particles are not very active in the isomerization, the presence of the first metal (Pt) will enhance

nickel reduction. Also the increase/enhancement in di-branched products suggests that there is a synergetic effect between Pt and Ni [45, 48].

The research in the dissertation has investigated the behaviour of mono- and bi-functional catalysts for hydroisomerization application for the purpose of enhancing the RON of gasoline. In addition, the deactivation of zeolite catalysts was also studied along with the relevant characterization and analytical techniques. The reaction of n-C₇ over Pt USY and Pt/Ni USY was carried out during this program.

CHAPTER THREE

EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES

3.1. Materials

The following is a list of material used in this dissertation:

- Sodium Aluminate (SA) (Fisher Scientific)
- Sodium Hydroxide (Sigma Aldrich, $\geq 98\%$)
- Ludox (Sigma Aldrich, 40% water)
- De-ionized Water
- Tetra-Ammine Platinum (II) Chloride (Aldrich, 99.5% purity)
- Nickel (II) Nitrate (Fisher Scientific, 98% purity)
- Ammonium Nitrate (Sigma Aldrich, $\geq 99\%$) and Ammonia solution.
- Zeolite Y (Si/Al 2.6) provided by Crosfield, Warrington, UK
- CBV-712 (Si/Al 6) provided by Zeolyst International
- n-heptane (Sigma-Aldrich, 99.33% purity)
- Hydrogen gas cylinders (BOC, 99.99% purity, (~ 200 bari))
- Nitrogen and air compressed gas cylinders (BOC)
- HC gravimetric, gas standard mixture cylinder (C₁-C₅ BOC limited)

3.2. Experimental

Experimental sections 1 and 2 deal with zeolite synthesis and characterization, giving detailed understanding of both areas. This research project focuses on the metal loading and the subsequent testing of the bi-functional mono and bi-metallic catalysts which are presented in Section 3.

3.2.1. Zeolite Y synthesis

The Y-zeolite recipe was developed in a previous work at University of Manchester [49]. The Chemical composition is as follow: $3\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:10\text{SiO}_2:120\text{H}_2\text{O}$. Calculation for the recipe is shown in Appindix-1.

It was prepared by mixing SA (Fisher Scientific) with de-ionized water and Sodium Hydroxide (Sigma Aldrich, $\geq 98\%$) in a plastic beaker. Then the required amount of Ludox (Sigma Aldrich, 40% water) was added to the mixture and stirred for 10 minutes by a magnetic stirrer to ensure that all ingredients have dissolved. Finally, the mixture was aged overnight at room temperature in a sealed plastic vessel. This was followed by the hydrothermal synthesis step which was carried out by adding the prepared mixture in a sealed polypropylene bottle and keeping the sample in a heating system shown in Figure 3-1 at 100 °C as indicated in the displayed screen, for 24 hours for crystallization. Finally, the synthesized NaY sample was centrifuged. The subsequent white zeolite product was then washed with de-ionized water. After several times centrifugation, the pH of the solution was measured. When it had dropped to 7, the sample was dried at 100 °C overnight. Then, the prepared sample was characterized using XRD in order to compare its XRD pattern with the commercial zeolite Y (Si/Al 2.6) from Crosfield Catalysts.

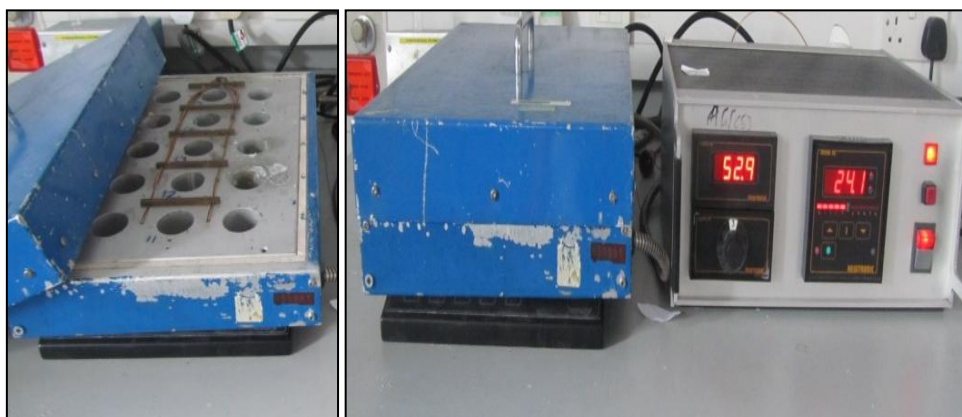


Figure 3-1: Heating system.

3.2.2. Ammonium ion exchange

As mentioned in the literature review, for catalytic applications, the ammonium form of the zeolite is required (Section 2.1.4) on heating ammonia is liberated and the proton form HY is generated for catalysis. One gram of the in-house synthesized NaY was then ion exchanged with 50 ml aqueous solution of ammonium nitrate (0.5M). This was repeated four times in order to completely remove the Na^+ ions to produce $\text{NH}_4\text{-Y}$ zeolite. For each ion exchange, the mixture was left stirring at 70 °C for 4 hours, after which the mixture was filtered and washed with 1 litre of de-ionized water followed by drying overnight at 90 °C. The sample was ready for XRD characterization and on this occasion the prepared $\text{NH}_4\text{-Y}$ was compared with the commercial CBV-712 NH_4USY zeolite ($\text{Si}/\text{Al} = 6$) supplied by the Zeolyst International Company.

3.2.3. Bi-functional catalyst preparations

The CBV-712 USY zeolite catalysts were provided as a powder in ammonium form with a bulk Si/Al mole ratio of 6. Five samples were loaded with Pt or Ni only or with varying levels of both metals (Figure 3-2).



Figure 3-2: Raw material used (CBV-712 catalyst, Pt and Ni compounds).

3.2.3.1. Monometallic catalysts

- **Platinum (1 wt% Pt)**

The catalyst was loaded with 1 wt% platinum by ion-exchanging with an amino complex of platinum as used by Weisz to exchange platinum into zeolite A [50]. In the loading procedure, 3 grams of the CBV-712 catalyst was mixed with a (1.04×10^{-3} M) aqueous solution of tetra-ammine platinum (II) chloride ($\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot 6\text{H}_2\text{O}$) (Aldrich, 99.5% purity), whose amount was calculated such that it resulted in 1 wt% platinum loading on the zeolite sample dissolved in 150 ml of de-ionized water. The initial pH was measured and was found to be 4. Then, the mixture was left stirring at room temperature overnight, after which the mixture was filtered and washed with 1 litre of de-ionized water followed by drying overnight at 90 °C.

- **Nickel (1 wt% Ni)**

For the catalyst loaded with 1 wt% Ni, the same methodology described above was used. However, nickel (II) nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (Fisher Scientific, 98% purity) (3.4×10^{-3} M) was used as a solution instead.

3.2.3.2. Bimetallic catalysts

- **Pt (1 wt%) - Ni (1 wt%) co-ion exchange**

The catalyst was loaded with 1 wt% Pt and 1 wt% Ni by competitive co- ion exchange method with an amino complex of platinum and nickel nitrate. In the loading procedure, the ammonium form of the catalyst was mixed with a (1.04×10^{-3} M) aqueous solution of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$, and a (3.4×10^{-3} M) aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ whose amounts were calculated such that it resulted in 1 wt% platinum and 1 wt% nickel loading on the zeolite sample dissolved in 150 ml of de-ionized water. The pH was measured and was found to be 4.

- **Pt (1 wt%) - Ni (1 wt%) co-ion exchange + pH**

The catalysts were loaded using the same method described above. However, the pH was increased to 9 by adding drops of ammonia solution to the mixture.

- **Pt (1 wt%) - Ni (4 wt%) co-ion exchange + pH**

The catalysts were loaded with 1 wt% Pt and 4 wt% Ni using the same method described above. The pH was increased to 7 by adding drops of ammonia solution to the mixture. All the mixture were left stirring at room temperature for 24 hours, after which the mixture was filtered and washed with 1 liter of de-ionized water to ensure that the catalyst was free of any residual chloride ions. The washed catalyst was then dried overnight at 90 °C.

3.3. Introduction to Characterization Techniques

The most commonly used characterization techniques are as follows: Inductively Coupled Plasma- Optical Emission Spectroscopy (ICP-OES), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), ThermoGravimetric Analyzer (TGA), Transmission Electron Microscopy (TEM).

3.3.1. Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

Inductively coupled plasma optical emission spectroscopy (ICP-OES) is an analytical technique used for the detection of trace concentrations of elements. The technique sometimes is referred to it as Wet-Sampling Method due to the fact that the sample is introduced in liquid form for analysis. In the optical emission spectrometry (OES), the sample is subjected to plasma as electrical discharge that provides high temperature to cause significant amounts of atoms excitation into high energy levels and ionization. In another words the high generated temperature causes elements in the analyzed sample to become thermally excited and emit light at their characteristic wavelengths.

It is highly an energetic thermal source and usually produced in inert gases such as Argon. When the atoms or ions are in their excited states, they can decline to lower states by emitting a light. In OES, the intensity of the light emitted at particular wavelengths is measured and used to determine the concentrations of the target elements. One of the main advantages of the ICP-OES technique is that many elements can be detected in the same run [51].

During the course of this study, Varian Vista MPX CCD Simultaneous Axial ICP-OES (Figure 3-3) of the MEDAC LTD Analytical Services was used to determine the actual contents of the metal loading zeolite catalysts. Prior to performing the analysis the sample was subjected to digestion process and then the solution was analyzed.

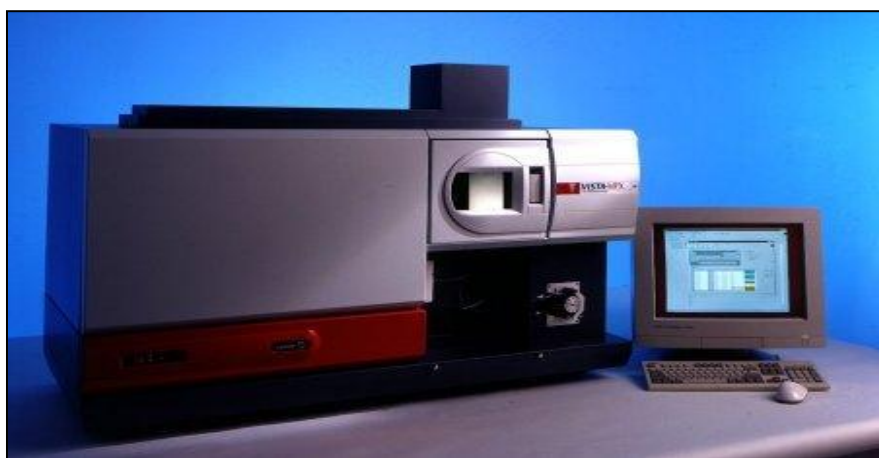


Figure 3-3: Varian Vista MPX CCD simultaneous Axial ICP-OES [52].

3.3.2. X-ray Diffraction (XRD)

Generally, X-ray diffraction is the most powerful, flexible and non-destructive technique. It provides significant information about the chemical composition and crystallographic structure of natural and synthesized materials [53]. The principle of the XRD technique is that crystal structure consists of planes produced by cyclic arrangements of atoms, which are capable of diffracting X-rays. The angles of diffraction vary for the different planes within the crystal and therefore each

compound or element has its own distinctive diffraction pattern, thus permitting the diffraction of diverse structures within the catalyst. It can be used for quantitative chemical phase analysis. The characterization of the crystal structure and the chemical phase composition by the diffraction of x-ray beam is measured as a function of the angle of the incident beam. Expansion of the diffraction peaks can be used to estimate crystallite diameter. It can be used to detect crystalline materials having crystal domains of greater than 3-5 nm [28].

When an X-ray beam hits a sample and is diffracted, the distances between the planes of the sample's atoms can be calculated by using Bragg's Law:

$$n \lambda = 2 d \sin \theta \quad (1)$$

Where n is the order of the diffracted beam, λ is the wavelength of the incident X-ray beam, d is the d -spacings the (distance between two planes of atoms), and θ is the angle of incidence of the X-ray beam (Figure 3-4).

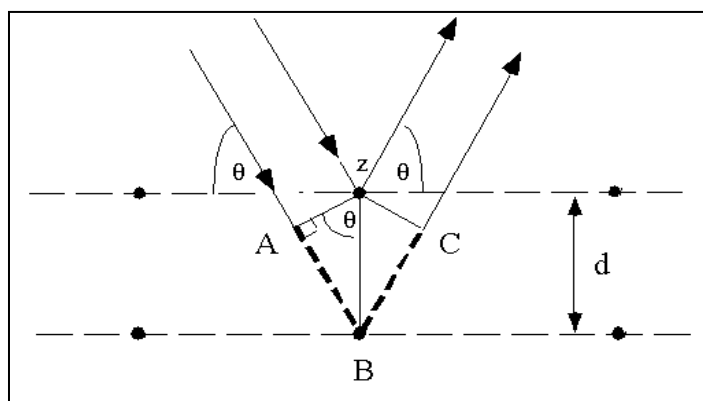


Figure 3-4: Diffraction of X-rays by a crystal [54].

For crystal with cubic symmetry such as Faujasite, the size of the unit cell a_0 can be determined from the angular positions of the reflections.

$$a_0 = \frac{\sqrt{h^2 + K^2 + I^2}}{2 \sin \theta} \quad (2)$$

The unique structure of different zeolites with regard to the positions of the atoms and unit cell dimensions is reflected in the characteristic positions and relative intensities of the examined peak. The XRD patterns of known structure types of zeolites are gathered in the “collection of simulated XRD patterns for zeolites” [55] and in the online database of the IZA [18, 56].

In the straightforward case, the structure of a zeolite sample can be identified by comparing its experimentally measured powder diffractogram with reference diffractograms. The integrated intensity of preferred reflections can be used to determine the crystallinity of the samples by normalizing their intensities to those of a reference sample. The crystallinity is defined as stated in the relevant ASTM standards on catalysts as [56, 57].

$$\text{Crystallinity\%} = (\text{intensity of sample peak} / \text{intensity of reference peak}) * 100 \quad (3)$$

To compare the crystallinity accurately of several samples run at different times, by different operator or on different instrument; a silicon reference can be mixed with a sample homogeneously and run in the XRD under the sample used conditions. The optimum 2θ value can be taken from the sharper peak [58]. However, this research, it was determined using the following two methods:

- **Method one** : the intensity of 9 main peaks of the sample were summed and compared with the intensity of the same 9 main peaks of the reference using equation (3) mentioned earlier.
- **Method two**: calculated as above but excluding the first peak at low 2θ (approximately at $6^\circ 2\theta$) was excluded.

XRD was carried out for this work using Philips X’pert Pro PW3719 X-ray Powder Diffractometer (Figure 3-5) in the scan range of 2θ between 5° and 50° at a wavelength of $1.54 \text{ \AA}$. The XRD experimental parameters are listed in Table 3-1.

Table 3-1: XRD run conditions.

Start angle	4.997
End angle	50.017
Step size	0.033
Time per step(s)	146.685
Scan Speed	0.0290
Number of steps	1347
Total scanning time (min)	27



Figure 3-5: Philips X'pert Pro PW3719 X-ray Powder Diffractometer.

3.3.3. Environmental Scanning Electron Microscopy (ESEM)

ESEM is the most versatile technique to study the morphology and particle size distribution of zeolite [56]. Electron microscope uses electrons to form an image of the material; magnifications in excess of 1,000,000 times can be obtained. The scanning electron microscope mainly consists of an electron gun to generate an electron beam which can be focused by magnetic lenses and condensers. A final lens then focuses the beam to as small as possible a spot onto the sample, which is located in the sample chamber [59, 60].

In a typical SEM, electrons can be emitted via field emission (FE). In the field emission gun, finely tipped tungsten is used and the electrons are generated from the filament tip by an intense potential field set up by an anode situated beneath the tip of the filament. The electron-sample interaction (Figure 3-6) can result in the generation of three types of electrons:

- **Secondary electrons:** A primary electron may interact with an electron in the sample ejecting it as a secondary electron. These secondary electrons carry little information about the elemental composition of the sample [59, 60].
- **Backscattered electrons:** If the primary electron interacts with the nucleus of the sample atom, they may be scattered in any direction with little loss of energy. Some will be scattered outside of the sample. These backscattered electrons are much more energetic than the secondary electrons and carry relevant information about the sample composition and topography [59, 60].
- **Characteristic x-rays:** An electron is ejected from an inner atomic shell by interaction with a high-energy electron beam to give an electron in the excited state. Upon relaxation, an electron from an outer shell drops into a vacancy in an inner shell and the resulting energy difference results in the

generation of an X-ray photon characteristic to the element or the compound [49, 50].

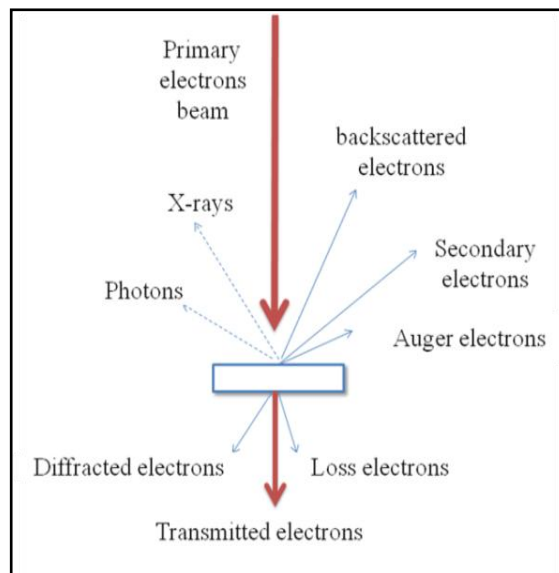


Figure 3-6: Interaction of primary electron beam with the sample (redrawn) [56].

The Energy Dispersive X-ray detector (EDAX) is a useful chemical analysis capable of detecting elements with an atomic number as low as 4 (Boron). The EDAX analysis has an advantage because it penetrates beneath the surface layer of the examined materials. The X-rays generated penetrate the surface under study to about 2 microns deep, and thus EDAX is a surface science technique. However, it can give representative bulk analysis especially for zeolite Y. By moving the electron beam across the sample, an elemental analysis of the sample can be acquired [56, 59]. For non-metallic samples, it is essential to make them conductive by coating them with conductive material such as gold or carbon which is done by a sputter coater. As zeolites are non-conductive, they must be coated to produce a thin coating layer over the zeolite sample to prevent the accumulation of static electric charge on the specimen (charging effect) during electron irradiation to obtain high quality image [60].

In this study, EDX analysis was applied using FEI Quanta 200 Environmental SEM with EDAX Genesis EDS X-Ray analysis to determine the bulk Si/Al ratio

of the zeolite samples (Figure 3-7). The Si/Al ratio was based on several individual analyses based on 4 or 5 spots on the sample. The samples had a thin gold film deposited on them in order to obtain high quality image and reduce the effect of charging.

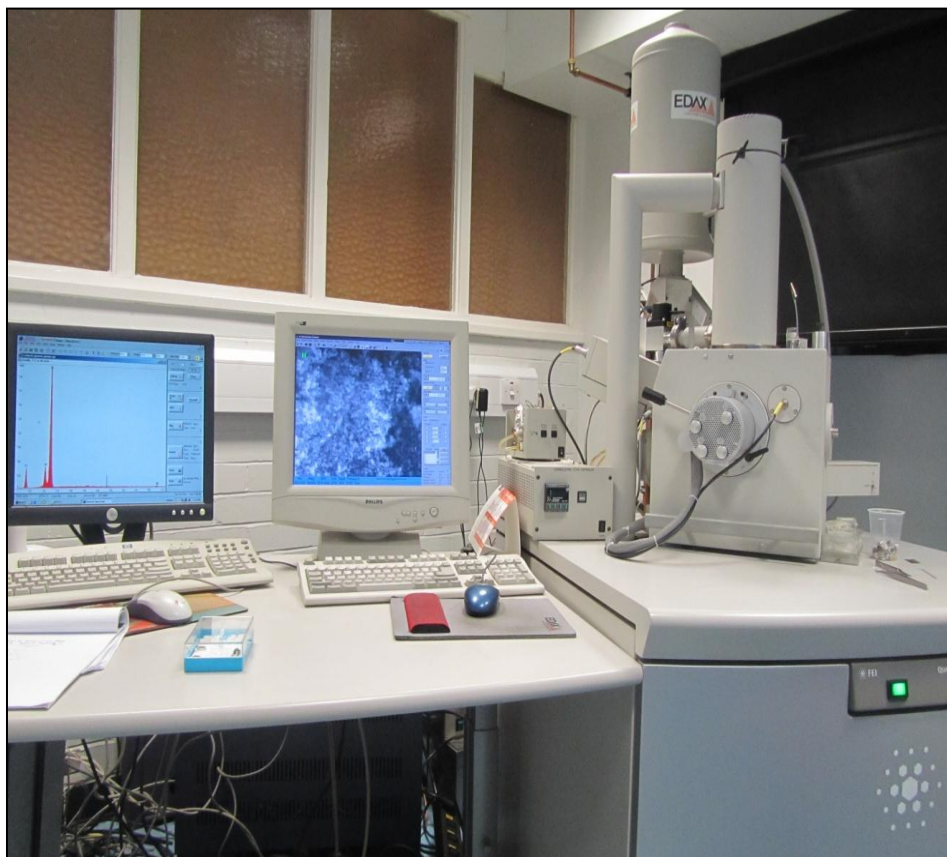


Figure 3-7: FEI Quanta 200 Environmental SEM.

3.3.4. Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) is a simple analytical technique that measures the amount and rate of weight change (loss or gain) of the sample as a function of temperature in a controlled atmosphere. The atmosphere used in the TGA experiment plays an important role and can be reductive, oxidizing or inert and can be changed during the experiment [61]. TGA provides information about decomposition of materials to predict their thermal stability [62]. It is suitable for use with all types of solid materials, including organic or inorganic materials. The

main components of the instrument are the microbalance, the furnace, the programmer controller, and a computer or data acquisition system. Typical arrangements of the components for TGA are shown in Figure 3-8. Balance sensitivity is usually around one microgram, with a total capacity of a few hundred milligrams [61].

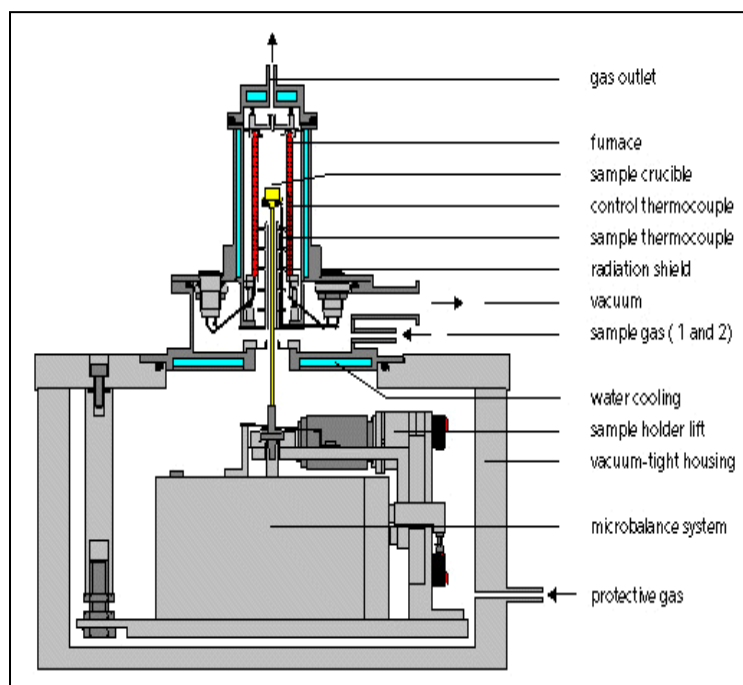


Figure 3-8: Typical arrangements of the components for TGA [63].

The sample is typically heated at a constant heating rate or held at a constant temperature (isothermal measurement). The result of a TGA measurement is usually displayed as a TGA thermogram in which mass or percent mass is plotted against temperature or time. An alternative and complementary presentation is to use the first derivative of the TGA thermogram with respect to temperature or time [61]. According to the literature, TGA can be used directly as a reactor in the catalytic cracking reaction to study in-situ coke formation. The catalyst sample weight is measured continuously while the rate of weight change is calculated by differentiation over time [64]. TGA can be used to identify the

adsorption of e.g. H_2O or NH_3 on zeolites and the buildup of coke from catalytic reactions. Data obtained can be used to estimate the acid site strength and distribution of different zeolites, for example, when using NH_3 [65].

In this work, TGA was run on the spent catalyst using a TA instrument Q500 to determine coke content (Figure 3-9). Thus the catalysts were subjected to a series of steps for this purpose as shown in Figure 3-10.



Figure 3-9: TGA-TA instrument Q500.

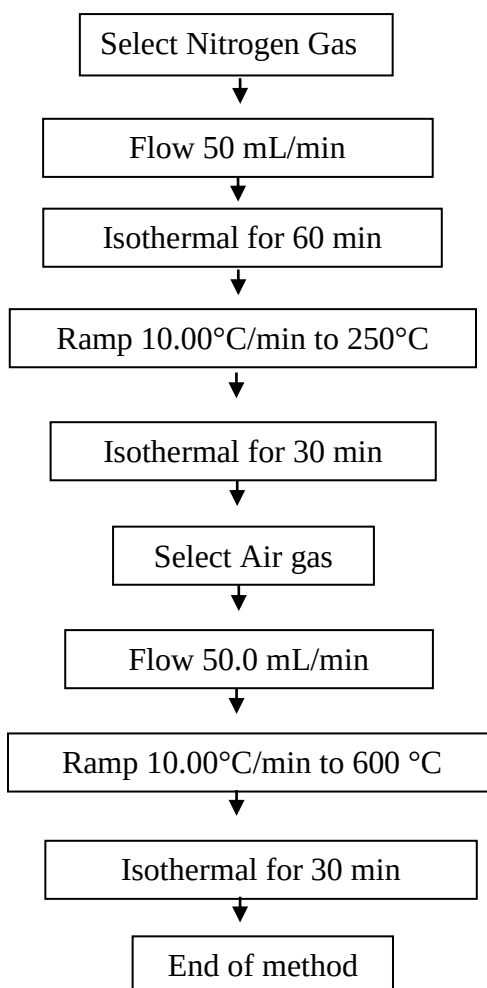


Figure 3-10: Coke analysis method used for spent catalyst.

3.3.5. Transmission Electron Microscopy (TEM)

TEM is a technique whereby a high intensity primary electron beam, approximately in the range from 100-300 keV, passes through the sample; the transmitted and diffracted electrons are collected. Therefore, the sample has to be very thin (in the range from 10-500 Å) and should be kept under vacuum typically $< 10^{-5}$ torr [12]. An image is formed from the interaction of the electrons transmitted through the specimen, which becomes ready for processing to improve the contrast. The image is magnified and focused on to an imaging tool. For example, a fluorescent screen, on a coating of photographic film or by a

sensor similar to a CCD camera [66, 67]. TEM is composed of several components (Figure 3-11), which include electron guns at the top down, which are capable of accelerating the electrons through a selected potential difference in the range of 60 to 200 kV, the condenser system which contains two or more condenser lenses that are below the electron gun. The main function of these condenser lenses is to reduce the beam diameter emitted by the gun and control it in the way that it hits the specimen [67].

A two dimensional projection of the sample is produced from the attenuation of the beam that is based on the density and thickness of the sample. If an aperture used to permit the transmitted electrons to share, yet rejects all diffracted electrons, the imaging mode bright field image is produced. For supported catalysts, dark field images mode appears to be an improved contrast for the metal particles [11]. The bright-field/dark-field imaging modes of the microscope operate at medium magnification. It is combined with electron diffraction and it helps to provide invaluable information about the morphology, crystal phases, composition or any defects occur in a microstructure material very high spatial resolution [67, 68].

TEM is a useful tool for determining crystalline size and size distribution for supported metals. For example, it is useful in examining the changes in an average crystalline size and size distribution for sintering of supported Ni and Pt catalysts. It is also useful for the determination of the microstructure of electron transparent samples by transmission of a focused corresponding electron beam to a fluorescent screen with a resolution higher than 0.2 nm. [28].

TEM was carried out in this research using a 300 kV FEI Tecnai TEM shown in Figure 3-12 to determine the metal loading particle size. After calcinations at 500 °C and reduction at 450 °C, the catalyst sample powder was suspended in ethanol by ultrasonic treatment. Drops of this dispersion were placed on to holy carbon TEM grids and then introduced to the microscope.

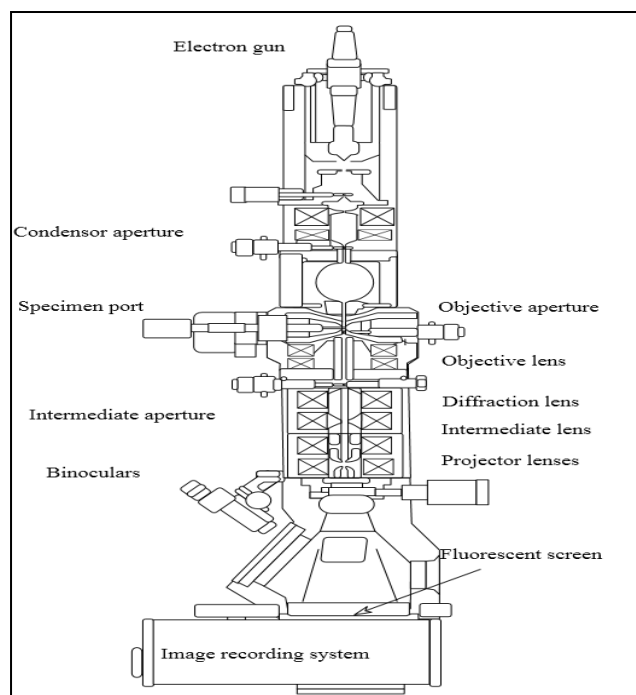


Figure 3-11: Transmission Electron Microscopy components [69].



Figure 3-12: FEI Tecnai Transmission Electron Microscopy.

3.4. Catalyst Testing

The catalysts were tested for the hydroisomerization of *n*-C₇ with a purity of 99.33 wt% (Sigma-Aldrich).

3.4.1. Catalytic fixed bed reactor design

Figures 3-13 and 3-14 show the fixed bed reactor set up for *n*-heptane hydroisomerization over CBV-712 zeolite catalyst. The fixed bed reactor consists of a vertical furnace heating the fixed bed reactor, with the temperature being controlled by a Carbolite temperature controller. In addition, mass flow controller (MFC), chiller cooler bath, and thermocouple located between the metal tube and the wall of the reactor column. Also, a digital thermometer connected to the thermocouple is installed to accurately measure the temperature profile of the catalytic reaction.

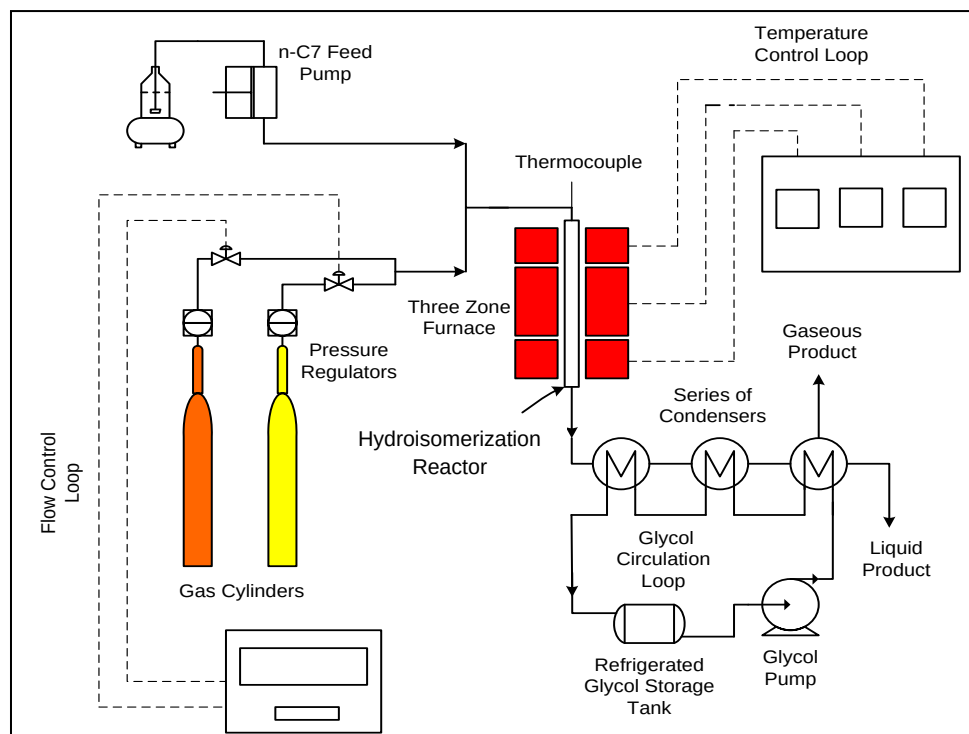


Figure 3-13: Fixed bed reactor setup for *n*-C₇ hydroisomerization modified [41].



Figure 3-14: Photograph of fixed bed reactor set-up for n-C₇ hydroisomerization.

3.4.2. Preparation and catalytic testing procedure

Following the ion-exchange, approximately one gram of each metal-loaded zeolite catalyst was pressed at a weight of approximately 10 tons to produce catalyst pellet form. Then, the obtained pellets were crushed using a pestle and mortar, and sieved in a mesh producing particles with sizes between 250 and 420 μm (Figure 3-15). This was followed by packing the prepared catalyst in the fixed bed reactor column (middle zone). The fixed bed glass micro-reactor column with 11.2 mm inner diameter and 600 mm length was used for all experimental work. Glass beads of 1-1.3 mm in diameter were used to fill the top and bottom of the reactor between the catalyst beds (top and bottom zone). Fine glass wool was used to separate the catalyst from the glass beads. The role of using glass beads is to uniformly distribute the flow over the catalytic bed. This packing method leads to a catalyst bed length of 2 cm (Figure 3-16).

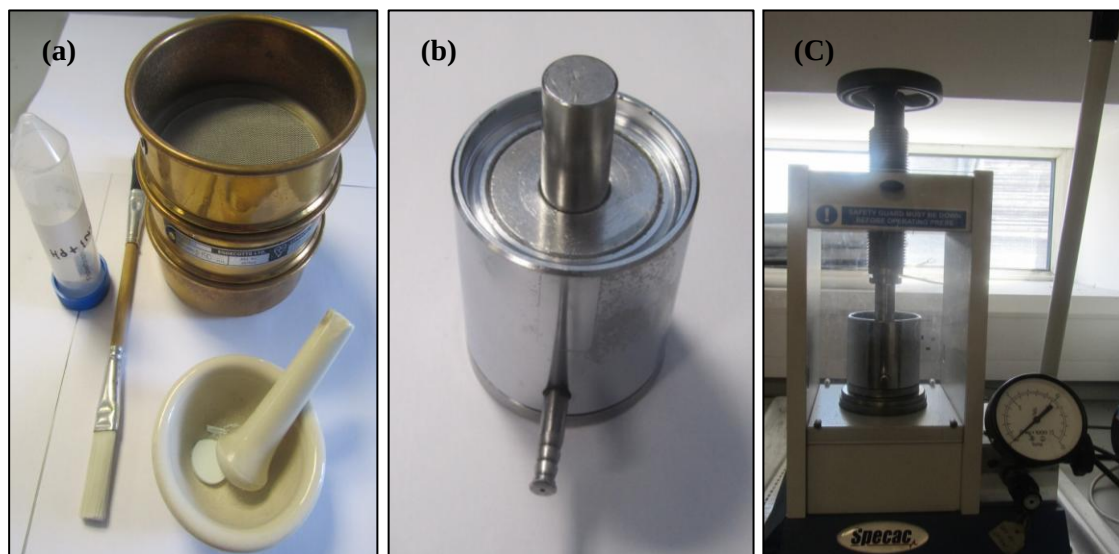


Figure 3-15: Equipment for pressing catalysts (a) mortar, pestle and sieves, (b) die for press and (c) die in the press

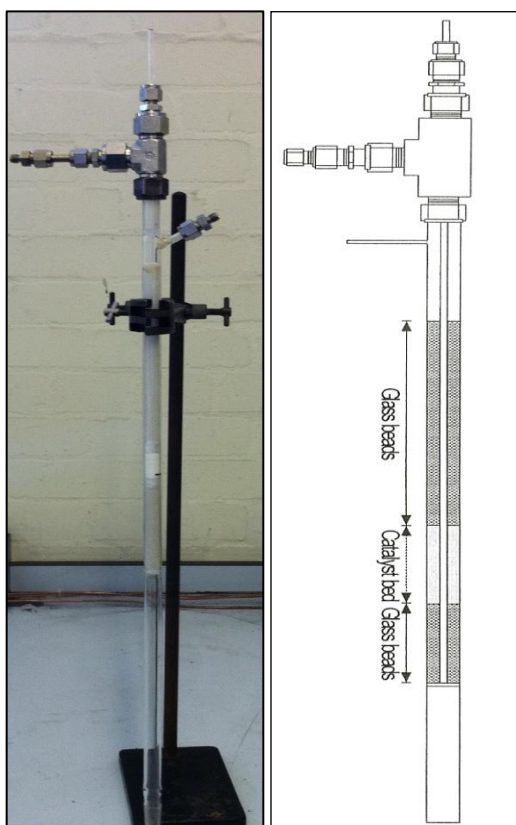


Figure 3-16: Photo and schematic of glass reactor packed with glass beads and catalyst [41].

The catalyst was activated in situ by first removing ammonium via calcinations at 500 °C for 2 hours under an air flow of 50 ml/min and heating rate of 3°C/min. Following the removal of ammonium, the catalyst was then reduced in a hydrogen atmosphere at 450 °C for 4 hours at a flow rate of 100 ml/min in order to convert the metal ions into their elemental form. A summary of the calcinations and reduction procedure for the catalyst is shown in Figure 3-17. A slow temperature heating rate of 3 °C/min was used during calcinations. This is due to the agglomeration of metal that could occur due to fast heating rates which leads to a poor catalyst performance.

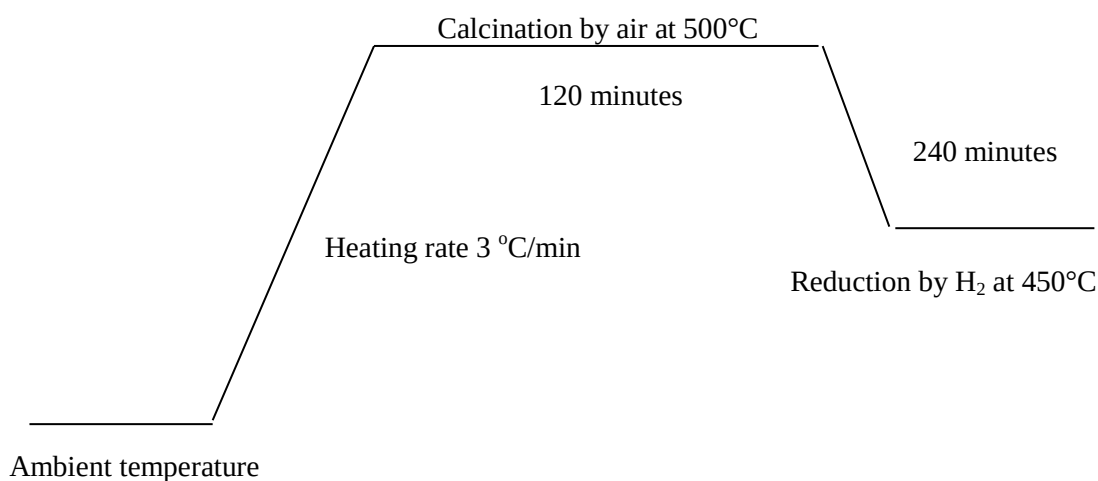


Figure 3-17: Furnace temperature ramping program for the catalyst activation.

The optimum reaction conditions were selected for n-heptane hydroisomerization based on previous work [41]. However, in this work, the reaction was carried out at 230 °C at atmospheric pressure and constant reaction parameters such as contact time (WHSV) and hydrogen to hydrocarbon molar ratio (H₂/HC) were carried out for all experiments. Table 3-2 shows the run condition of the n-heptane hydroisomerization deactivation reactions for both of the zeolite catalysts at the different temperatures.

Table 3-2: n-C₇ hydroisomerization reaction conditions.

Reaction Conditions	
T, °C	230
P, bar	1
Cat. Weight, g	1
Bed Length, cm	2
Feed	n-C ₇ (99.3%)
Liq. Flow, ml/hr	7.50
Pump Setting, ml/min	0.132
H ₂ /HC, mol/mol	9.03
WHSV, h ⁻¹	5.13
W/F, g.s/mol	70323
H ₂ Flow, ml/min	187.50

In each experiment, the temperature profile across the catalyst bed was measured. The required hydrogen flow was adjusted by a MFC. Calibration of the MFC is shown in Appendix-2. In addition, as furnace consisting of three separately heating zones, it was first calibrated and tested in order to identify the most stable zone. Calibration of the furnace is given in Appendix-3. This was followed by introducing the feedstock n-heptane in to the reactor by starting the high performance liquid chromatography (HPLC) pump at the desired flow rate. Calibration of the HPLC pump is given in Appendix-4. The pump was first primed by using a syringe to fill the feed lines to and from the pump. All of the deactivation experiments were run for at least five days. During the deactivation run, liquid and gas product samples were taken after 30, 60 and 120 minutes until bed temperature profile became stable. In addition, the temperature profile across the bed was also recorded with each sampling. The measurement of the H₂ gas outlet flow rate was also performed at the same intervals time using a bubble meter (0-100 ml volume, SGE) in order to calculate the mass balance. The reaction products were passed through a condenser in an ice-cold condition and

then were collected. The condenser tube was installed and operated at -2 °C in order to separate the liquid products from the gas products. A wall condenser tube was used to separate the light ends from the product stream and recover the *n*-heptane and its isomers with the liquid product by circulating a cooled solution of water and glycol around the tube (Figure 3-18).

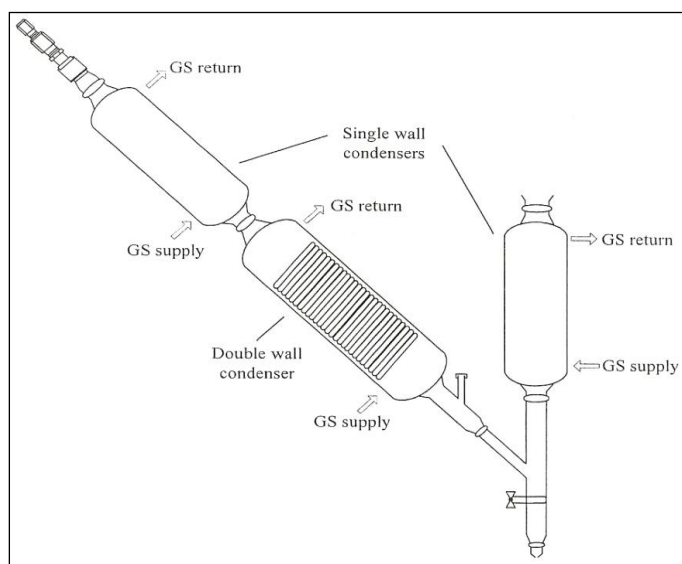


Figure 3-18: Liquid-gas separation section [41].

The collected liquid samples were then analyzed on a Varian GC fitted with an FID detector. Finally, the reactor temperature was reduced to the ambient temperature and the spent catalysts were collected after each reaction and sealed in suitable containers for further analysis. Also the isomers were identified using GC-MS.

3.4.2. Gas Chromatography-Flame Ionization Detector (GC-FID)

Gas Chromatography is a powerful and versatile existing technique to the analyst. In a single step process, it can separate a mixture into its individual components and simultaneously provide a quantitative indication of each compound [70]. Samples may be in the gaseous or liquid form and can range from a simple mixture of two components (e.g. benzene and toluene [71]) to a multi component containing broadly diverse chemical species (e.g. naphtha [72]). In gas

chromatography there are different phases: a gaseous mobile phase (a carrier gas often helium or nitrogen) and a liquid or solid stationary phase. In gas-liquid chromatography, all compounds pass through the column; some of these components that interact with the stationary phase take more time there to go through the column. For instance, a non-polar compound would strongly interact with a non-polar stationary phase. Therefore, they would have a longer retention time which can be described as the time from injection of the sample to the time which a particular compound in the sample is detected. While polarity is the main element in the separation, the boiling points of components of the sample are also important for determining the retention time. Whereas components with higher volatility (lower boiling points) have a tendency to spend more time in the mobile gas phase and hence have shorter retention time. After going out of the column, the separated components are detected and a detector response is recorded. A typical gas chromatogram is shown below Figure 3-19 [70, 73].

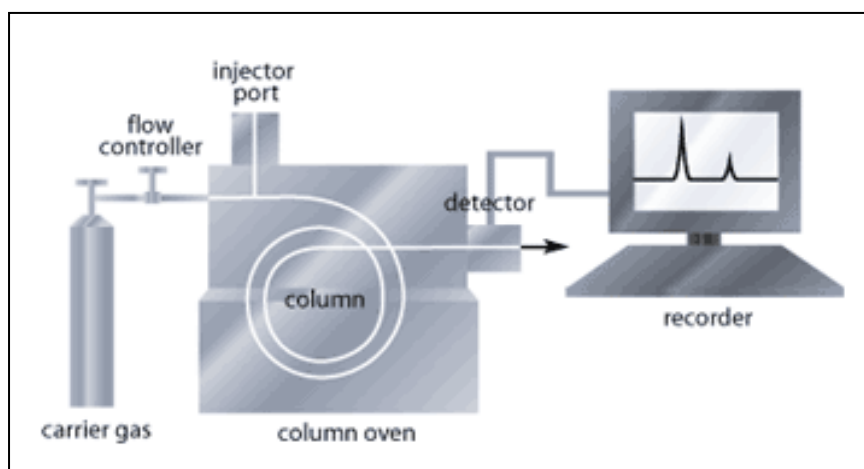


Figure 3-19: Diagram of GC apparatus [74].

Different detectors can be fitted to GC based on the required application. For instance, the Flame Ionization Detector (FID) is the most useful and commonly used GC detector. The FID has a very broad range and a high sensitivity which make it a powerful in the separation of hydrocarbons and hence its wide applications in the petroleum industry [70, 75, 76].

The collected liquid samples were analyzed by injecting 0.1 μl into a Varian 450-GC gas chromatograph (Figure 3-20) with a capillary column (100m long, 0.25mm i.d. PONA CB) attached to a flame ionization detector (FID). However, the gas sample was collected in a gas bag. The analysis was carried out on the same instrument with a 50m $\times$ 0.32mm i.d. PLOT $\text{Al}_2\text{O}_3/\text{KCl}$ capillary column. Helium (99.99% purity) @ 30 psi was used as a Carrier-gas. Table 3-3 lists the temperature program applied for the analyses:

Table 3-3: Experimental conditions used for GC-FID analysis.

Conditions	Gaseous samples	Liquid samples
Split Ratio	50:1	
Oven Temperature 1 ($^{\circ}\text{C}$)	110	70
Isothermal Time 1 (min)	5	16
Ramp Rate 1 ($^{\circ}\text{C}/\text{min}$)	7.5	5
Oven Temperature 2 (min)	225	100
Isothermal Time 2 (min)	5	2
Injector temperature ($^{\circ}\text{C}$)	250	250
Detector temperature ($^{\circ}\text{C}$)	250	250
Total run time (min)	30	24

The GC was first calibrated by injecting a gas sample (500 μl) containing hydrocarbons ranging from C_1 - C_5 . This analysis was carried out three times and the response factor was calculated based on the average peak area obtained for each hydrocarbon. Calibration of GC-FID is shown in Section 4.4.2.

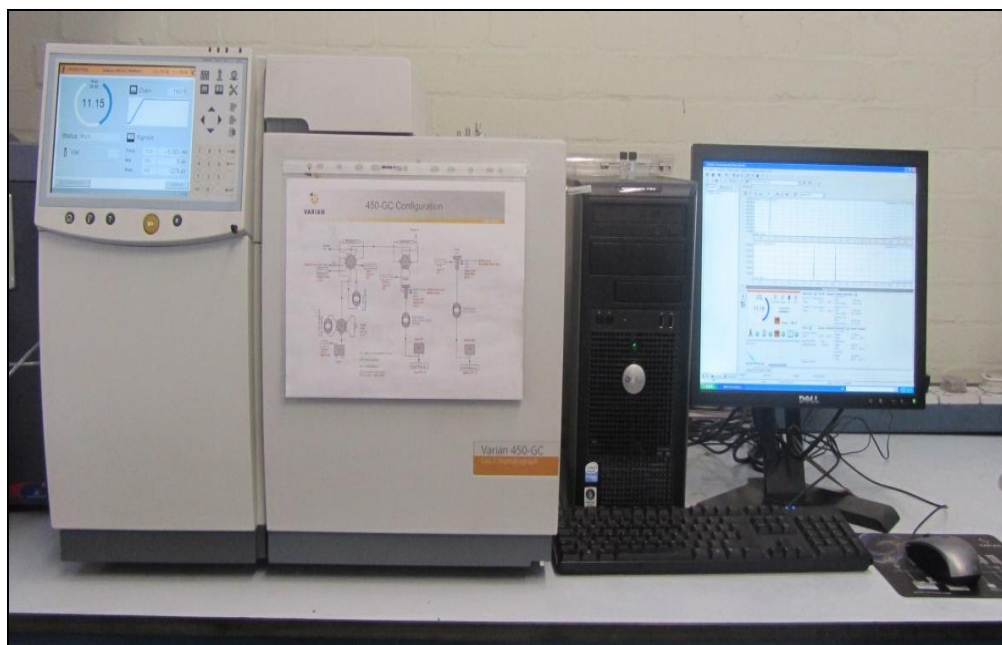


Figure 3-20: Varian 450-Gas Chromatograph.

3.4.3. Gas Chromatography-Mass Spectrum (GC-MS)

A Gas Chromatograph connected to a mass spectrometer (GC-MS) provides structural information of organic compounds. This detailed information can be obtained using electron ionization spectrometers achieved by fragmenting the peaks eluting from a GC column. These compounds are ionized using a 70 eV electron beam which lead to the formation of ions with different masses. These ions produce from breaking bonds in the molecules of each compound. The ions are then separated and the resulting fingerprint used to identify mass spectrum characteristic of the individual compound (Figure 3-21) [73, 75].

In this work, GC-MS was carried out on the liquid products to identify the resultant isomers. The analysis was performed using an Agilent 6890N GC-5973MSD with a PONA CB capillary column (100m × 0.25mm i.d.) shown in (Figure 3-22). Table 3-4 details the GC-MS experimental conditions used for the analysis:

Table 3-4: Experimental conditions used for GC-MS analysis.

Conditions	Liquid samples
Split/ Fraction Mode	50:1
Oven Temperature 1 (°C)	40
Isothermal Time 1 (min)	16
Ramp Rate 1 (°C/min)	2
Oven Temperature 2 (min)	220
Isothermal Time 2 (min)	10
Injector temperature (°C)	250
Total run time (min)	86

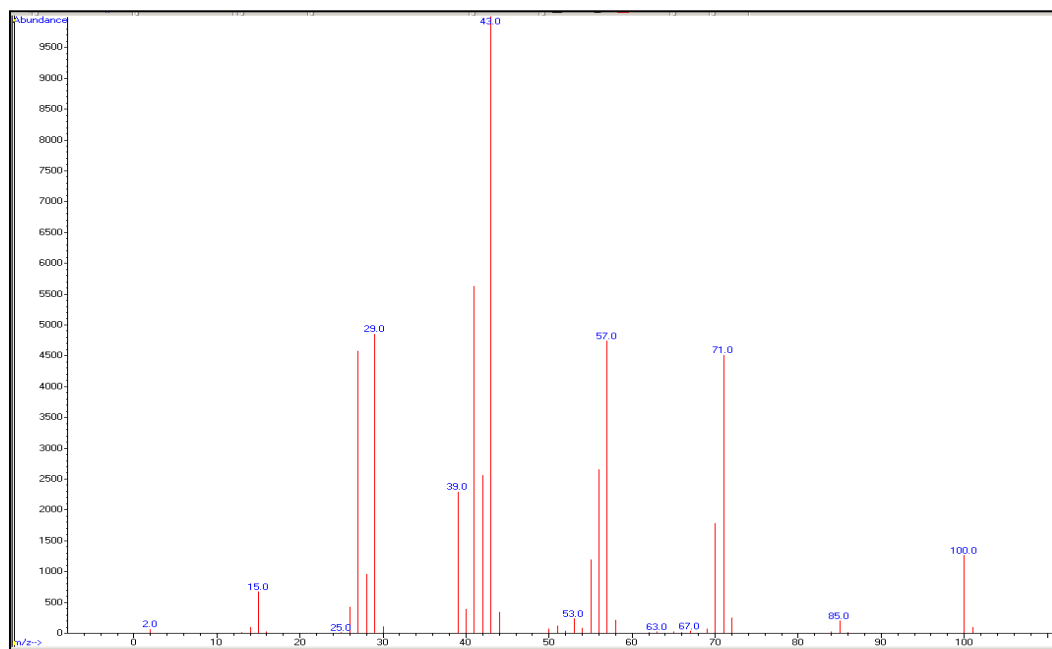


Figure 3-21: GC-MS trace for n-heptane.



Figure 3-22: Agilent 6890N GC-5973MSD.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1. Comparison of Zeolite Y Synthesized with a Commercial Sample

The prepared sample was characterized using XRD in order to compare its XRD pattern with the commercial zeolite Y (Si/Al 2.6) that was supplied by Crosfield Catalysts. Both catalysts were analyzed using Philips XRD using X'pert Pro PW3719 x-ray powder diffractometer and under the same conditions. The XRD pattern of the in-house synthesized zeolite NaY sample was consistent with the XRD pattern of the commercial one and compares well with the pattern of a typical zeolite Y sample referenced by IZA (Figure 4-1).

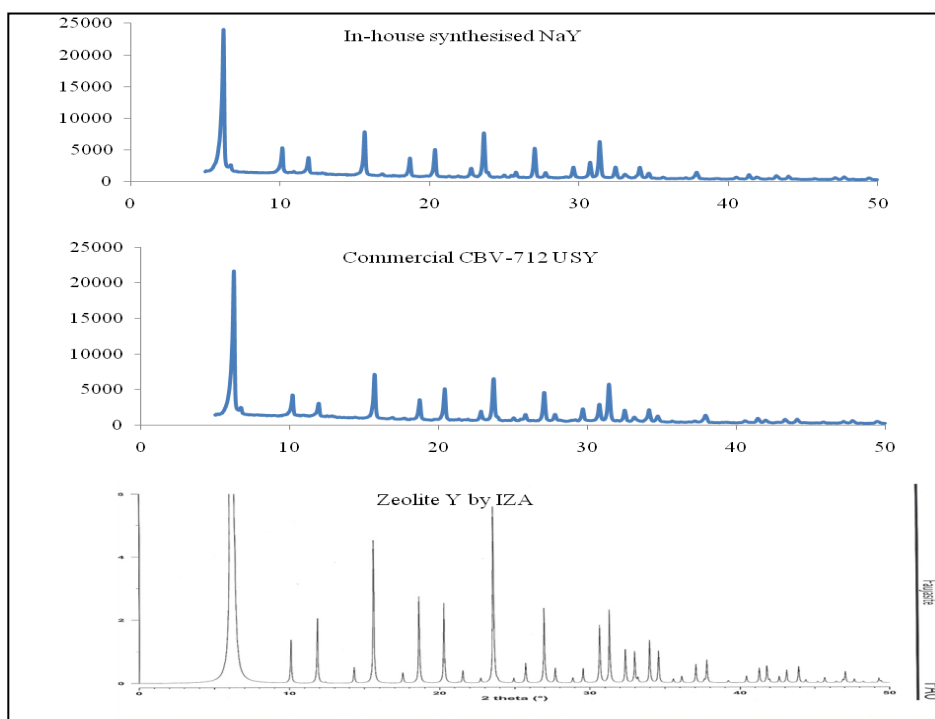


Figure 4-1: XRD pattern of the in-house synthesized, commercial NaY and typical zeolite Y sample [77].

The XRD analysis revealed that the prepared sample has a pure phase of zeolite Na-Y which is confirmed from XRD patterns. Furthermore, the unit cell of both samples was calculated and found that the unit cells of the in-house synthesized and commercial sample were very close and as expected which are 24.7 and 24.6 Å respectively. A typical of unit cell calculation is shown in Appendix-5.

In addition, the SEM and EDX analysis of in-house synthesized and commercial zeolite catalysts were used to determine the bulk Si/Al ratio, Average Na contents and an approximate average of crystal diameter (Table 4-1). The obtained results were based on the average of 3 spots of 100 µm diameter at 800X magnification. The results show that the Si/Al ratio (mol %), Na content and crystal diameter of both samples were very close as shown in the table below.

Table 4-1: SEM and EDAX analysis of in-house synthesized and commercial NaY.

ESEM and SEM Data	In-house synthesized NaY	Commercial NaY	Expected Range
Si/Al ratio (mol%)	2.5	2.7	1.5 – 3 [78]
Na content (wt%)	6.7	6.5	n/a
Crystal diameter (nm)	409	393	n/a

The morphology of the in-house synthesized NaY and the commercial zeolite Y was very similar (Figure 4-2).

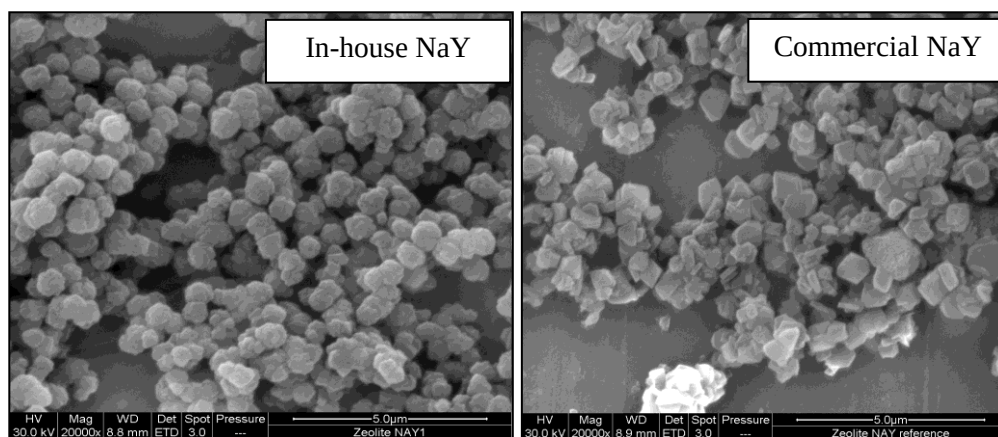


Figure 4-2: SEM images for in-house synthesized NaY and commercial Y.

4.2. Comparison of In-house Synthesized NH_4Y with a Commercial NH_4USY CBV-712 Sample.

4.2.1. Study of ion exchange of in-house synthesized NaY

The ion exchange was studied by taking a small sample after each of the ion exchanges and applying XRD, SEM and EDAX analysis. As can be seen in Figure 4-3, the XRD pattern changed slightly with each ion exchange. Overall the unit cell was 24.73 Å and very close to NaY shown in Section 4.1 (Figure 4-1). However, the slight increase shown was due to replacing the sodium ions by ammonium ions [79].

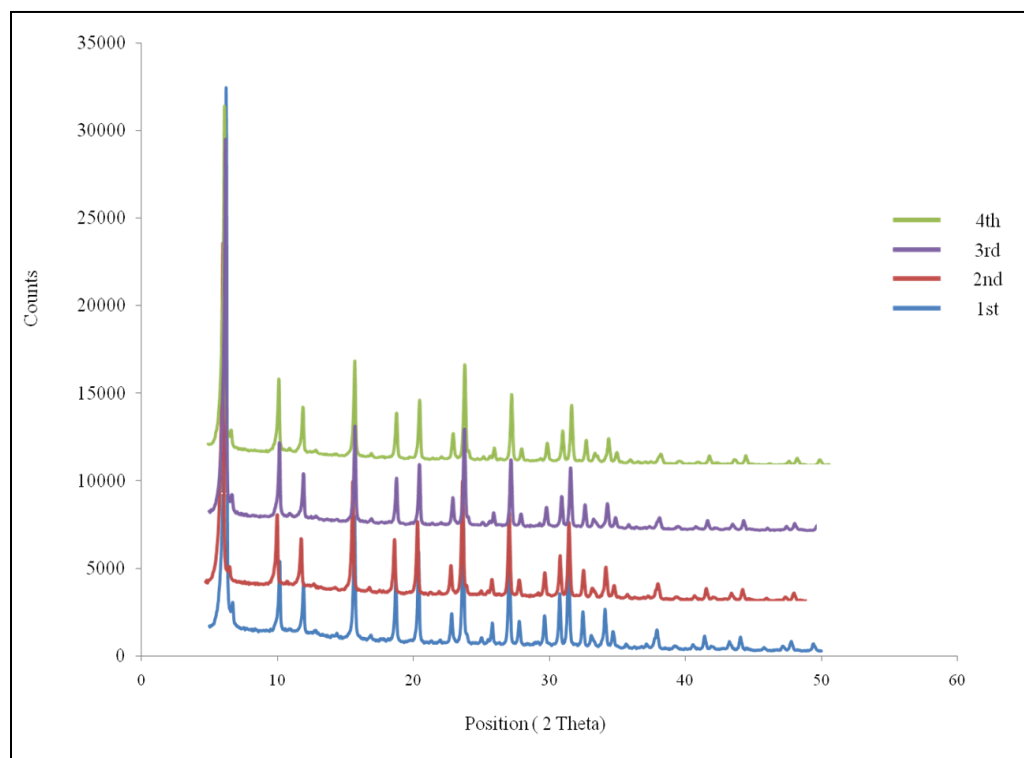


Figure 4-3: XRD pattern of in-house synthesized NH_4Y zeolite after 1- 4 ion exchanges.

As for the SEM/ EDAX analysis, it clearly shows the change in Si/Al ratio and Na content with each ion exchange (Table 4-2). Four EDAX spot analyses were

acquired for each of the mentioned ion exchanges (1 to 4), and then the averages were calculated, as shown in the table below.

Table 4-2: EDAX analysis of the in-house synthesized NH_4Y after 1- 4 ion exchanges.

Element (wt %)	spot #	Ion Exchange				SD
		1 st	2 nd	3 rd	4 th	
Si	1	38.3	41.5	44.0	38.4	
	2	36.2	36.7	48.2	36.3	
	3	39.3	45.7	33.5	36.2	
	4	-	40.7	41.0	37.3	
Average	-	37.9	41.1	41.9	37.0	± 2.4
Al	1	13.7	14.4	14.8	14.8	
	2	13.2	13.4	15.2	13.9	
	3	14.0	15.3	15.7	13.8	
	4	-	14.2	14.3	14.0	
Average	-	13.6	14.3	15.0	14.1	± 0.6
Na	1	2.14	1.2	1.0	0.6	
	2	2.21	1.5	0.8	0.8	
	3	2.48	1.2	0.5	1.0	
	4	-	1.5	1.1	0.7	
Average	-	2.3	1.4	0.8	0.7	± 0.7
Si/Al	1	2.8	2.9	3.0	2.6	
	2	2.7	2.7	3.2	2.6	
	3	2.8	3.0	2.1	2.6	
	4	-	2.9	2.9	2.7	
Average	-	2.8	2.9	2.8	2.6	± 0.7

EDAX is only designed for surface analysis about 2 μm deep as stated earlier (Section 3.3.3.) and clearly its use is indicative of bulk analysis. The variation in the analysis for Si, Al and Na ranges from approximately 7-25% dependent on the amount of the element under study. However, a reasonable indication of Si/Al and of falling Na content with each ion exchange was obtained (Figure 4-4). The conclusion for the Na analysis is that 3-4 ion exchanges are sufficient to extract the available Na^+ from the channels and β – cages.

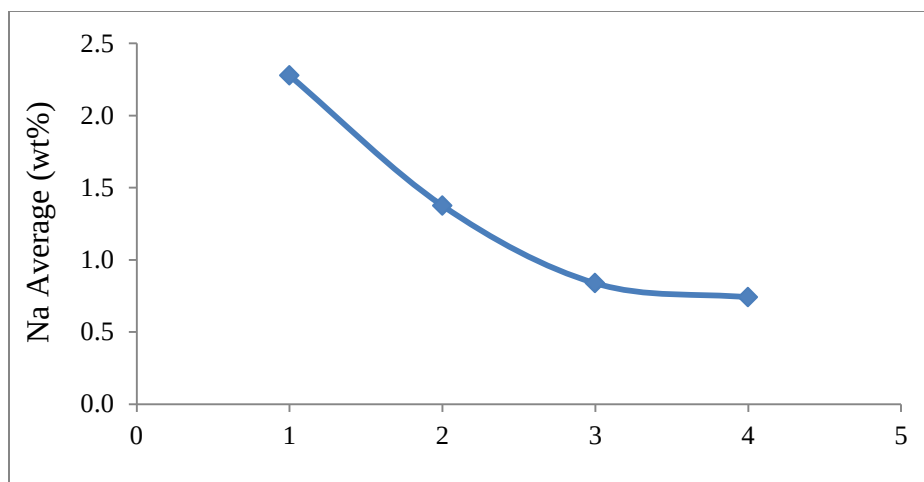


Figure 4-4: Average of Na with each ion exchange.

4.2.2. Comparison of in-house synthesized NH_4Y and a commercial CBV-712

The in-house synthesized NH_4Y sample was compared with a new commercial NH_4USY CBV-712 zeolite using XRD. In this work, both catalysts were studied using the same XRD methodology mentioned in Section 3.3.2 and under the same conditions. The XRD pattern of the in-house synthesized NH_4Y sample was consistent with the XRD pattern of the commercial one. The unit cells of both samples were calculated found to be 24.73 and 24.3 Å, respectively. The difference in the unit cells can be accounted for by the difference of Si/Al ratios, where the Si/Al of the in house synthesized NH_4Y is 2.6, and for the CBV-712 sample is 6. Since the atomic radius of Al is bigger than that of Si atom. As the aluminum was removed to produce USY from the commercial zeolite structure by steaming or chemical treatment, the unit cell size dimension shrinks [79]. The XRD patterns of in-house synthesized NH_4Y and commercial NH_4USY CBV-712 are shown in Figure 4-5.

To check the Si/Al ratio and Na content, EDAX was carried out for comparison and the obtained results were based on the average of 4 spots (Table 4-3).

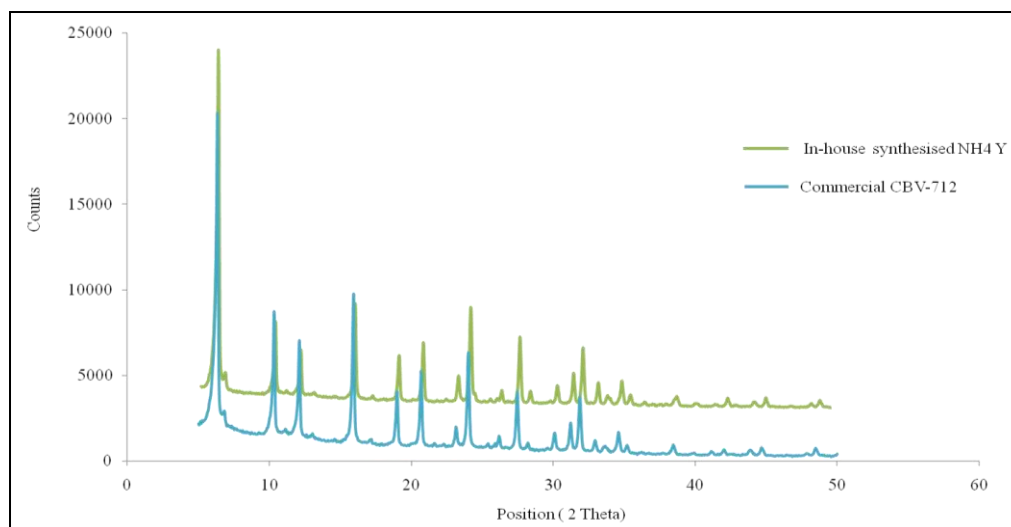


Figure 4-5: XRD patterns of in-house synthesized NH₄Y and NH₄USY CBV-712.

Table 4-3: EDAX analysis of in-house synthesized NH₄Y and NH₄USY CBV-712.

Element (wt%)	Spot #	CBV-712	NH ₄ Y (4 th ion exchange)
Si	1	40.3	38.4
	2	41.5	36.3
	3	40.5	36.2
	4	-	37.3
Average	-	40.8	37.0
Al	1	7.2	14.8
	2	7.2	13.9
	3	7.0	13.8
	4	-	14.0
Average	-	7.1	14.1
Si/Al	1	5.6	2.6
	2	5.8	2.6
	3	5.8	2.6
	4	-	2.7
Average	-	5.7	2.6
Na	1	0.1	0.6
	2	0.1	0.8
	3	0	1.0
	4	-	0.7
Average	-	0.1	0.7

As stated earlier, the Na content of the in-house synthesized sample was 0.8% which was high compared to the commercial CBV-712. The steaming (100% steam, $T_s > 500\text{ }^{\circ}\text{C}$) [79] and leaching (acid leaching) process which produces the ultra-stabilized Y will loosen Na^+ ions and hence the Na content has fallen to 0.1%. The morphology of the in-house synthesized and the commercial CBV-712 was very similar (Figure 4-6).

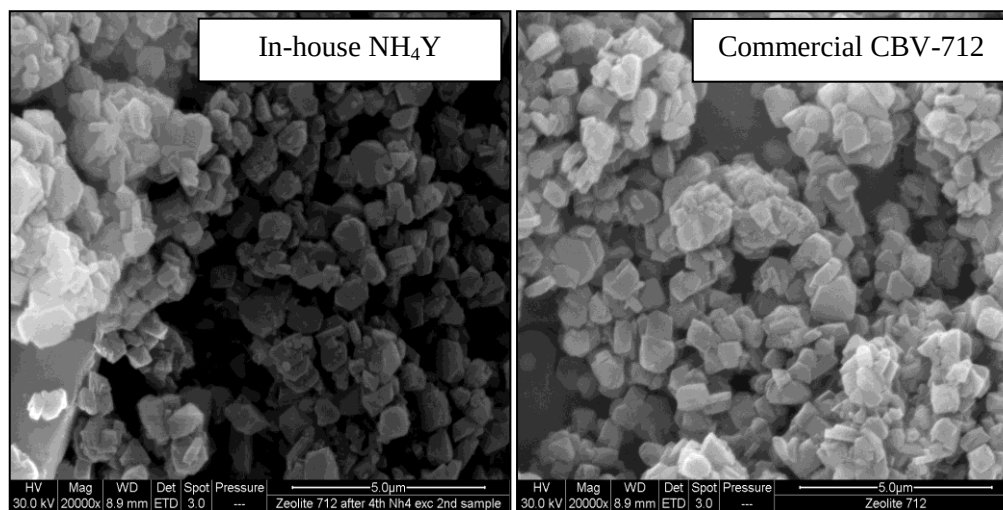


Figure 4-6: SEM images for in-house synthesized NH_4Y and commercial CBV-712.

4.3. Metal Loading and Subsequent Testing of the Bi-Functional Catalysts

This section relates to the characterization of the metal loading of Pt or Ni only and Pt-Ni catalysts and the subsequent testing of the bi-functional mono- and bi-metallic catalysts using CBV-712 USY zeolite as the parent (Section 3.3.3).

4.3.1. ICP- OES analysis

As mentioned earlier, EDAX analysis is not the proper technique to detect elements as it is only a surface technique and hence is less useful at lower levels. Acid digestion followed by ICP-OES was used to determine the actual content of metal loading of the zeolite catalysts. Table 4-4 below summarizes the results obtained noting the quoted instrument elemental analysis error ($\pm 0.3\%$).

Table 4-4: ICP-OES analysis of the zeolite catalysts.

Code	CBV712 + metal loading	Target (wt %)		ICP results (wt %)		ICP error (wt %)
		Pt	Ni	Pt	Ni	
A	CBV712	-	-	-	-	±0.3
B	Pt	1	-	1	-	±0.3
C	Ni	-	1	-	0.5	±0.3
D	Pt, Ni	1	1	0.9	0.5	±0.3
E	Pt, Ni +pH	1	1	0.8	1.1	±0.3
F	Pt, Ni+ pH	1	4	0.8	2.2	±0.3

The results showed that when targeting 1 wt% of Pt, the amount loaded was 1 wt% (catalyst B). However, there appears have been only 50% of the expected Ni loaded content loaded in catalyst C. This was further shown when both Pt and Ni were ion exchanged in catalyst D. Evidence in the literature suggested that some level of pH control was required to a homogeneous distribution within particles as reported [68]. When the pH was adjusted to pH 9 using ammonia solution, the Pt loaded reduced by 10-20%, but the Ni was as expected (1%) as shown in catalyst E. A further increase in Ni concentration however did double the Ni ion exchange in catalyst F however not all the Ni was incorporated. It should be noted that the pH was not monitored during the ion exchange only at the start.

4.3.2. SEM-EDAX characterization of catalysts

The morphology of all the catalysts (A-F) was very similar suggesting no damage during ion exchange as shown in Figure 4-7. In addition, the EDAX results are shown in Figure 4-8 and confirm the presence of the Pt and Ni.

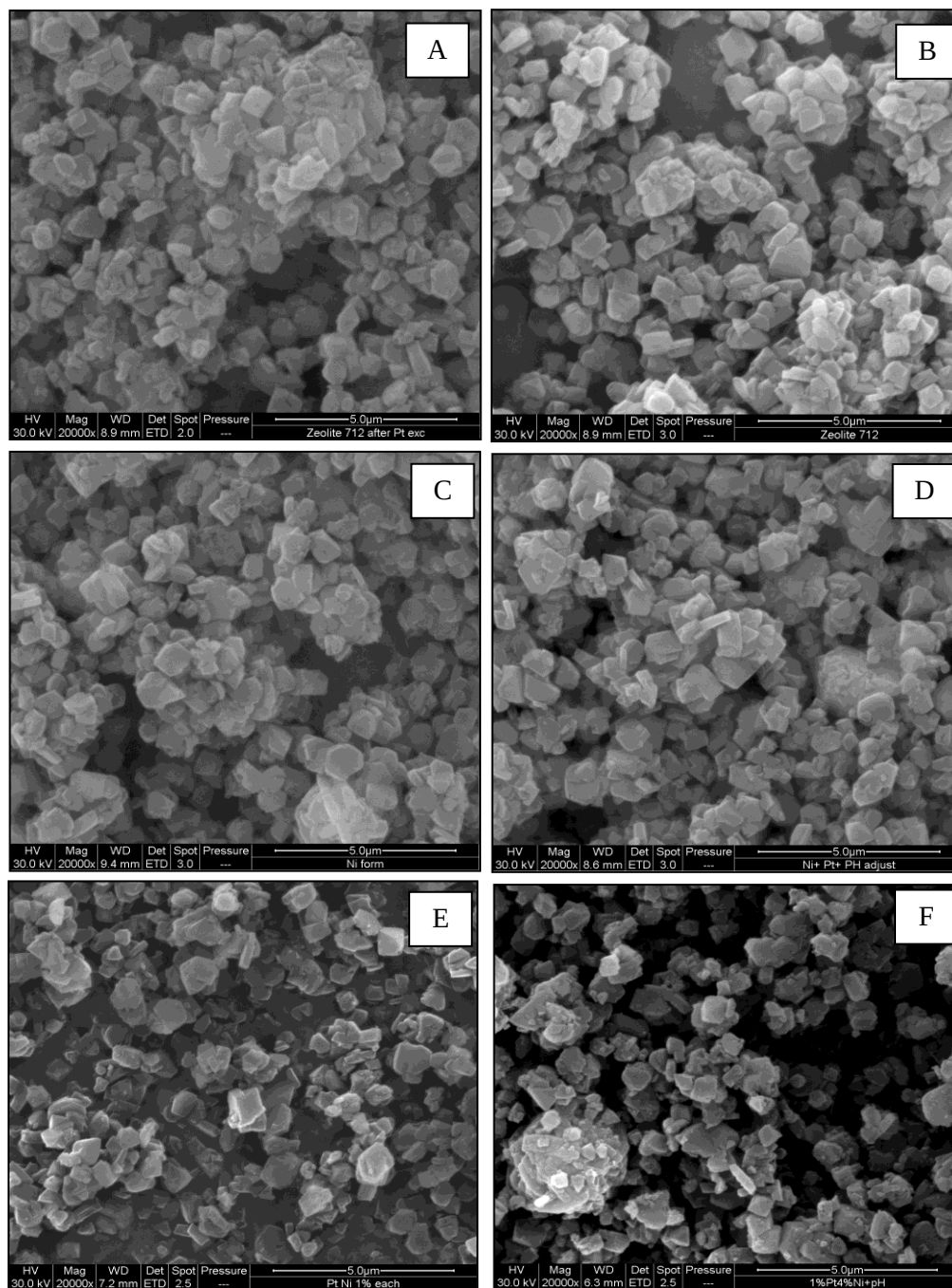


Figure 4-7: SEM images of catalysts (A-F).

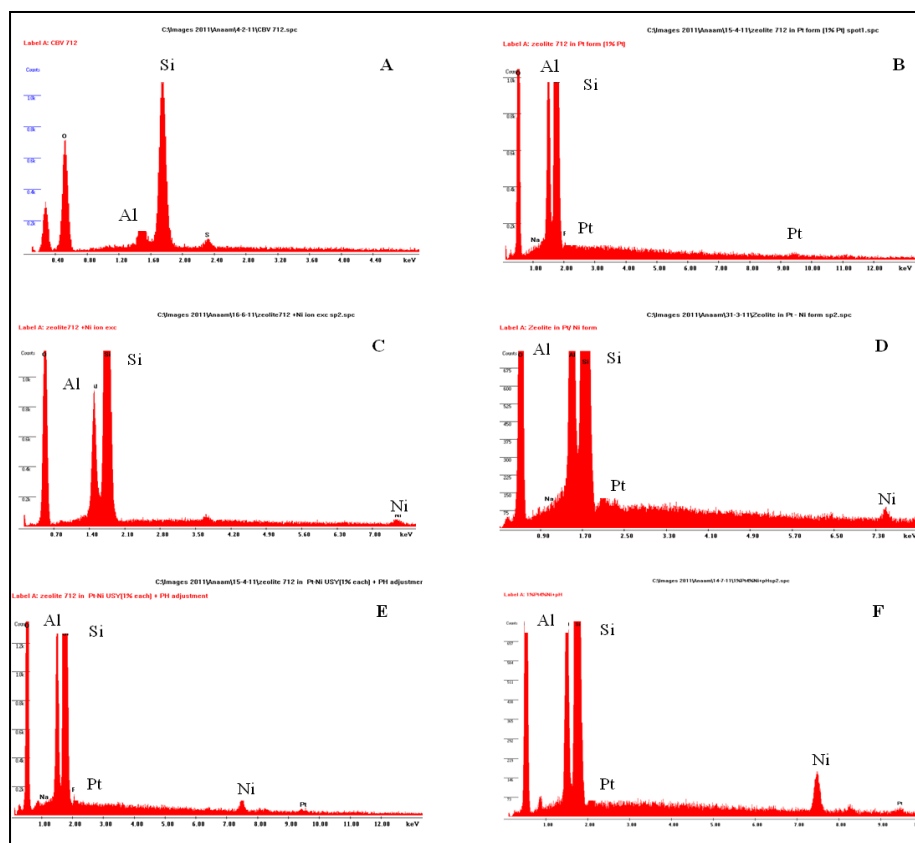


Figure 4-8: Typical EDAX spectra for all the samples.

4.3.3. XRD characterization of catalysts

XRD of the zeolites were used to determine the unit cell and the degree of crystallinity. Where the unit cell calculated using equation 2, the degree of crystallinity can be calculated from the relative intensities of the main peaks using method one / two as mentioned in Section 3.3.2. Method two was found to be more reliable as the first XRD peak is sensitive to the orientation and size distribution of the particles. XRD pattern indicates that the position of peaks and the intensity of all the samples are found to be almost similar with slight changes as shown in Figure 4-9. No further peaks were found which suggests that the samples contain no impurities. Assuming that the crystallinity of CBV-712 USY sample to be 100%, the crystallinity of all the samples relative to CBV-712 USY are in the range between 83.3 and 106.7 % as shown in Table 4-5. This suggests that all the samples were highly crystalline and contains single phase. The

decrease or increase in crystallinity was more than likely due to machine conditions as the samples were not analyzed in the same time. In addition, inadvertent errors in sample preparation might account also for some of the differences. To avoid these problems, a silicon standard could be used as mentioned in Section 3.3.2 [58]. However, since insufficient catalyst was available this was not carried out here. The unit cell for all the samples were cubic and found to range from 24.3 to 24.4 Å, indicating that the unit cell was not affected by the metal loading.

Table 4-5: XRD results of all metal loading catalysts including parent sample.

Catalysts	Unit Cell (Å)	SD	Crystallinity % (method 1)	Crystallinity % (method 2)
A	24.3	0.014	100.0	100.0
B	24.3	0.018	118.1	106.7
C	24.3	0.018	111.3	101.1
D	24.3	0.027	99.1	102.4
E	24.4	0.012	118.3	102.0
F	24.4	0.015	91.6	83.3

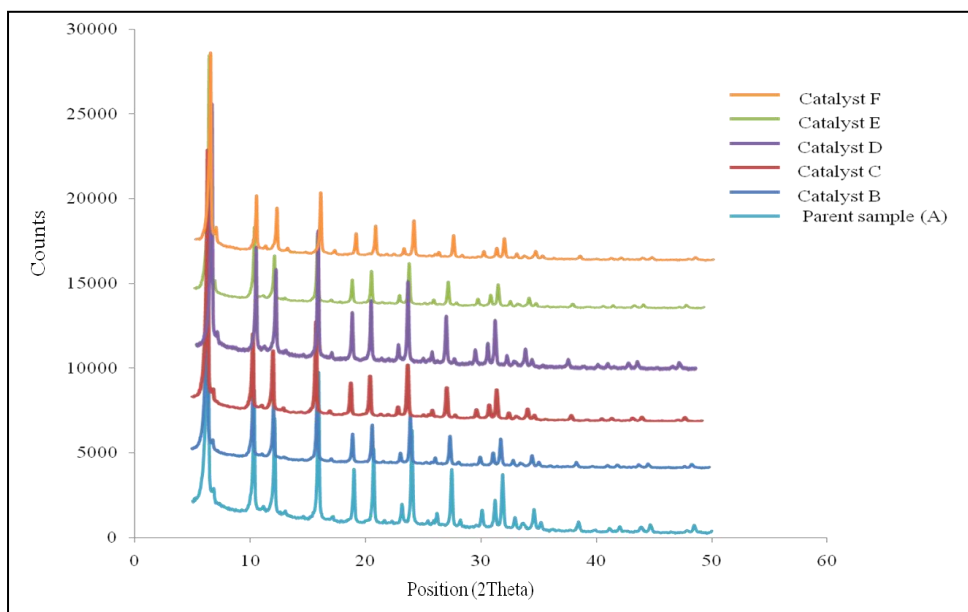


Figure 4-9: XRD pattern of the metal loading catalysts including the parent sample.

4.3.4. TEM characterization of catalysts

The TEM images for the B, D and E samples are shown in Figures 4-10 – 4-12. The black dots are assumed to be Pt and Ni/Pt clusters as mono and bi metallic particles. The average size of the clusters was also measured at 20 nm diameter and found to be 6-10 nm. Based on the atomic radius of Pt and Ni which are 0.138 nm and 0.124 nm, a rough estimation of the number of atoms in a cluster is presented in Table 4-6. Such clusters are considered big in size compared to the pore of the parent sample which can be subjected to thermal mobility during the reduction. Therefore, it is assumed that these metal particles are located outside the pores as reported [8, 48, 80]. In addition, the largest clusters were obtained with Pt only ion exchange. However the clusters were decreased in the case of bimetallic catalysts and hence less surface area and more dispersion therefore more reaction occur according to the literature [40].

Also, it was found that the pH control lead to increasing the clusters size slightly compared to the one without pH control (23 $\rightarrow$ 30). TEM analysis indicated that the average clusters size of the metal increases with increasing the addition of Pt or Ni loading. Table 4-6. It was also found that the metal particles shows various size and shape that lead to lower degree of dispersion of the catalysts as reported [46].

Table 4-6: Estimated cluster size and number of atoms in a cluster by TEM.

Catalyst	B	D	E
Cluster size (nm)	9-10	6-7	8-9
No. of atoms in one cluster	~32	~23	~30

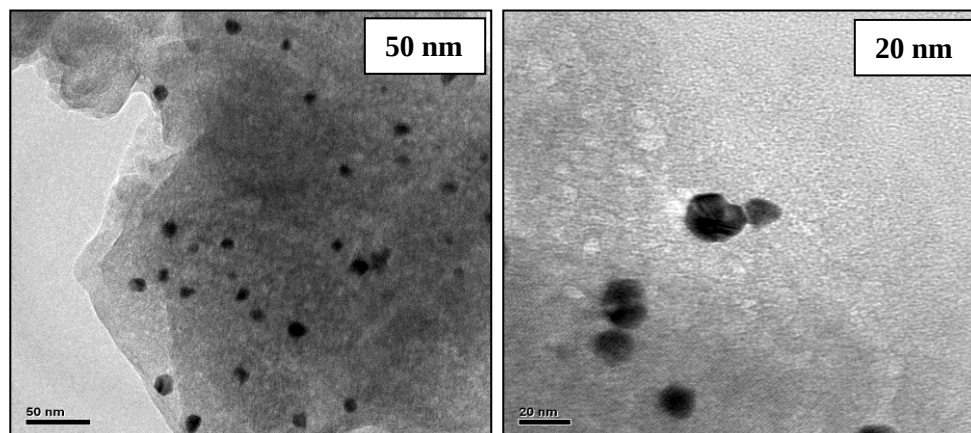


Figure 4-10: TEM images for Pt loading catalyst (B).

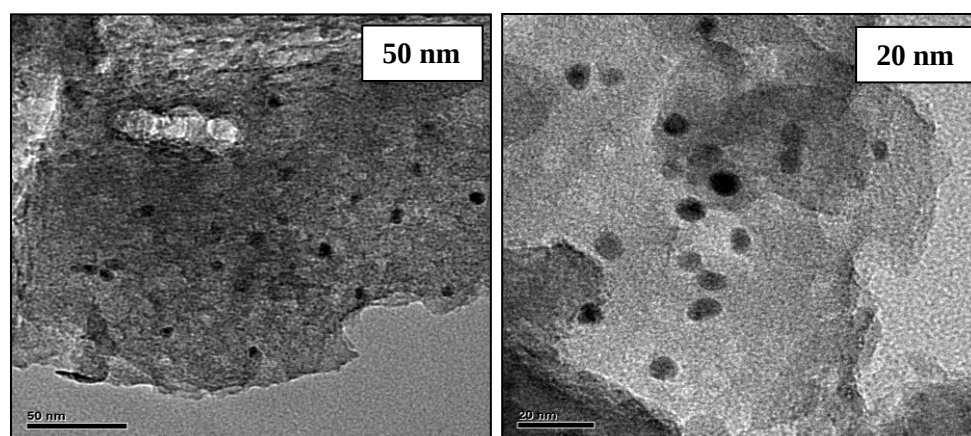


Figure 4-11: TEM images for Pt-Ni loading catalyst (D).

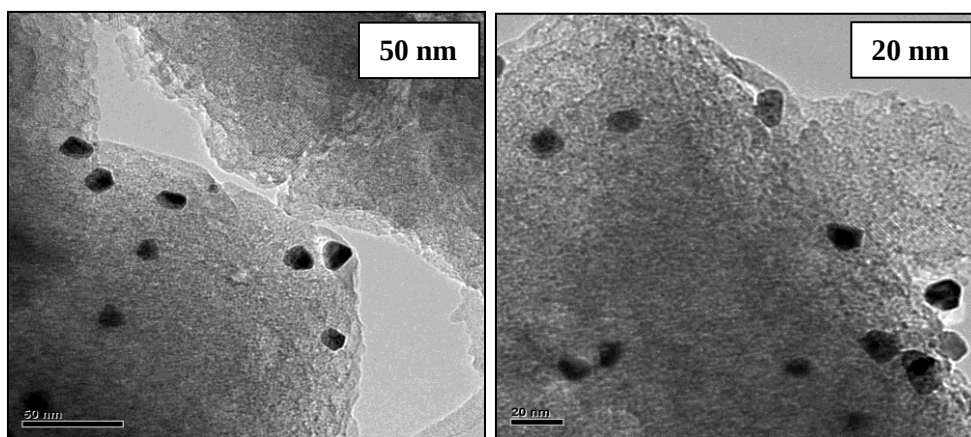


Figure 4-12: TEM images for Pt-Ni loading with pH control catalyst (E).

4.4. Catalytic Testing - Hydroisomerization of *n*-Heptane

The results of hydroisomerization of *n*-heptane are described for a series of metal loaded CBV-712 USY catalysts (B-F) at 230 °C (see Section 3.4.2.).

4.4.1. Calibration of the GC-FID

The GC-FID was calibrated by injecting three times a standard gas mixture containing 1% of C₁-C₅, and the results of the gas analysis are presented in Table 4-7.

Table 4-7: GC-FID results of the standard gas mixture.

Run	Name	Time [Min]	Area [μ V.Min]	Area % [%]
1	C ₁	3.03	4011.4	4.26
	C ₂	3.32	8122.0	8.62
	C ₃	4.22	11978.4	12.71
	iC ₄	5.74	15991.2	16.97
	nC ₄	5.92	15772.7	16.74
	iC ₅	7.80	19378.4	20.56
	nC ₅	8.02	18987.8	20.15
	Total		94242.0	100.00
2	C ₁	3.03	4123.7	4.22
	C ₂	3.32	8349.9	8.54
	C ₃	4.22	12341.6	12.64
	iC ₄	5.74	16504.8	16.89
	nC ₄	5.92	16330.8	16.71
	iC ₅	7.79	20176.3	20.64
	nC ₅	8.01	19916.9	20.38
	Total		97743.9	100.00
3	C ₁	3.03	3928.0	4.35
	C ₂	3.32	7929.4	8.77
	C ₃	4.22	11660.1	12.90
	iC ₄	5.74	15499.5	17.15
	nC ₄	5.93	15165.7	16.78
	iC ₅	7.81	18413.9	20.38
	nC ₅	8.02	17777.2	19.67
	Total		90373.8	100.00

The average of the area under the peaks for each component in each of the three samples was determined as shown in Table 4-8. Then the response factor (RF) was determined by plotting the log of carbon number (log C) of each hydrocarbon of standard gas against the relevant log of response factor (log RF) as shown in Figure 4-15.

Table 4-8: Average of the areas and response factor for each component.

Name	Time [Min]	Average Area [μ V.Min]	Mole (%)	RF (%mole/Area)	log C	log RF
C ₁	3.03	4021.0	1	2.487E-04	0.00	-3.60
C ₂	3.32	8133.8	1	1.229E-04	0.30	-3.91
C ₃	4.22	11993.4	1	8.338E-05	0.48	-4.07
iC ₄	5.74	15998.5	1	6.251E-05	0.60	-4.20
C ₄	5.92	15756.4	1	6.347E-05	0.60	-4.19
iC ₅	7.80	19322.9	1	5.175E-05	0.70	-4.20
C ₅	8.02	18894.0	1	5.293E-05	0.70	-4.28

Using the response factors for the standard gas mixture (C₁-C₅) and applying the straight line equation shown in Figure 4-13, the response factors of higher hydrocarbons (C₆-C₈) were also estimated as shown in the Table 4-9. This allowed the analysis of every component in the gas produced from the fixed bed reactor taking (FBR).

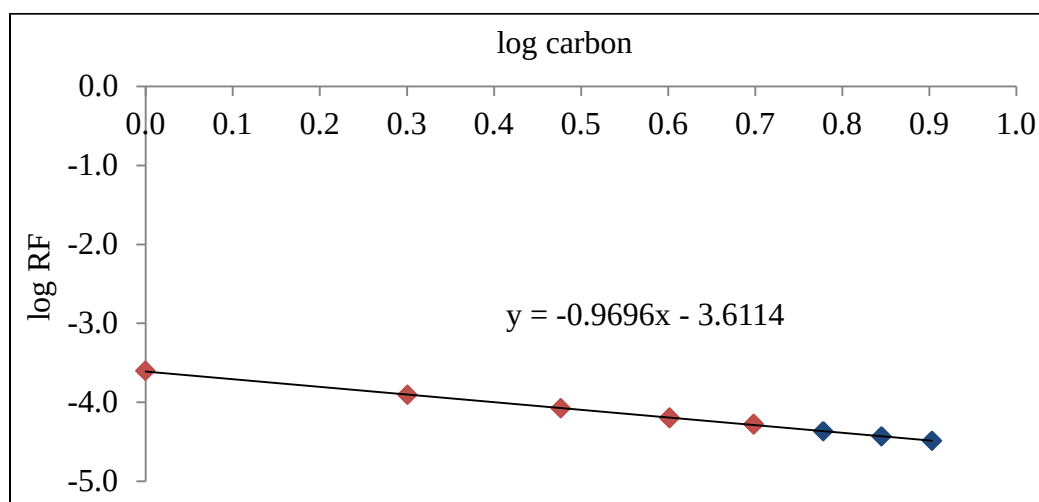


Figure 4-13: Log carbon number against log response factor.

Table 4-9: Response factor of C₆-C₈ hydrocarbons extrapolated from the C₁-C₅ calibration.

C no.	log C	log RF	RF
6	0.78	-4.37	4.306E-05
7	0.85	-4.43	3.708E-05
8	0.90	-4.49	3.258E-05

4.4.2. Mass balance

The mass balances for all catalytic reactions were determined based on the amount of liquid pumped into the reactor and the observed gas and liquid products, where the liquid in and out was measured gravimetrically and the liquid out was calculated from GC results. Then, the errors were calculated based on the obtained mass balance which is presented in Table 4-10.

Mass balances for all runs at 30 minutes-on-stream were expected to be low (typically 37-46%) as the reactor stabilized. By 60 minutes-on-stream constant mass balances were obtained.

Overall, the mass balances were lower than expected as 90% $\pm$ 5% was the target. However, a hair-line fracture was discovered in a joint under the condenser. On replacing this part of the reactor, the mass balances for catalyst F were close to the expected range (typically 85 $\pm$ 10%). For all experiments when excluding the 30 minutes-on-stream value, the mass balances averaged $\sim$ 80% and the results for the conversion and selectivity were seen as representative of the catalyst performance.

Table 4-10: Mass balances for all catalytic reactions.

Catalyst	TOS, mins	Liquid in, g	Liquid out, g	Gas out, g	All out, g	HC Mass Balance, %	Error (%)
B	30	2.6	1.0	0.10	1.2	46	54
	60	2.6	1.6	0.30	1.9	74	26
	120	5.1	3.6	0.30	4.0	76	24
	1440	2.6	1.6	0.10	1.7	65	35
	2880	2.6	1.6	0.10	1.7	65	35
	4425	2.6	1.7	0.10	1.8	69	31
	5855	2.6	1.7	0.20	1.9	73	27
D	30	2.6	0.8	0.15	1.0	38	62
	60	2.6	1.5	0.36	1.9	73	27
	1704	2.6	1.5	0.16	1.7	66	34
	2880	2.6	1.7	0.16	1.8	72	28
	5040	2.6	1.9	0.17	2.0	79	21
	6360	2.6	1.9	0.14	2.0	79	21
E	30	2.6	1.0	0.20	1.1	44	56
	60	2.6	1.7	0.30	2.0	79	21
	120	5.1	3.2	0.70	4.0	77	23
	1410	2.6	1.5	0.20	1.7	66	34
	2880	2.6	1.6	0.10	1.8	69	31
	4320	2.6	1.6	0.20	1.8	70	30
	6420	2.6	1.8	0.20	2.0	78	22
F	30	2.6	0.8	0.10	0.9	37	63
	60	2.6	2.0	0.40	2.4	92	8
	120	5.1	3.6	0.40	4.0	79	21
	1560	2.6	2.3	0.20	2.5	98	2
	3000	2.6	1.8	0.20	1.9	74	26
	4440	2.6	1.9	0.20	2.1	80	20
	5880	2.6	2.0	0.20	2.2	84	16

4.4.3. Temperature profile across the catalytic bed

The temperature profile across the catalytic bed was measured as described in Section 4.3.2 before starting the reaction and then, at 30, 60 and 120 minutes

(min) from the time n-heptane was introduced into the reactor. Subsequently the profile was measured once a day until testing was complete. Clearly all datasets showed a warming of the catalyst bed (~ 2.5 - 3.0 °C) due to the slightly exothermic hydroisomerization reaction [81] as seen for the catalyst shown in Figure 4-14.

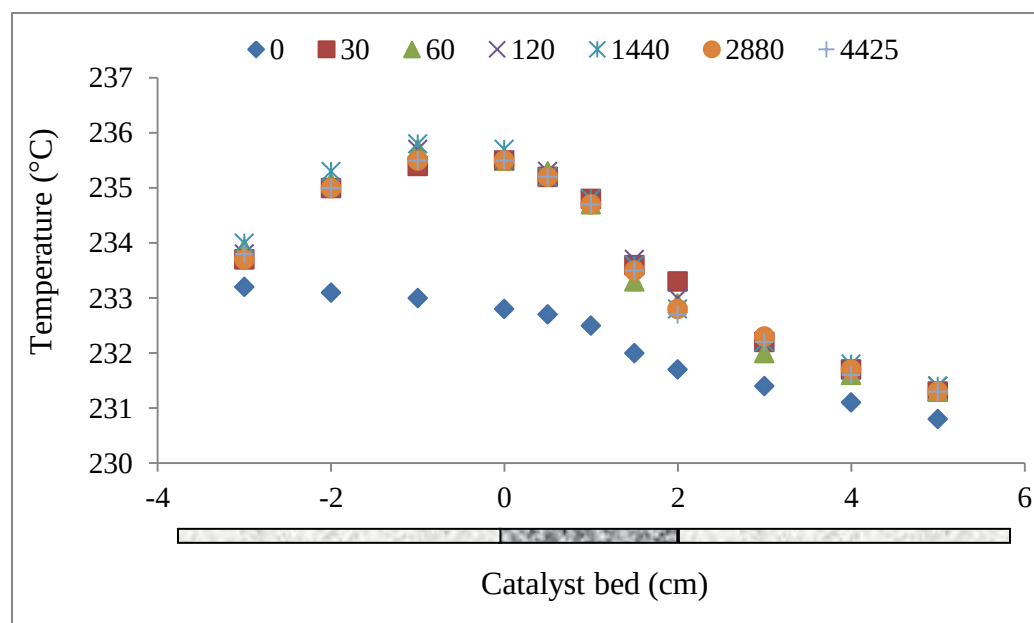


Figure 4-14: Temperature profiles across the catalytic bed at different times-on-stream for the 1% Pt catalyst (B) .

The reaction using the Ni only catalyst (C) showed very low conversion (typically 2-3%) and deactivated rapidly and will not be discussed further. The temperature profiles for all catalytic runs were compared from the start until end of the experiment. Each point shown in Figure 4-15 represents an average of the 5 points in the bed and was plotted against time-on-stream. The experiments were only compared from 120 minutes-on-stream to allow for the reactor to have stabilized.

Before introducing the feedstock, the temperature profile of the catalytic bed was always in the range 231 to 232 °C. The catalyst bed temperature increased when feed was introduced into the reactor. For catalysts B, E and F, the bed temperature rose to ~ 234.4 °C ± 0.1 °C and stabilized after 120 minutes of starting the reaction. The bed temperature for catalyst 1% Pt (B) continued to be stable until end of the

reaction (~6000 min) and this can probably be attributed to Pt suppressing deactivation. However, catalyst E and F were stable up to 4320 and 4440 minutes then the temperature started falling. This might be due to the presence of Ni and might indicate that the Ni or Pt-Ni sites are deactivating. Catalyst D had a different behavior when compared to catalysts B, E and F, where the temperature increased initially but was not stable and started dropped noticeably.

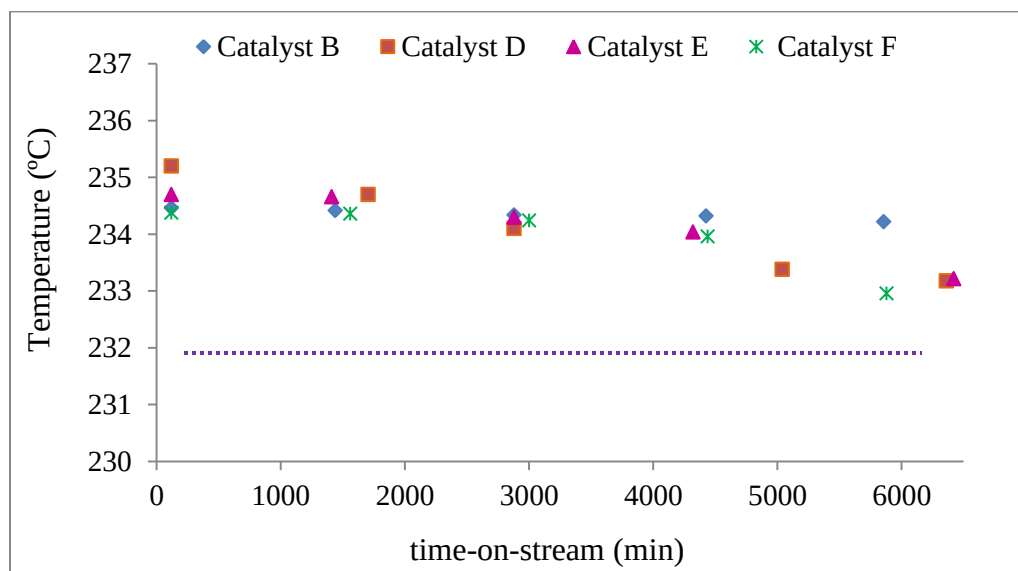


Figure 4-15: Average of temperature profiles across the catalytic bed at different times-on-stream for all the catalytic testings (the dotted line represents the temperature for no reaction).

4.4.4. Overall *n*-Heptane conversion (wt%)

The conversions in wt% are plotted against times-on-stream in minutes for the catalytic reactions B, D, E and F are presented in Figure 4-16. The overall conversion was determined as shown in equation (4). The yield calculation method and W/F calculation are shown in Appendix 6.

$$((C_{7 \text{ in}} - C_{7 \text{ unreacted}}) / C_{7 \text{ in}}) \times 100 \quad (4)$$

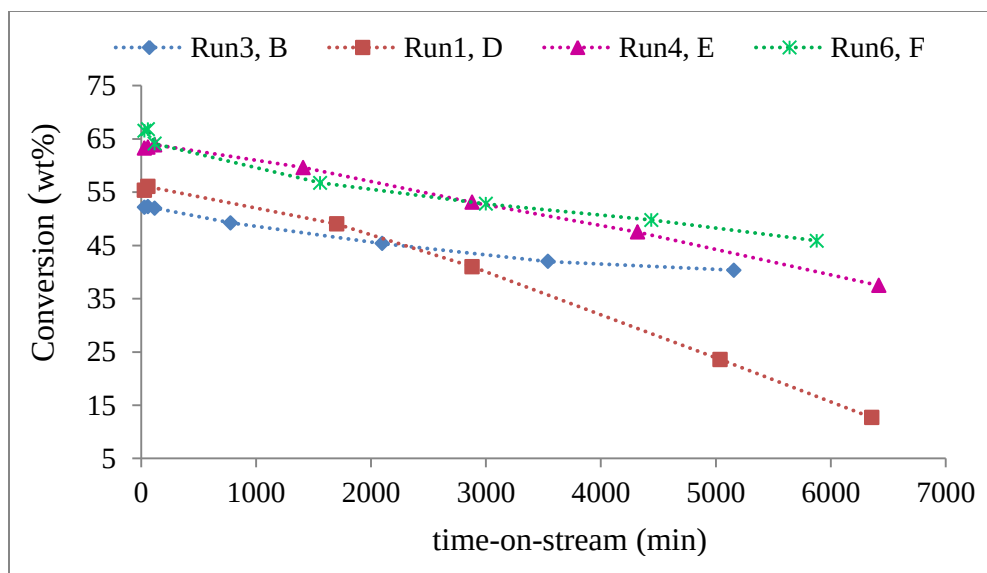


Figure 4-16: Conversion (wt%) vs. time-on-stream (min) for reactions B, D, E and F.

The lowest initial conversion was obtained with catalyst 1% Pt (B). However, it was the most stable range from 52.2 wt%, and 40.3 wt% at the end of the experiment. The initial conversion of the bimetallic catalysts E and F was better than catalyst B. Both catalysts had similar behavior throughout the experiment up to 4000 min). The highest initial conversion of the bimetallic catalysts was shown in catalyst F (66.5 wt%) followed by E (63.3 wt%), both with pH control when metal loading and then D (55.3 wt%). In terms of stability of these bimetallic catalysts, catalyst F (1% Pt 2% Ni with pH control) was the most stable followed by catalyst E indicating that the control of pH on ion exchange leads to improved conversion. However, increased Ni content in F namely double catalyst E seemed to have little influence. Catalyst D was the least stable of all the catalysts with a very low conversion after 6000 minutes due to catalyst deactivation and this was attributed to the lack of pH control during ion exchange leading to poorly dispersed large metal particles.

4.4.5. Selectivity to isomerization (wt%)

The selectivity to isomerization in wt% against time-on-stream in minutes for catalysts B, D, E and F are shown in Figure 4-17 and as expected the C₇ isomers are the major products under the reaction conditions used in this dissertation. The selectivity to isomerization was determined according to equation (5).

$$\text{Selectivity to isomerization (wt \%)} = (\Sigma iC_7 / \Sigma \text{ products}) \times 100 \quad (5)$$

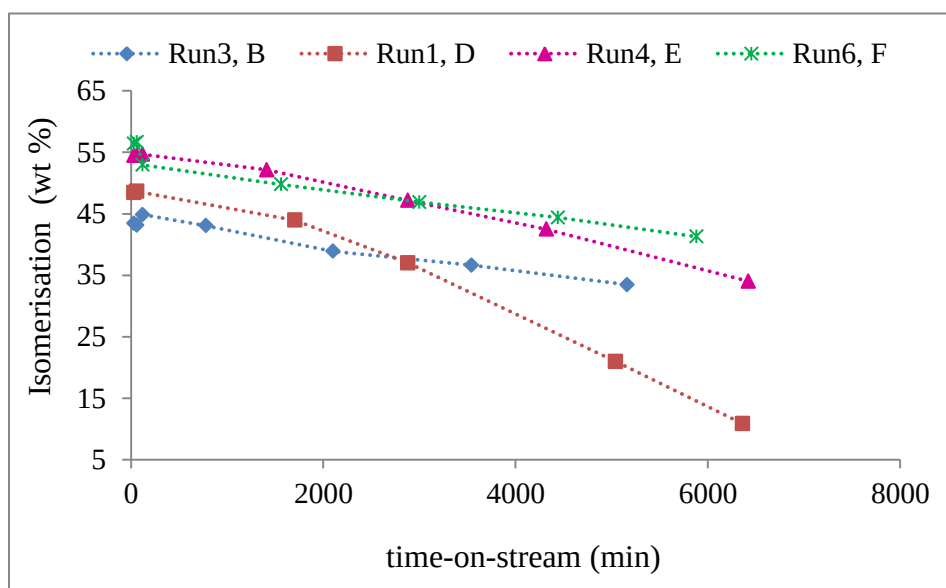


Figure 4-17: Isomerization (wt%) vs. time-on-stream (min) for reactions B, D, E and F.

Catalyst B and F showed similar trends with an initial drop in isomerization activity following long term stability in isomerization activity. Catalyst D and E were also similar to each other but deactivated to different degrees, where D was much more than E from the initial introduction of *n*-heptane. Maximum isomerization was attained in catalysts E and F which were 56.4 and 54.5 wt% isomers, respectively. These were followed by catalyst C which gave 48.4 wt% isomers and the least isomers was obtained with catalyst D. This indicates that the bi-metallic catalysts enhance the selectivity to isomers and that the isomer selectivity increased with pH control. Using GC-MS, the following isomers were identified; 2-methyl pentane (2MP), 3-methyl pentane (3MP), 3-ethyl pentane (3EP) 2-methyl hexane (2MH), 3-methyl hexane (3MH), 2,2-dimethyl pentane

(2,2DMP), 2,3-dimethyl pentane (2,3DMP), 3,3-dimethyl pentane (3,3DMP), 2,4-dimethyl pentane (2,4DMP) and 2,2,3-trimethyl butane (2,2,3TMB) are the major obtained products due to structural rearrangement (conversion) of n-heptane. Very small amounts of cyclised and aromatized products were also detected such as toluene, methyl cyclohexane and ethyl cyclopentane. See Appendix-7 a typical GC-MS data of the isomers obtained (catalyst B). Unfortunately time did not allow completing a full comparison of the individual isomers using GC-MS; this could form part of a subsequent dissertation.

4.4.6. Selectivity to cracking (wt%)

The selectivity to cracking in wt% against time-on-stream in minutes for catalysts B, D, E and F are shown in Figure 4-18. The selectivity to cracking was calculated as shown in equation (6).

$$\text{Selectivity to cracking (wt\%)} = (\Sigma \text{ cracked} / \Sigma \text{ products}) \times 100 \quad (6)$$

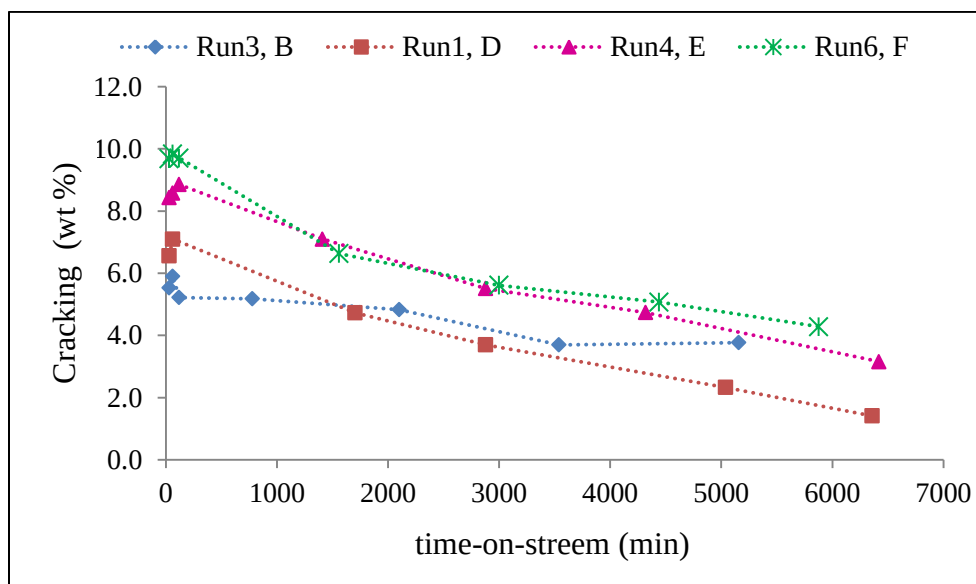


Figure 4-18: Cracking (wt%) vs. time-on-stream (min) for reactions B, D, E and F.

The results showed that some of the catalysts are stable with respect to cracked products. All catalysts showed a decrease in cracked products with time-on-

stream. Catalyst B decreased much less than catalyst D, E and F. Catalysts D, E and F were all similar but the Ni-Pt catalyst D without pH was showing the greatest decrease. Also, it was observed that catalysts E and F (pH treatment) gave maximum cracked products. For catalysts D and E, although the initial percentage of the cracked products formation was different, it was found that both catalysts had similar behavior and they decrease rapidly over time. Overall, the formation of cracked products can be attributed to increased activity and potentially acidity. Increased activity will lead to an increase in coke formation and hence lead to active site poisoning and subsequent reduction in activity.

4.5. Characterization of the Spent Catalysts

4.5.1. TGA analysis

As catalyst deactivation was caused predominantly by coke formation in this work by means of poisoning active sites and blocking catalyst pores [54], TGA analysis was carried out on all spent catalysts in order to determine the coke content. Each sample was divided into 3 parts; top, middle and bottom of the catalyst bed. For the all catalysts the coke contents were generally low. As can be clearly seen in Table 4-11 and 4-12, the amount of coke on the top is higher compared to other parts as the reaction takes place mostly on the top then on the middle of the catalysts. The highest coke content was obtained with catalyst C (Ni) obtained after 120 minutes confirming the quick deactivation of Ni loaded catalyst and was probably due to the acidic function of catalyst dominating. The level of Ni was comparable with that of Pt catalyst (B) but the activity for hydrogenation-dehydrogenation was much lower.

Table 4-11: Coke content for spent catalysts B and C.

Spent Catalyst	Coke Content wt%		
	Top	Middle	Bottom
1% Pt (B)	0.5	0.4	0.3
0.5% Ni (C)	2.3	1.8	1.6

Catalyst D showed the next highest coke content (0.9 at the top) and again indicates a lower hydrogen transfer potential. This has improved when the ion exchange was pH controlled for catalyst E and F. Catalyst B, E and F have comparable coke content. The TGA thermograms for the coke content of catalyst B and C are shown in Figure 4-19 and 4-20. The TGA thermograms for catalysts (D-F) are presented in Appendix-8.

Table 4-12: Coke content for spent catalysts B, D, E and F.

Spent Catalyst	Coke Content wt%		
	Top	Middle	Bottom
1% Pt (B)	0.5	0.4	0.3
0.9% Pt, 0.5% Ni (D)	0.9	0.8	0.6
0.8% Pt, 1.1% Ni (E)	0.6	0.5	0.4
0.8% Pt, 2.2% Ni (F)	0.8	0.4	0.3

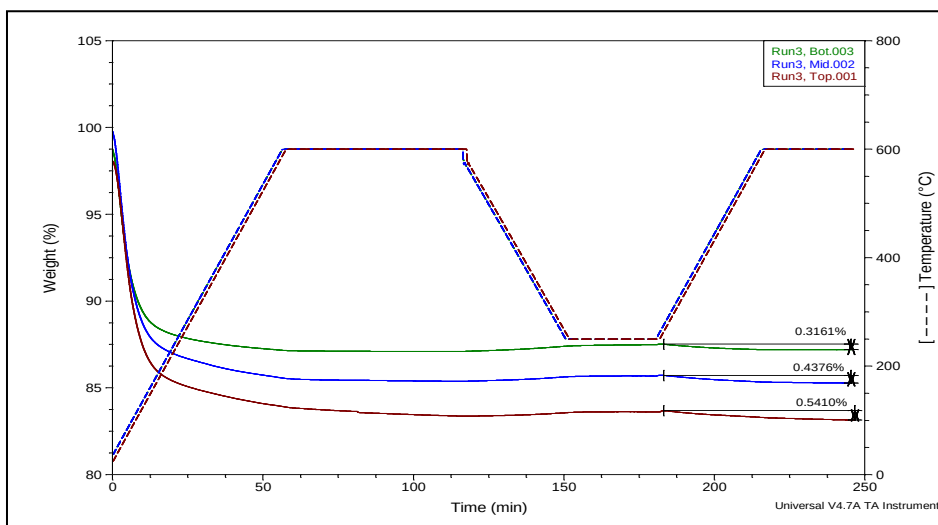


Figure 4-19: TGA analysis for spent catalyst B (bottom, middle and top).

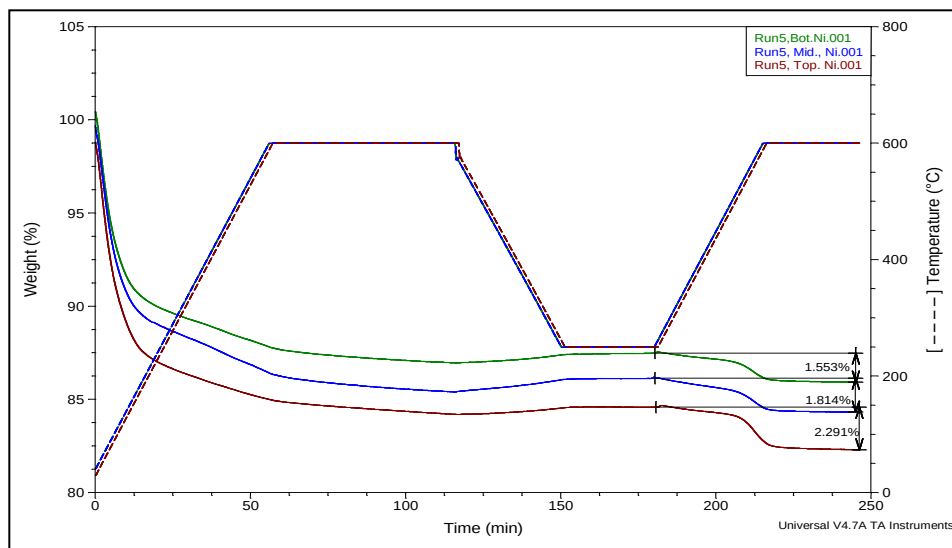


Figure 4-20: TGA analysis for spent catalyst C (bottom, middle and top).

4.5.2. XRD analysis

XRD was also carried out on the spent catalysts to determine any change in crystallinity and the unit cell after the catalytic testing as shown in Figure 4-21. The position of peaks and the intensity of all the samples are found to be almost similar. The decrease in crystallinity post catalysts could be due to the fact that a part of the framework structure has collapsed leading to an increased amount of amorphous phase. The unit cell for all the samples remains the same. The following Table 4-13 summarizes the XRD results of the spent catalysts.

Table 4-13: XRD results of all the spent catalysts.

Catalysts	Unit Cell (Å)	SD	Crystallinity % (method 1)	Crystallinity % (method 2)
B	24.3	0.02	87.1	78.8
C	24.3	0.02	89.5	73.9
D	24.3	0.03	74.0	72.9
E	24.3	0.01	77.5	72.7
F	24.3	0.02	79.7	77.8

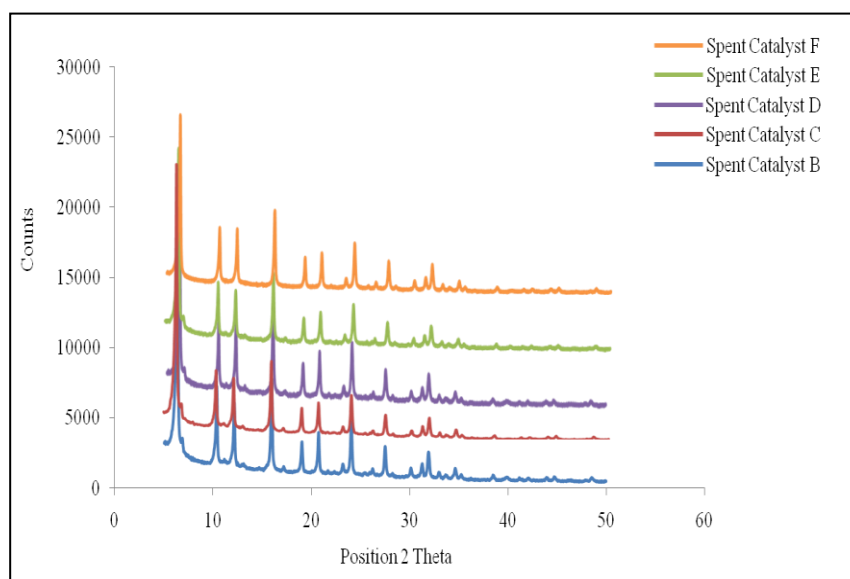


Figure 4-21: XRD pattern of spent catalysts (B-F).

4.5.3. TEM analysis

TEM analysis for the spent catalysts B, D and F after the catalytic testing show no differences compared to the fresh catalyst before reaction in terms of metal cluster size (Figures 4-22- 4-24).

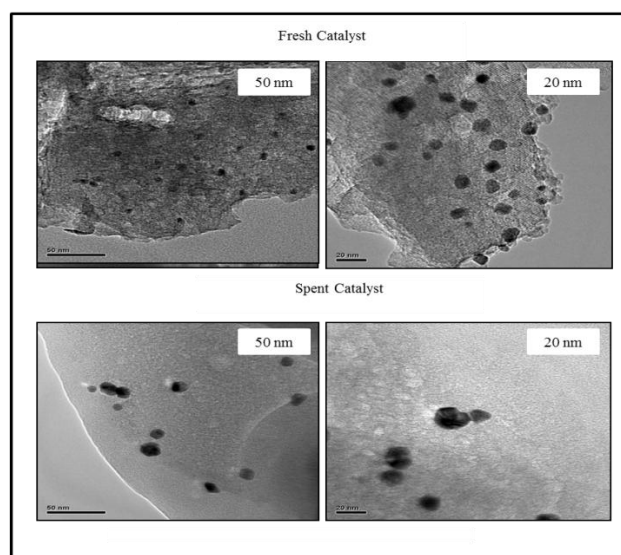


Figure 4-22: TEM images for catalyst B before and after testing.

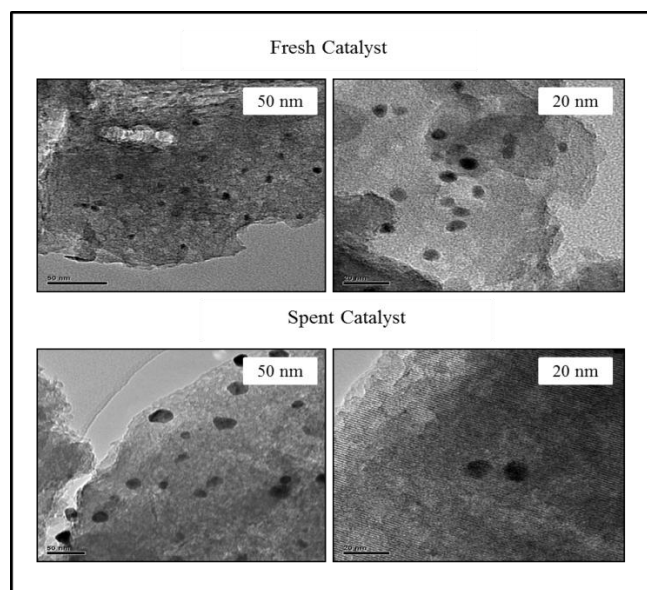


Figure 4-23: TEM images for catalyst D before and after testing.

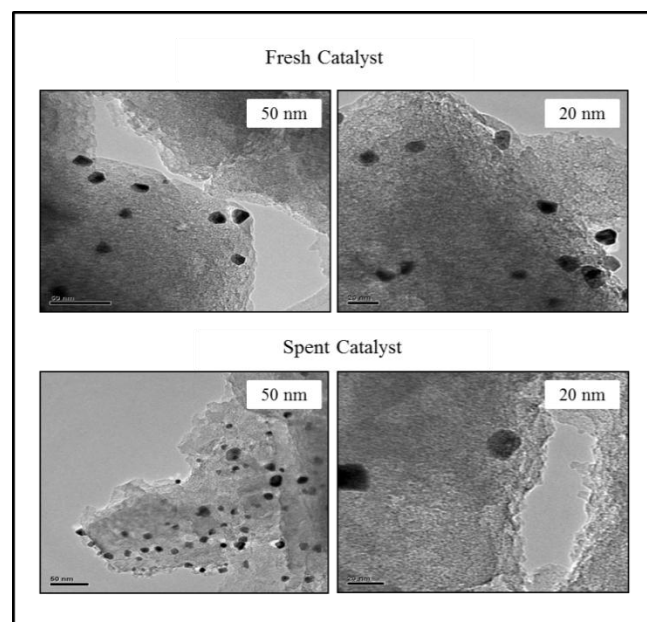


Figure 4-24: TEM images for catalyst E before and after testing.

CHAPTER FIVE

CONCLUSIONS AND FUTURE WORK

In this dissertation, the synthesis and characterization of a range of Pt / Pt-Ni CBV-712 USY catalysts was carried out. In addition, selected catalysts were tested for n-heptane hydroisomerization reaction at 230 °C and contact time (WHSV of 5.13, h⁻¹) to determine their activity and lifetime. The following conclusions could be drawn:

1. The in house synthesized zeolite Y was successfully synthesized and this was confirmed by XRD, SEM and EDAX and by comparison with a commercial zeolite Y. A crystallization time of 24 hours was sufficient for the producing pure Y phase of zeolite.
2. The results suggested that three to four times ion exchanges were sufficient to extract the available Na⁺ from the channels and β – cages of zeolite structure and produce NH₄Y (with Na level at 0.7 wt%).
3. The in-house synthesized NH₄Y sample was compared with a new commercial NH₄USY CBV-712 zeolite using XRD and SEM. Difference in the unit cells observed can be accounted for by the difference of Si/Al ratios, where higher unit cell was obtained for the in house synthesised due to its low Si/Al ratio when compared to the commercial CBV-712. As the aluminum was removed by steaming or chemical treatment from USY, the reference CBV-712 zeolite structure, the unit cell size dimension contracts. In addition, steaming and acid leaching process is required to loosen Na ions to 0.1% from zeolite structure to produce the ultra-stabilized Y catalyst.

4. Catalytic testing showed that although Pt-Ni catalysts were initially more active, their activity decreased, and the 1 wt% Pt catalyst was stable up to 6000 minutes although it was initially less active.
5. The competitive Pt and Ni ion exchange was problematic and clear evidence for pH control during competitive ion exchange was obtained. When pH was not controlled, the Pt-Ni catalyst deactivated significantly over the period of testing.
6. As stated the 1 wt% Pt catalyst was the most stable catalyst whereas the 0.5 wt% Ni catalyst showed poor activity and deactivated immediately.
7. Ignoring the Ni only catalysts and the Pt-Ni without pH control, selectivity to isomers was similar in all other catalysts Overall, Pt-Ni bimetallic catalysts with some pH control are appropriate for the isomerization. However, there are problematic with long term stability.

The results in this dissertation point to three key areas which could be covered further for the hydroisomerization:

1. Activation of the metals on the catalyst

The catalysts were reduced in a hydrogen atmosphere at 450 °C for 4 hours at a flow rate of 100ml/ min in order to convert the metal ions into their elemental form. However, it was found by coincidence that the sintering temperature for Ni and Pt are 500 °C and 570 °C, respectively [82] which are relatively close to the used reduction temperature. Therefore, finding the optimum condition for reduction could be a subject of further investigation

2. Control of pH during ion exchange

Since some pH control using ammonia solution has improved the catalytic and the stability of the bi-metallic Pt-Ni catalysts, study the optimum pH control might be an interesting part of future research. It could also be interesting to

compare between the competitive and sequential ion exchange with pH control.

3. Investigation of the isomers

A full investigation of the individual isomers obtained using GC-MS to determine the level of mono-, di- and tri- branched alkanes. The investigation of isomers is also a key for determining the influence of acidity, metal function and structure sensitivity in a range of USY catalysts from different post-synthetic treatments (e.g. acid leaching and streaming). The study could be extended to investigate other zeolite structures such as zeolite β and mordenite. Optimization of GC-MS methods to allow optimum separation could also be needed.

REFERENCES

1. Van de Runstratt, A., 1997. *Adsorption effects in acid catalysis by zeolites*. Thesis. Eindhoven University of Technology, pp. 1-41.
2. Guisnet, M., and Ribeiro, F. R., 2011. *Deactivation and regeneration of zeolite catalysts*. Imperial College Press, pp. 3-29.
3. Flanigen, E. M., Zeolites and molecular sieves. An historical perspective. In: Bekkum, H., et al., ed. 2001. *Studies in surface science and catalysis 137*. Amsterdam: Elsevier Science, pp. 10-32.
4. Degnan, T.F., 2000. Applications of zeolites in petroleum refining. *Topics in Catalysis* **13**, pp. 349-356.
5. Rahman, M. M., Hasnida, N., and Wan Nik, W. B., 2009. Preparation of zeolite Y using local raw material rice husk as a silica source. *Journal of Scientific Research*, **1**(2), pp. 285-291.
6. Ruren, X., et al., 2007. Chemistry of zeolites and related porous materials synthesis and structure. Wiley-Interscience, pp. 1-50.
7. Fúnez, A., et al., 2008. Assessment of dominant factors affecting liquid phase hydroisomerization on bifunctional zeolites. *Applied Catalysis A*, **349**(1-2), pp. 29-39.
8. Eswaeamoorthi, I., and Lingappan, N., 2004. Ni-Pt loaded silicoaluminophosphate molecular sieves for hydroisomerisation of n-heptane. *Journal of Molecular Catalysis A: Chemical*, **218**, pp. 229-239.
9. Crønstedt, A.F., and Stockholm, A. H., 18 (1756) 120. Refrenced in: Bekkum, H., et al., 2001. *Introduction to zeolite science and practice 137*. 2nd ed, Amsterdam: Elsevier Science, pp. 5.

10. Wong, T.W., 2009. *Handbook of zeolite: structure, properties and applications*. Nova Science, pp. preface.
11. Wachter, W.A., and Rouge, B., 1982. Exxon Research & Engineering Co. *Method of ion exchange zeolites*. United States Patent 4,346,067.
12. Moscou, L., The zeolite scene. In: Bekkum, H., et al., ed. 1991. *Studies in surface science and catalysis 58*. Amsterdam: Elsevier Science, pp. 2-7.
13. Roland, E., and Kleinschmit, P., 2005. Zeolite. In: *Ullmann's Encyclopedia of Industrial Chemistry*. Wiley, pp. 1-7.
14. Barrer, R.M., 1982. *Hydrothermal chemistry of zeolites*. London: Academic Press, Inc, pp. 151-156.
15. Sato, K., et al., 2003. Structural changes of Y zeolites during ion exchange treatment: effects of Si/Al ratio of the starting NaY. *Microporous and Mesoporous Materials*, **59**(2-3), pp. 133-146.
16. Weitkamp, J., 2000. Zeolites and catalysis. *Solid State Ionics*, **131**(1-2), pp. 175-188.
17. McCusker, L. B., Zeolites structures. In: Bekkum, H., et al., ed. 2001. *Studies in surface science and catalysis 137*. Amsterdam: Elsevier Science, pp. 37-44.
18. Available via Google <<http://www.iza-structure.org/databases/>> [Accessed: 4 April 2011].
19. Koningsveld, H., Structural subunits in silicate and phosphate structures. In: Bekkum, H., et al., ed. 1991. *Studies in surface science and catalysis 58*. Amsterdam: Elsevier Science, pp. 36.
20. Niwa, M., Katada, N., and Okumura, K., 2010. *Characterization and design of zeolite catalysts: solid acidity, shape selectivity and loading properties*. Springer Series in Materials Science, pp. 1-6.

21. Htay, M. M., and Oo, M. M., 2008. Preparation of zeolite Y catalyst for petroleum. *World Academy of Science, Engineering and Technology*, **48**, pp. 114-120.
22. Baerlocher, C., Meier, W., and Olson, D., 2007. *Atlas of zeolite framework types*. 6th ed. Elsevier, pp. 140-141.
23. Marques, J.P., et al., 2003. Infrared spectroscopic study of the acid properties of dealuminated BEA zeolites. *Microporous and Mesoporous Materials*, **60**(1-3), pp. 251-262.
24. Ribeiro, F. R., and Rodrigues, A., 1984. *Zeolites: science and technology*. Martinus Nijhoff, pp. 327-338.
25. Beyer, H. K., 2002. Dealumination techniques for zeolites. In: *Molecular sieves*, vol. 3. Springer-Verlag, pp. 204-248.
26. Tanabe, k., et al., 1990. *New solid acids and bases: their catalytic properties (Studies in surface science and catalysis 51)*. Elsevier B.V, pp.160.
27. Stöcker, M., 2005. Gas phase catalysis by zeolites. *Microporous and Mesoporous Materials*, **82**(3): p. 257-292.
28. Bartholomew, C. H., and Farrauto, R. J., 2006. *Fundamentals of industrial catalytic process*. 2nd ed., Wiley Interscience, pp. 4-151.
29. Available via Google image
<http://www.google.com.sa/imgres?imgurl=http://www.catcracking.com/images/FCC_Flow_Diagram.png&imgrefurl=http://www.catcracking.com/operations/Process> [Accessed: 4 April 2011].
30. Barrer, R. M., and Makki, M. B., 1964. Molecular sieve sorbents from clinoptilolite. *Canadian Journal of Chemistry*, **42**(6), pp. 1481.

31. Jansen, J. C., The preparation of molecular sieves: A. Synthesis of zeolites. In: Bekkum, H., et al., ed. 2001. *Studies in surface science and catalysis 137*. Amsterdam: Elsevier Science, pp. 181.
32. Kouwenhoven, H. W., and de Kroes, B., Preparation of zeolite catalysts. In: Bekkum, H., et al., ed. 2001. *Studies in surface science and catalysis 137*. Amsterdam: Elsevier Science, pp. 678- 687.
33. Skeels, G. W., and Breck, D. W., 1985. Union Carbide Corporation. *Silicon substituted zeolite compositions and process for preparing same*. United States Patent 4,610,856.
34. Maher, P. K., Hunter, F. D., and Scherzer, J., 1971. Crystal structures of ultrastable Faujasites. *Advances Chemistry Series*, **101**, pp. 266.
35. Kerr G. T., 1967. Intracrystalline rearrangement of constitutive water in hydrogen zeolite Y. *Journal of Physical Chemistry*, **71**(12), pp. 4255.
36. Cusumano, J. A., 1995. Environmentally sustainable growth in the 21st century: the role of catalytic science and technology. *Journal of Chemical Education*, **72**(11), pp. 959-964.
37. Bousquest, J., and Valais, M., 1996. Trends and constraints of the European refining industry. *Applied Catalysis. A*, **134**(2), pp. N8-N18.
38. De Gauw, F., 2002. *Kinetic studies of alkane hydroisomerization over solid acid catalysts*, in Eindhoven PhD. Technische University, pp. 1-3.
39. Denayer, J. F., et al., 2000. Evidence for alkylcarbenium ion reaction intermediates from intrinsic reaction kinetics of C₆–C₉ n-alkane hydroisomerization and hydrocracking on Pt/H–Y and Pt/USY zeolites. *Journal of Catalysis*, **190**, pp. 469-473.
40. Jordão, M. H., et al., 2000. Bifunctional Ni, Pt zeolite catalysts for the isomerization of n-hexane. In: Corma, A., et al., *12th international*

- congress on catalysis. Studies in surface science and catalysis 130*, Elsevier Science, pp. 2387-2392.
41. Abudawood, R. H., 2010. *Hydroisomerization of alkanes over metal-loaded zeolite catalysts*. PhD. University of Manchester, pp. 1-204.
42. Blomsma, E., Martens J. A., and Jacobs P. A., 1996. Mechanisms of heptane isomerization on bifunctional Pd/H-Beta zeolites. *Journal of Catalysis*, **159**(2), pp. 323-331.
43. Fúnez, A., et al, 2008. Hydroisomerization in liquid phase of a refinery naphtha stream over Pt-Ni/H-beta zeolite catalysts. *Chemical Engineering Journal*, **136**, pp. 267-275.
44. Barsi, F. V., and Cardoso, D., 2008. Bimetallic Pt-Ni catalysts supported on USY zeolite for n-hexane isomerization. *Brazilian Journal of Chemical Engineering*, **26**(2), pp. 353-360.
45. Martins, A., et al, 2006. Hydroisomerization of n-hexane over Pt-Ni/HBEA using catalysts prepared by different methods. *Catalysis Letters*, **109**(1-2), pp. 83-87.
46. Eswaeamoorthi, I., and Lingappan, N., 2003. Hydroisomerization of n-hexane over bimetallic bifunctional silicoaluminophosphate based molecular sieves. *Applied catalysis A: General*, **245**, pp. 119-135.
47. Vazquez, M. I., et al., 1987. Activity and selectivity of Ni-MO/HY ultrastable zeolites for hydroisomerization and hydrocracking of alkanes. *Industrial and Engineering Chemistry Research*, **26**(8), pp. 1495-1500.
48. Eswaeamoorthi, I., and Lingappan, N., 2003. Ni-Pt/H-Y zeolite catalysts for hydroisomerization of n-hexane and n-heptane. *Catalysis Letters*, **87**(3-4), pp. 133-141.
49. Al-Rubaye, R., 2010. *Developing of novel catalyst*. First year transfer report. University of Manchester. pp. 54.

50. Weisz, P. B., and Frillette V. J., 2002. Intracrystalline and molecular-shape-selective catalysis by zeolite salts. *The Journal of Physical Chemistry*, **64**(3): pp. 382-382.
51. Boss, C. B., and Fredeen, K. J., 1997. *Concepts, instrumentation, and techniques in inductively coupled plasma optical emission spectroscopy*. 2nd ed., Perkin-Elmer Corporation, pp. 1-8.
52. Available via Google <http://www.speciation.net/md/000/000/524/th_Varian_Vista_MPX-with-PC.jpg> [Accessed: 6 January 2012].
53. Available via Google <<http://www.panalytical.com/index.cfm?pid=519>> [Accessed: 4 April 2011].
54. Available via Google image <<http://serc.carleton.edu/details/images/20375.html>> [Accessed: 7 April 2011].
55. Treacy, M. M., Higgins, J. B., and von Ballmoos, R., 1996. *Collection of simulated XRD powder patterns for zeolites*. Elsevier, pp. 643.
56. Jentys, A., and Lercher, J., Techniques of zeolite characterization. In: Bekkum, H., et al., ed. 2001. *Studies in surface science and catalysis 137*. Amsterdam: Elsevier Science, pp. 347-363.
57. American Society for the Testing of Materials (ASTM), 2003. ASTM D3906, Edition: 3. *Standard test method for determination of relative x-ray diffraction intensities of Faujasite-type zeolite-containing materials*, West Conshohocken, US.
58. McCusker, L. B., Product characterization by x-ray powder diffraction. In: Robson, H., Lillerud, K.P., 2001. *Verified synthesis of zeolitic materials*. Elsevisor, 2nd revised ed., pp. 47.

59. Goldstein, J., et al., 2003. *Scanning electron microscopy and X-ray microanalysis*. 3rd ed. Kluwer Academic, pp. 1-24.
60. Dunlap, M., and Adaskaveg, J., 1997. SEM Manual. *Facility for Advanced Instrumentation*, pp. 1-28. Available via Google <<https://imf.ucmerced.edu/downloads/semmanual.pdf>> [Accessed: 10 September 2011].
61. Bottom, R., Thermogravimetric analysis. In: Gabbott, P., ed. 2008. *Principles and applications of thermal analysis*. Blackwell, pp. 88-91.
62. Brown, M. E., 2001. *Introduction to thermal analysis: techniques and applications*. 2nd ed. Kluwer Academic, pp. 19-20.
63. Gideon Analytical Labs, Inc. [Website]. Available via Google <<http://www.gideonlabs.com/thermal.htm>> [Accessed: 7 October 2010].
64. Chen, S., and Manos, G., 2004. In situ thermogravimetric study of coke formation during catalytic cracking of normal hexane and 1-hexene over ultrastable Y zeolite. *Journal of Catalysis*, **226**(2), pp. 343-350.
65. TA instruments, Thermal analysis applications brief: TGA evaluation of zeolite catalysts, TA no. 231. Available via Google. <http://www.tainstruments.co.jp/application/pdf/Thermal_Library/Applications_Briefs/TA231.PDF> [Accessed: 5 April 2011].
66. Available via Google <<http://micron.ucr.edu/public/manuals/Tem-intro.pdf>> [Accessed: 9 October 2011].
67. Goodhew, P. J., and Humphreys, F. J., 1988. *Electron microscopy and analysis*. 2nd ed., Taylor and Francis, pp. 64-73.
68. Transmission Electron Microscope Facility [website]. Available via Google <<http://www.stanford.edu/group/snl/tem.htm>> [Accessed: 18 July 11].

69. Available via Google
<http://en.wikipedia.org/wiki/File:Scheme_TEM_en.svg> [Accessed: 19 July 11].
70. Scott, R.P.W., 2003. *Chrom-Ed Book Series: Book2, Gas Chromatography*. [E-book]. Library 4 Science. Available via Google
<<http://www.chromatography-online.org/3/contents.html>> [Accessed: 4 April 2011].
71. American Society for the Testing of Materials (ASTM) 2004. ASTM D3606. *Standard test method for determination of benzene and toluene in finished motor and aviation gasoline by Gas Chromatography*, West Conshohocken, US.
72. American Society for the Testing of Materials (ASTM) 2004. ASTM D710. *Standard test method for boiling distribution of gasoline and gasoline fractions by Gas Chromatography*, West Conshohocken, US.
73. Karasek, F. W., and Clement, R. E., 1988. *Basic gas chromatography-mass spectrometry principles and techniques*. Elsevier, pp. 3-44.
74. Available via Google image
<<http://students.ycp.edu/~danders7/Instrument%20Portfolios/GC%20Block%20Diagram.bmp>> [Accessed: 31 October 2011].
75. Hites, R. A., Gas chromatography-mass spectrometry In: Settle, F. A., 1997. *Handbook of instrumental techniques for analytical chemistry*. Prentice Hall PTR, pp. 609-615.
76. Scott, R.P.W., 2003. *Chrom-Ed Book Series: Book4, Gas Chromatography Detectors* [e-book]. Library 4 Science. Available via Google
<<http://www.chromatography-online.org/GC-Detectors/Time-Constant/rs16.html>> [Accessed: 4 April 2011].

77. Treacy, M. M. J., and Higgins, J. B. 2001. *Collection of simulated XRD powder patterns for zeolites*. Amsterdam: Elsevier, pp. 149.
78. Carrado, K. A., 2003. *Hand book of zeolite science and technology*. Marcel Dekker, pp. 6.
79. Szostak, R., Secondary Synthesis. In: Bekkum, H., et al., 2001. *Studies in surface and catalysis 137*. Elsevier Science, pp. 263-272.
80. Canizares, P., et al., 1998. Characterization of Ni and Pd supported on H-mordenite catalysts: influence of the metal loading method. *Applied Catalysis A- General*, **169**(1), pp. 137-150.
81. Mohamed, L. K., and El Kady, F.Y., 2010. Influence of operating conditions on the product distribution in the hydroconversion of n-heptane over Pt/HM+Al₂O₃ catalyst. *Journal of Applied Sciences Research*, 6(2), pp. 144-150.
82. Missen, R. W., Mims, C. A., and Saville, B. A., 1999. *Introduction to chemical reaction engineering and kinetics*. John Wiley and Sons, Inc, pp. 216.

APPENDIX-1:

CALCULATION FOR THE ZEOLITE Y RECIPE

The mass balance to determine the required weight of zeolite Y synthesis was shown below. The batch composition was presented by: $3\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:10\text{SiO}_2:120\text{H}_2\text{O}$.

- For one mole Al_2O_3 from feedstock the required amount are(x gm) of sodium aluminates (SA). The SA contains; 50.9 wt% Al_2O_3 , 31.2 wt% Na_2O and 17.9 wt% H_2O .
- In 1 gm SA there is 0.509 gm (0.005 mol of Al_2O_3). So, X =1 mole of Al_2O_3 in the feedstock/ 0.005 mole of Al_2O_3 in the 1 gm of SA. Therefore, X= 200.32 gm of SA
- To calculate the required amount of Na_2O (3 mol), one gram of SA, there are 0.312 gm of Na_2O and $(0.312)(200) = 62.4$ gm (1.0133 mol) of Na_2O will be required. Then $3-1.0133= 1.967$ mol of Na_2O . Therefore to complete the required amount of Na_2O a 99 wt% sodium hydroxide (NaOH) will be added. If we knew that for 2 (No. of mol of Na_2O) = No. of mole of NaOH and that will be 3.932 mol of NaOH which equal to 157.36 gm of NaOH.
- In Ludox, there are 40 wt% SiO_2 and 60 wt% H_2O . Therefore, to get 10 mol of SiO_2 , 600 gm of SiO_2 is required from Ludox $[(10)(60.0840)]$ from that the amount required from Ludox will be $(600.84/0.4) = 1502.1$ gm.
- In 200.32 gm of SA there are $[0.179(200.32)] = 35.8575$ gm. The Hydrogen estimations in SA $[(35.8575)(2)/18.0148] = 3.98$ mol and (3.932 mol) from NaOH. In Ludox there are $[(0.6)(1502.1)] = 901.26$ gm and for Hydrogen $[(901.26)(2)/18.0148] = 100.057$ mol. Then the total mol of Hydrogen $[(3.981 + 3.932 + 100.057) = 110.62$ mol. Therefore, the amount of the de-ionized water required will be: $[2(120)-$

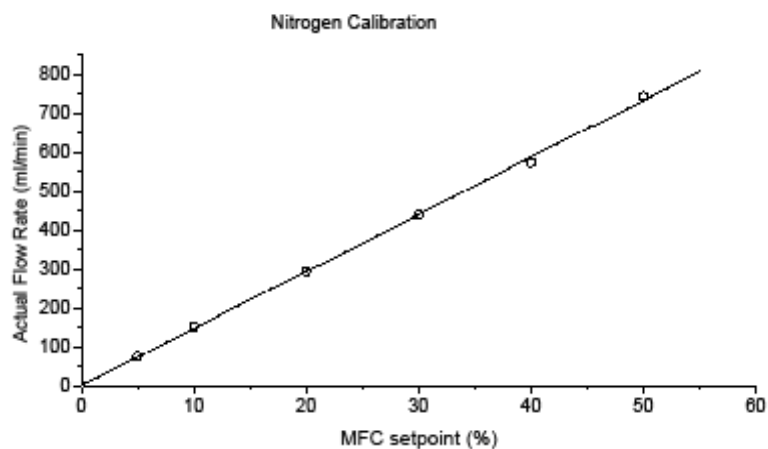
$[(200(0.179)^{2/18})+(1502(0.6)^{2/18})+ 3.98] = 131.92/2 = 69.89$ mol which is equivalent to 1187.28 gm.

APPENDIX -2: MASS FLOW CONTROLLER CALIBRATION

MFC Set point	t1	Time (sec/10ml)		Average	Flow rate ml/min
		t2	t3		
0.0	0.00	0.00	0.00	0.00	0
5.0	7.92	7.91	7.89	7.91	76
10.0	3.93	3.94	3.92	3.93	153
20.0	2.02	2.03	2.05	2.03	295
30.0	1.35	1.36	1.38	1.36	440
40.0	1.05	1.02	1.06	1.04	575
50.0	0.81	0.80	0.81	0.81	744

$$y = 14.650x + 1.696$$

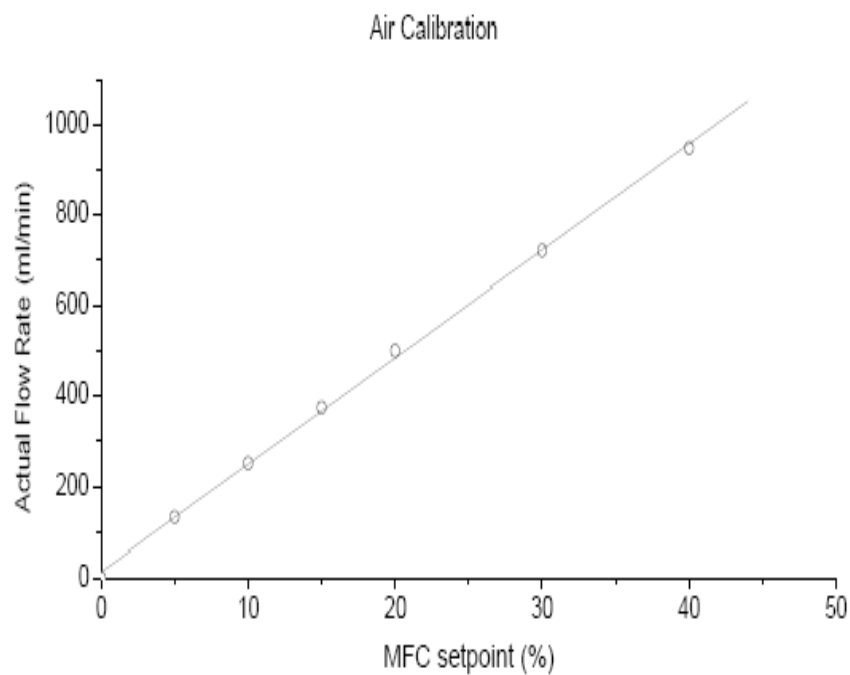
$$r^2 = 0.9994$$



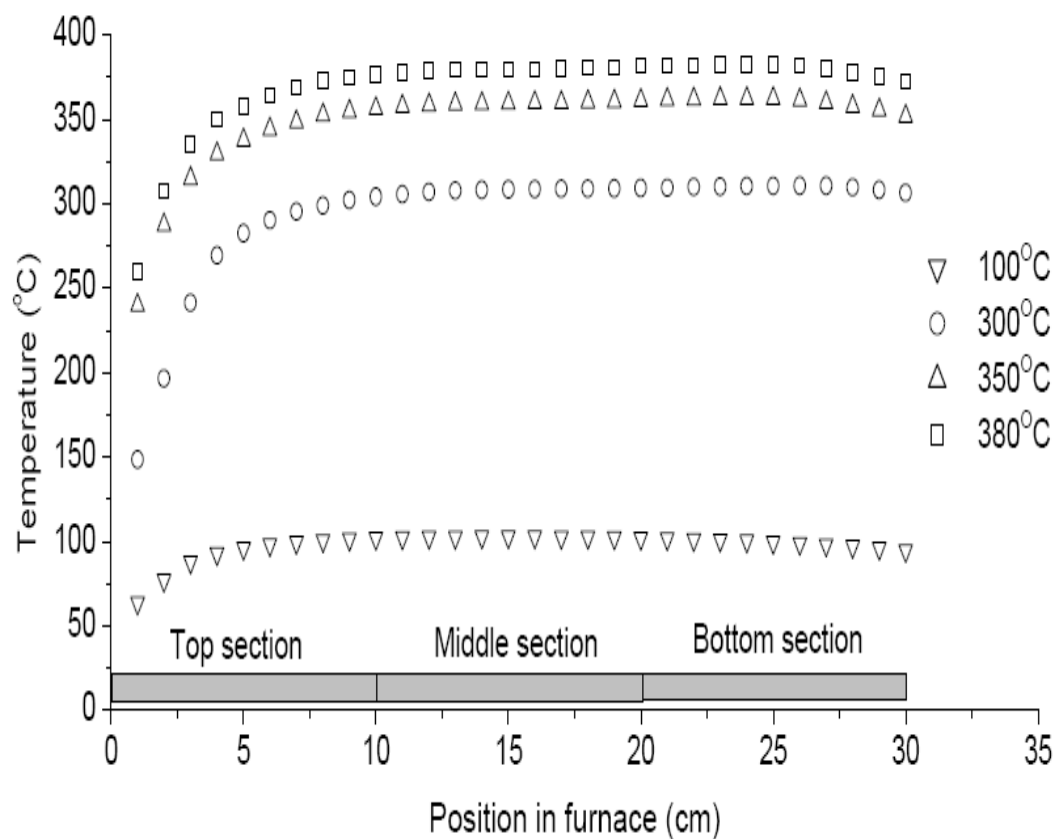
MFC Set point	Time (sec/10ml)				Flow rate ml/min
	t1	t2	t3	Average	
0.0	0.00	0.00	0.00	0.00	0.0
5.0	4.53	4.55	4.57	4.55	131.9
10.0	2.37	2.38	2.41	2.39	251.4
15.0	1.58	1.61	1.61	1.60	375.0
20.0	1.18	1.20	1.21	1.20	501.4
30.0	0.83	0.82	0.85	0.83	720.0
40.0	0.64	0.63	0.63	0.63	947.4

$$y = 23.593x + 13.692$$

$$r^2 = 0.9991$$



APPENDIX-3: FURNACE CALIBRATION



APPENDIX-4:

Setpoint 30.00 ml/h	Start 308.89	Flow rate ml/h	
Time /hr			
1	285.69	23.2	30.13
2	264.95	43.94	28.53
3	243.08	65.81	28.49
4	218.61	90.38	29.34
5	195.12	113.77	29.55
6	175.17	133.72	28.94
Average		29.17	

Setpoint 25.02 ml/h	Start 174.17	Flow rate ml/h	
Time /hr			
1	155.39	18.78	24.39
2	137.12	37.05	24.06
3	118.63	55.54	24.04
4	99.13	75.04	24.36
5	81.58	92.59	24.05
6	62.83	111.34	24.10
Average		24.17	

Setpoint 19.98 ml/h	Start 303.58	Flow rate ml/h	
Time /hr			
1	288.39	15.19	19.73
2	273.92	29.66	19.26
3	258.96	44.62	19.32
4	245.18	58.4	18.96
5	231.47	72.11	18.73
6	216.25	87.33	18.90
Average		19.15	

Setpoint 15.00 ml/h	Start 216.25	Flow rate ml/h	
Time /hr			
1	205.16	11.09	14.40
2	193.86	22.39	14.54
3	182.37	33.88	14.67
4	171.73	44.52	14.45
5	160.02	56.23	14.61
6	149.35	66.9	14.48
Average		14.52	

Setpoint 10.02 ml/h	Start 301.63	Flow rate ml/h	
Time /hr			
1	294.45	7.18	9.32
2	286.83	14.8	9.61
3	279.13	22.5	9.74
4	272.64	28.99	9.41
5	264.18	37.45	9.73
6	258.04	43.59	9.44
Average		9.54	

Setpoint 7.50 ml/h	Start 149.35	Flow rate ml/h	
Time /hr			
1	143.79	5.56	7.22
2	138.51	10.84	7.04
3	133.19	16.16	7.00
4	127.23	22.12	7.18
5	121.39	27.96	7.26
6	116.23	33.12	7.17
Average		7.14	

Setpoint 5.04 ml/h	Start 116.21	Flow rate ml/h	
Time /hr			
1	112.57	3.64	4.73
2	108.97	7.24	4.70
3	105.18	11.03	4.77
4	102.09	14.12	4.58
5	97.77	18.44	4.79
6	93.73	22.48	4.87
Average		4.74	

APPENDIX-5: UNIT CELL CALCULATION FOR CBV-712 CATALYST

The unit cell was determined using equation (3) $a_0 = \frac{\sqrt{h^2 + k^2 + l^2}}{2\sin\theta}$ as mentioned in Section 3.3.2

Where: $h^2 + k^2 + l^2 = N$

2θ	θ	$\sin \theta$	$\sin 2\theta$	$\sin^2\theta/\sin^2\theta_1$	N	N	h	k	l	d	a (unit cell Å)
18.97	9.49	0.165	0.027	8.90	26.70	27	3	3	3	4.68	24.30
20.66	10.33	0.179	0.032	10.53	31.60	32	4	4	0	4.30	24.32
23.99	11.99	0.208	0.043	14.15	42.46	43	5	3	3	3.71	24.33
27.42	13.71	0.237	0.056	18.41	55.23	56	6	4	2	3.25	24.34
31.84	15.92	0.274	0.075	24.66	73.98	75	5	5	5	2.81	24.34

Average of a (unit cell) = 24.33 Å

SD= 0.01

APPENDIX-6:

W/F AND YIELD CALCULATIONS

W/F (contact time) Calculations

- The weight of catalyst used was always $W = 1$ grams
- nC_7 flow at 7.5 ml/hr
- The density of nC_7 at room temperature is 0.684 g/ml,

W	F	$W/F = (1 / (F * 0.684)) / (100.21 * 3600)$
g	ml/h	g.s/mol
1	7.5	70323

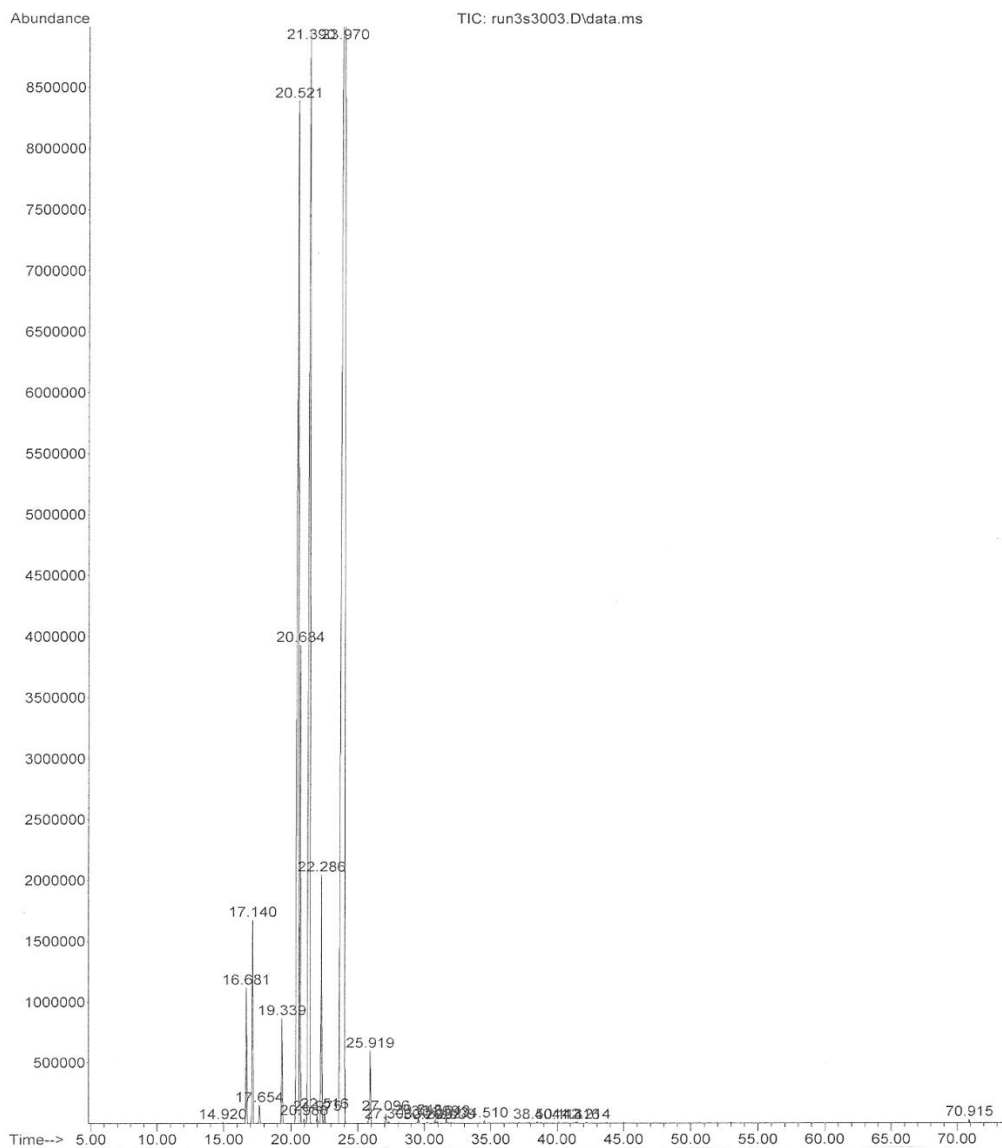
Yield Calculations

1. GCs separate each component in the injected sample into peaks, and for liquid samples each peak corresponds to the weight % of its related product. For example, one sample of liquid product, nC_7 wt% is multiplied by the total liquid sample weight to get the yield in gm.
2. The yield in gm is converted to moles to allow the calculation of nC_7 conversion w%.
3. In case of gas samples, the GC produces peaks for individual components of the injected sample. Each peak area is multiplied by the RF of its corresponding component to get its mol% of the gas product.
4. Then, the mol% of the individual component is divided by the total mol% of components to get the mol% of the individual component for the total hydrocarbon content of the gas product
5. The mol% of each component in the hydrocarbon mixture is multiplied by its molecular weight, and the resultant values for all components are summed to get the average molecular weight of hydrocarbons in the gas product.

6. After that, the average flow rate of gas during the testing time is determined in liters per hour and then multiplied by the testing time to get the volume of total product, which is multiplied by the total mol% of the gas sample to determine the hydrocarbons volume during the testing time. The hydrocarbons volume is multiplied by the sample average molecular weight and divided by 24.2 (liters per mol using the idea gas law) to give the hydrocarbons total mass in the gas product.
7. Finally, to determine the yield in gm for each individual component of gas product, its mole ratio in the hydrocarbon content of the gas product is multiplied by its molecular weight and the obtained value is multiplied by the total mass of hydrocarbons in the gas product then divided by their average molecular weight [60].

APPENDIX-7:
GC-MS ANALYSIS FOR ISOMERS OBTAINED
(Catalyst B)

File : C:\MSDCHEM\1\DATA\ARTHUR\24aug\run3s3003.D
Operator : liz
Acquired : 24 Aug 2011 20:06 using AcqMethod PONA2MS.M
Instrument : Instrument #1
Sample Name: run3s3 Catalyst (B)
Misc Info :
Vial Number: 57



n-Heptane Hydroisomerization over Bifunctional Zeolite Catalysts

Area Percent Report

Data Path : C:\MSDCHEM\1\DATA\ARTHUR\24aug\
Data File : run3s3003.D
Acq On : 24 Aug 2011 20:06
Operator : liz
Sample : run3s3 Catalyst (B)
Misc :
ALS Vial : 57 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : C:\MSDCHEM\1\METHODS\pona3manmS.M
Title :

Signal : TIC: run3s3003.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	14.920	2465	2531	2561	BB 4	8372	323295	0.02%	0.009%
2	16.681	2775	2834	2862	BV	1122040	48108748	2.76%	1.325%
3	17.140	2891	2913	2941	VB	1639053	71639615	4.11%	1.973%
4	17.654	2978	3001	3031	BB 2	147456	6314109	0.36%	0.174%
5	19.339	3224	3290	3327	BB	870371	42235827	2.42%	1.163%
6	20.521	3394	3493	3508	BV	8274396	651046636	37.32%	17.931%
7	20.684	3508	3521	3558	VV	3876171	165781281	9.50%	4.566%
8	20.988	3558	3574	3593	VV 3	40220	1909193	0.11%	0.053%
9	21.390	3593	3643	3711	VV	9064220	749158525	42.95%	20.633%
10	21.975	3711	3743	3767	VV 2	74578	3240178	0.19%	0.089%
11	22.286	3767	3797	3819	VV	2055538	94801949	5.43%	2.611%
12	22.516	3819	3836	3887	VB 3	94265	4351368	0.25%	0.120%
13	23.970	3964	4086	4187	BV 3	11168051	1744301939	100.00%	48.041%
14	25.919	4351	4421	4456	BV 2	596080	29005575	1.66%	0.799%
15	27.096	4557	4623	4643	BV 3	78246	3517152	0.20%	0.097%
16	27.306	4643	4659	4734	VB 5	13778	627263	0.04%	0.017%
17	29.543	4960	5043	5094	BB	44535	2064412	0.12%	0.057%
18	30.202	5127	5156	5177	BV 4	7345	340396	0.02%	0.009%
19	30.809	5214	5260	5276	BV 2	34378	1456924	0.08%	0.040%
20	30.982	5276	5290	5309	VV 5	13549	590937	0.03%	0.016%
21	31.643	5370	5404	5418	BV 3	36240	1589634	0.09%	0.044%
22	32.000	5443	5465	5487	VV 3	8532	389623	0.02%	0.011%
23	34.510	5850	5896	5923	BV 4	20354	868509	0.05%	0.024%
24	38.501	6513	6582	6610	BV 7	8740	445696	0.03%	0.012%
25	40.113	6810	6859	6896	BV 6	6708	280626	0.02%	0.008%
26	41.416	7060	7082	7163	BB 9	8259	693808	0.04%	0.019%
27	42.214	7166	7219	7279	BV 4	8381	432816	0.02%	0.012%
28	70.915	12088	12149	12228	BB 2	28994	1247082	0.07%	0.034%
29	108.856	17975	18665	18678	PV 2	531	133864	0.01%	0.004%
30	111.376	18678	19098	19125	PV 2	717	362806	0.02%	0.010%
31	111.848	19125	19179	19188	VV 2	858	87721	0.01%	0.002%
32	117.183	19188	20096	20108	PV 2	1465	3499858	0.20%	0.096%

Sum of corrected areas: 3630847360

pona3manmS.M Thu Aug 25 11:16:57 2011

n-Heptane Hydroisomerization over Bifunctional Zeolite Catalysts

Library Search Report

Data Path : C:\MSDCHEM\1\DATA\ARTHUR\24aug\
Data File : run3s3003.D
Acq On : 24 Aug 2011 20:06
Operator : liz
Sample : run3s3
Misc :
ALS Vial : 57 Sample Multiplier: 1

Search Libraries: C:\DATABASE\NIST02.L Minimum Quality: 0

Unknown Spectrum: Apex
Integration Events: ChemStation Integrator - autoint1.e

pk#	RT	Area%	Library/ID	Ref#	CAS#	Qual
1	14.918	0.01	C:\DATABASE\NIST02.L			
			Hexane	1796	000110-54-3	64
			Hexane	1797	000110-54-3	50
			Butyl aldoxime, 2-methyl-, syn-	4032	049805-56-3	40
2	16.682	1.33	C:\DATABASE\NIST02.L			
			Pentane, 2,2-dimethyl-	3916	000590-35-2	83
			Pentane, 2,2-dimethyl-	3915	000590-35-2	74
			Pentane, 2,2-dimethyl-	3914	000590-35-2	74
3	17.142	1.97	C:\DATABASE\NIST02.L			
			Pentane, 2,4-dimethyl-	3908	000108-08-7	91
			Pentane, 2,4-dimethyl-	3903	000108-08-7	91
			Pentane, 2,4-dimethyl-	3909	000108-08-7	83
4	17.654	0.17	C:\DATABASE\NIST02.L			
			Butane, 2,2,3-trimethyl-	3919	000464-06-2	90
			Pentane, 2,2-dimethyl-	3906	000590-35-2	83
			Pentane, 2,2-dimethyl-	3914	000590-35-2	83
5	19.337	1.16	C:\DATABASE\NIST02.L			
			Pentane, 3,3-dimethyl-	3910	000562-49-2	83
			Pentane, 3,3-dimethyl-	3911	000562-49-2	83
			Pentane, 3,3-dimethyl-	3904	000562-49-2	83
6	20.519	17.93	C:\DATABASE\NIST02.L			
			Hexane, 2-methyl-	3899	000591-76-4	91
			Hexane, 2-methyl-	3898	000591-76-4	91
			Hexane, 2-methyl-	3896	000591-76-4	91
7	20.682	4.57	C:\DATABASE\NIST02.L			
			Pentane, 2,3-dimethyl-	3913	000565-59-3	91
			Pentane, 2,3-dimethyl-	3912	000565-59-3	91
			Pentane, 2,3-dimethyl-	3905	000565-59-3	90
8	20.990	0.05	C:\DATABASE\NIST02.L			
			Cyclopentane, 1,1-dimethyl-	3329	001638-26-2	91
			Cyclopentane, 1,1-dimethyl-	3332	001638-26-2	83
			1-Hexene, 3-methyl-	3258	003404-61-3	49
9	21.392	20.63	C:\DATABASE\NIST02.L			
			Hexane, 3-methyl-	3897	000589-34-4	95
			Hexane, 3-methyl-	3900	000589-34-4	91
			Hexane, 3-methyl-	3894	000589-34-4	91
10	21.974	0.09	C:\DATABASE\NIST02.L			
			Cyclopentane, 1,3-dimethyl-, trans	3355	001759-58-6	94
			Cyclopentane, 1,3-dimethyl-	3333	002453-00-1	94
			Cyclopentane, 1,3-dimethyl-	3331	002453-00-1	90
11	22.288	2.61	C:\DATABASE\NIST02.L			
			Butane, 1,1'-oxybis[3-methyl-	28270	000544-01-4	83
			Pentane, 3-ethyl-	3901	000617-78-7	72
			Pentane, 3-ethyl-	3895	000617-78-7	64

n-Heptane Hydroisomerization over Bifunctional Zeolite Catalysts

Library Search Report

Data Path : C:\MSDCHEM\1\DATA\ARTHUR\24aug\
Data File : run3s3003.D
Acq On : 24 Aug 2011 20:06
Operator : liz
Sample : run3s3
Misc :
ALS Vial : 57 Sample Multiplier: 1

Search Libraries: C:\DATABASE\NIST02.L Minimum Quality: 0

Unknown Spectrum: Apex
Integration Events: ChemStation Integrator - autoint1.e

PK#	RT	Area%	Library/ID	Ref#	CAS#	Qual
1	14.918	0.01	C:\DATABASE\NIST02.L			
			Hexane	1796	000110-54-3	64
			Hexane	1797	000110-54-3	50
			Butyl aldoxime, 2-methyl-, syn-	4032	049805-56-3	40
2	16.682	1.33	C:\DATABASE\NIST02.L			
			Pentane, 2,2-dimethyl-	3916	000590-35-2	83
			Pentane, 2,2-dimethyl-	3915	000590-35-2	74
			Pentane, 2,2-dimethyl-	3914	000590-35-2	74
3	17.142	1.97	C:\DATABASE\NIST02.L			
			Pentane, 2,4-dimethyl-	3908	000108-08-7	91
			Pentane, 2,4-dimethyl-	3903	000108-08-7	91
			Pentane, 2,4-dimethyl-	3909	000108-08-7	83
4	17.654	0.17	C:\DATABASE\NIST02.L			
			Butane, 2,2,3-trimethyl-	3919	000464-06-2	90
			Pentane, 2,2-dimethyl-	3906	000590-35-2	83
			Pentane, 2,2-dimethyl-	3914	000590-35-2	83
5	19.337	1.16	C:\DATABASE\NIST02.L			
			Pentane, 3,3-dimethyl-	3910	000562-49-2	83
			Pentane, 3,3-dimethyl-	3911	000562-49-2	83
			Pentane, 3,3-dimethyl-	3904	000562-49-2	83
6	20.519	17.93	C:\DATABASE\NIST02.L			
			Hexane, 2-methyl-	3899	000591-76-4	91
			Hexane, 2-methyl-	3898	000591-76-4	91
			Hexane, 2-methyl-	3896	000591-76-4	91
7	20.682	4.57	C:\DATABASE\NIST02.L			
			Pentane, 2,3-dimethyl-	3913	000565-59-3	91
			Pentane, 2,3-dimethyl-	3912	000565-59-3	91
			Pentane, 2,3-dimethyl-	3905	000565-59-3	90
8	20.990	0.05	C:\DATABASE\NIST02.L			
			Cyclopentane, 1,1-dimethyl-	3329	001638-26-2	91
			Cyclopentane, 1,1-dimethyl-	3332	001638-26-2	83
			1-Hexene, 3-methyl-	3258	003404-61-3	49
9	21.392	20.63	C:\DATABASE\NIST02.L			
			Hexane, 3-methyl-	3897	000589-34-4	95
			Hexane, 3-methyl-	3900	000589-34-4	91
			Hexane, 3-methyl-	3894	000589-34-4	91
10	21.974	0.09	C:\DATABASE\NIST02.L			
			Cyclopentane, 1,3-dimethyl-, trans	3355	001759-58-6	94
			Cyclopentane, 1,3-dimethyl-	3333	002453-00-1	94
			Cyclopentane, 1,3-dimethyl-	3331	002453-00-1	90
11	22.288	2.61	C:\DATABASE\NIST02.L			
			Butane, 1,1'-oxybis[3-methyl-	28270	000544-01-4	83
			Pentane, 3-ethyl-	3901	000617-78-7	72
			Pentane, 3-ethyl-	3895	000617-78-7	64

n-Heptane Hydroisomerization over Bifunctional Zeolite Catalysts

12	22.516	0.12	C:\DATABASE\NIST02.L		
			Cyclopentane, 1,2-dimethyl-	3330	002452-99-5 95
			Cyclopentane, 1,2-dimethyl-, trans	3354	000822-50-4 94
			Isopropylcyclobutane	3274	000872-56-0 91
13	23.971	48.04	C:\DATABASE\NIST02.L		
			Heptane	3892	000142-82-5 91
			Heptane	3891	000142-82-5 86
			Heptane	3893	000142-82-5 78
14	25.922	0.80	C:\DATABASE\NIST02.L		
			Cyclohexane, methyl-	3276	000108-87-2 94
			Cyclohexane, methyl-	3280	000108-87-2 94
			Cyclohexane, methyl-	3278	000108-87-2 94
15	27.098	0.10	C:\DATABASE\NIST02.L		
			Cyclopentane, ethyl-	3279	001640-89-7 91
			Cyclopentane, ethyl-	3275	001640-89-7 91
			3-Methyl-3-hexene	3255	003404-65-7 43
16	27.307	0.02	C:\DATABASE\NIST02.L		
			Hexane, 2,4-dimethyl-	7438	000589-43-5 87
			Hexane, 2,4-dimethyl-	7446	000589-43-5 64
			Hexane, 2,4-dimethyl-	7445	000589-43-5 64
17	29.543	0.06	C:\DATABASE\NIST02.L		
			Toluene	2405	000108-88-3 91
			Toluene	2400	000108-88-3 91
			Toluene	2403	000108-88-3 87
18	30.201	0.01	C:\DATABASE\NIST02.L		
			Hexane, 2,3-dimethyl-	7457	000584-94-1 59
			Heptane, 4-methyl-	7431	000589-53-7 59
			Hexane, 2,3-dimethyl-	7448	000584-94-1 38
19	30.806	0.04	C:\DATABASE\NIST02.L		
			Heptane, 2-methyl-	7429	000592-27-8 94
			Heptane, 2-methyl-	7432	000592-27-8 91
			Heptane, 2-methyl-	7437	000592-27-8 87
20	30.981	0.02	C:\DATABASE\NIST02.L		
			Heptane, 4-methyl-	7435	000589-53-7 78
			Heptane, 4-methyl-	7436	000589-53-7 72
			Pentane, 2,3,4-trimethyl-	7464	000565-75-3 64
21	31.645	0.04	C:\DATABASE\NIST02.L		
			Heptane, 3-methyl-	7430	000589-81-1 90
			Hexane, 2,3,3-trimethyl-	12296	016747-28-7 64
			Heptane, 3-methyl-	7433	000589-81-1 64
22	32.000	0.01	C:\DATABASE\NIST02.L		
			Cyclohexane, 1,3-dimethyl-, cis-	6637	000638-04-0 72
			3-Hepten-2-one	6298	001119-44-4 72
			2-Pentene, 3,4,4-trimethyl-	6586	000598-96-9 72
23	34.509	0.02	C:\DATABASE\NIST02.L		
			Octane	7423	000111-65-9 90
			Octane	7425	000111-65-9 87
			Heptane, 2,4-dimethyl-	12286	002213-23-2 59
24	38.503	0.01	C:\DATABASE\NIST02.L		
			1-Hexanol, 3,5,5-trimethyl-	20282	003452-97-9 32
			2(3H)-Furanone, 5-ethenyldihydro-5	10850	001073-11-6 25
			-methyl-		
			Piperazine, 1,4-bis(diethylphospho	152865	101098-23-1 25
			natomethyl)-		
25	40.116	0.01	C:\DATABASE\NIST02.L		
			Cyclohexane, 1,2,4-trimethyl-, (1.	11271	007667-60-9 83
			alpha.,2.beta.,4.beta.)-		
			Cyclohexane, 1,2,4-trimethyl-	11221	002234-75-5 72
			Cyclohexane, 1,3,5-trimethyl-, (1.	11277	001795-26-2 72

			alpha.,3.alpha.,5.beta.)-			
26	41.415	0.02	C:\DATABASE\NIST02.L			
			Octane, 4-methyl-	12259	002216-34-4	64
			Octane, 4-methyl-	12263	002216-34-4	59
			Hexane, 2,3,4-trimethyl-	12303	000921-47-1	53
27	42.212	0.01	C:\DATABASE\NIST02.L			
			Octane, 3-methyl-	12266	002216-33-3	64
			Heptane, 4-(1-methylethyl)-	18485	052896-87-4	53
			Octane, 3-methyl-	12258	002216-33-3	53
28	70.916	0.03	C:\DATABASE\NIST02.L			
			Dodecane	36159	000112-40-3	94
			Dodecane	36158	000112-40-3	94
			Dodecane	36157	000112-40-3	91
29	108.854	0.00	C:\DATABASE\NIST02.L			
			Cyclotetrasiloxane, octamethyl-	115616	000556-67-2	27
			Benzoic acid, 5-methyl-2-trimethyl-	115080	1000153-59-4	27
			silyloxy-, trimethylsilyl ester			
			Cyclotetrasiloxane, octamethyl-	115617	000556-67-2	27
30	111.375	0.01	C:\DATABASE\NIST02.L			
			1,3-Bis(trimethylsilyl)benzene	70584	002060-89-1	38
			Methyltris(trimethylsiloxy)silane	122473	017928-28-8	32
			Tetrasiloxane, decamethyl-	122472	000141-62-8	32
31	111.846	0.00	C:\DATABASE\NIST02.L			
			Methyltris(trimethylsiloxy)silane	122473	017928-28-8	38
			Cyclotrisiloxane, hexamethyl-	71176	000541-05-9	35
			1,3-Bis(trimethylsilyl)benzene	70584	002060-89-1	32
32	117.185	0.10	C:\DATABASE\NIST02.L			
			Tetrasiloxane, decamethyl-	122472	000141-62-8	43
			Cyclotrisiloxane, hexamethyl-	71175	000541-05-9	38
			Cyclotrisiloxane, hexamethyl-	71177	000541-05-9	38

pona3mannS.M Thu Aug 25 11:17:36 2011

APPENDIX-8:

TGA THERMOGRAMS FOR SPENT CATALYST D- F

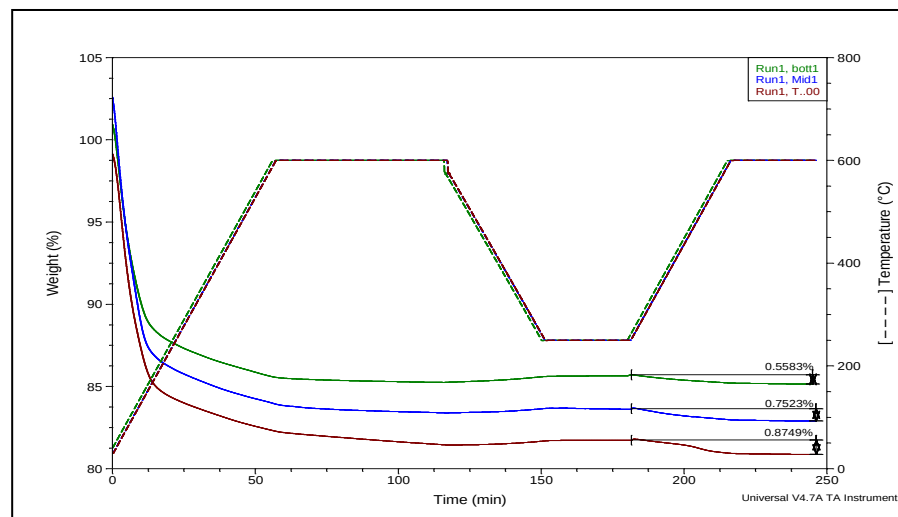


Figure 4-21: TGA analysis for spent catalyst D.

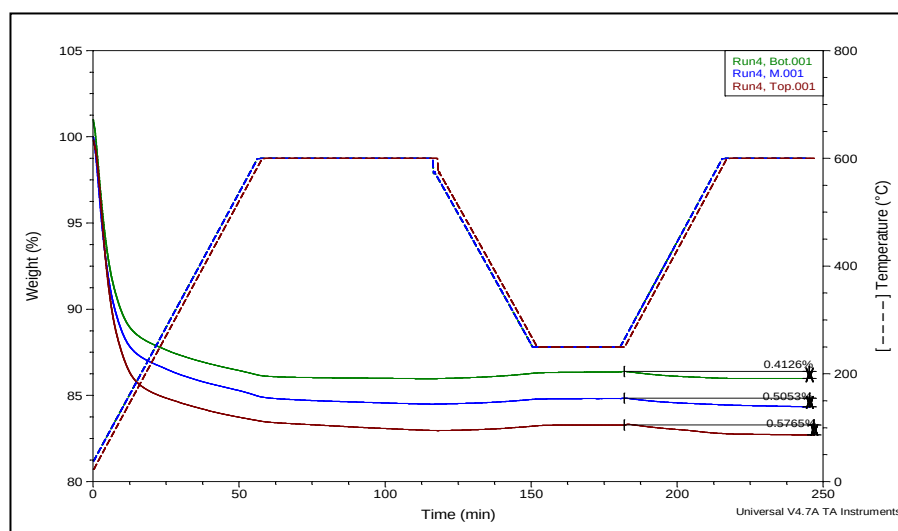
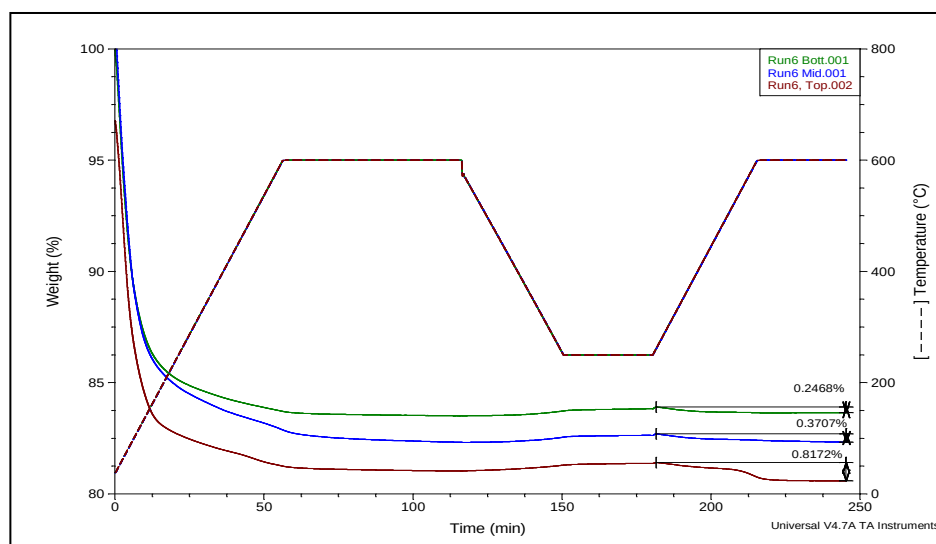


Figure 4-22: TGA analysis for spent catalyst E.



TGA analysis for spent catalyst F.

APPENDIX-9: RISK ASSESSMENT FORMS

RISK ASSESSMENT 1 for Management of Health and Safety at Work Regulations 1999

Status: Approved by SSA.

Printed on: 31 October 2011 at 23:36

TITLE OF EXPERIMENT/PROCEDURE

Synthesis of zeolite Y

Assessor

Al- Shaikh Ali

Supervisor

Dr Arthur Garforth

PERSONS AFFECTED

Arthur Garforth (supervisor), Anaam Al-Shaikhali (MSc by research student)

Other laboratory users - technical staff, academic staff, other PhD students,
visitors, contractors

SITE OF EXPERIMENT

Jacksons Mill/D42

HAZARDS IDENTIFIED

Furnace - heat hazard

2. See associated COSHH form

3. Burns, scalds, cuts and eye injuries

4. (Hazard is manual handling) risks are strains, sprains and crush injuries

5. Sprains, strains, cuts bruise broken bones

6. Electrical burns, shock and ignition source

RISKS ASSOCIATED

1. cause skin burn, L=3, S=3,PR=P2
2. cause caustic skin burn, irritation, L=3, S=3,PR=P2
2. electrical shock, L=2, S=3,PR=P3

GENERAL RISK ASSESSMENT PRIORITY RANKING

3.9

CONTROL MEASURES

1. Wear furnace gloves when handling hot surfaces
2. See COSHH
3. Training - follow standard operating procedure when using autoclave
4. Training manual handling course required if you lifting, pushing, pulling, moving heavy weights
5. Clean up spills remove and make safe tripping hazards
6. Pat testing, checks before use for wear and damage

EMERGENCY PROCEDURES

First aid contacts:

Des Doocey E63 - ext 63987

Loris Doyle D43a The Mill - ext 64543

Security can be contacted on 01613069966

If the fire alarm comes off, follow path to find the nearest fire exit to get out of the building, do not look behind.

LEVEL OF SUPERVISION

A. Those where work may not be started without direct supervision, and where such supervision will continue until it is clear the student is competent to proceed alone.

LONE WORKING

It is not permitted to work alone.

REVIEW DATE

30 November 2011

REVIEW PERIOD AFTER FIRST REVIEW

1 Month

FINISH DATE

20 January 2012

1 Associated COSHH Form(s):

CO#4800 Synthesis of zeolite Y

COSHH 1 for Control of Substances Hazardous to Health Regulations

COSHH Form for RA#5806 Synthesis of zeolite Y

Status: Approved by SSA.

Printed on: 28 October 2011 at 14:48

TITLE OF COSHH FORM

Synthesis of zeolite Y

Assessor

Al- Shaikh Ali

Supervisor

Dr Arthur Garforth

PERSONS AFFECTED (AND STATUS)

Msc by research student, Anaam Al-Shaikhali

AIM

IS THERE A LESS HAZARDOUS SUBSTANCE? WHY NOT USE IT?

None

PRECAUTIONS / CONTROL MEASURES TO BE ADOPTED

1. Use safety goggle, lab coat, PVC gloves and adequate ventilation.
2. Wear lab coat, safety goggle and flush with water immediately for 15 minutes if enters eyes. Conduct experiment in fume cupboard.
3. Wear lab coat, safety goggle and flush with water immediately for 15 minutes if enters eyes. Avoid inhalation.
4. Use safety goggle, lab coat, gloves and adequate ventilation.
5. Wear lab coat, safety goggle and flush with water immediately for 15 minutes

if enters eyes. Avoid inhalation and move to fresh air if exposed. If swallowed, get medical help immediately.

CHECKS ON EFFECTIVENESS OF THESE CONTROLS AND FREQUENCY

Supervisor conducts check after six months.

INFORMATION SOURCES

MSDS

DISPOSAL PROCEDURES AND ESTIMATED COST

N/A

ACCOUNT CODE FOR DISPOSAL CHARGES

N/A

EMERGENCY PROCEDURES

SPILLAGE AND UNCONTROLLED RELEASE

Flush skin and eyes for 20 minutes or until medical help arrives

FIRE

Potential electrical fire is unlikely. Sounds fire alarm and evacuate if necessary.

FIRST AID FOR AFFECTED PERSONNEL

Des Doocey E63- ext 63987

Loris Doyle D43a The Mill- ext 64543

Out of working hour

Security can be contacted on 01613069966

REVIEW DATE

30 November 2011

REVIEW PERIOD AFTER FIRST REVIEW

1 Month

FINISH DATE

20 January 2012

RISK ASSESSMENT 2 for Management of Health and Safety at Work Regulations 1999

Status: Approved by SSA.

Printed on: 28 October 2011 at 14:24

TITLE OF EXPERIMENT/PROCEDURE

Thermogravimetric analysis using the Q5000IR supplied by TA Instruments

Assessor

Al- Shaikh Ali

Supervisor

Dr Arthur Garforth

PERSONS AFFECTED

Anaam (MSc by research) Dr Arthur Garforth Aaron Akah (Post Doc) Chandni Rallan (PhD), other postgraduate in the same group and Technical staff

SITE OF EXPERIMENT

Jacksons Mill/D43

HAZARDS IDENTIFIED

1. Temperature - hot and cold surfaces -90 to 1000
2. Pressure gas purge facility low bleed required at all times
3. Chemical
4. Electric Shock

RISKS ASSOCIATED

1. After analysis the sample pan will be at a very high temperature, this can cause burns.
2. Gas flow rate is automatically selected by equipment and this is controlled by computer settings. A malfunction can cause equipment failure from pressurised cylinder/valve skin rupture.
3. see COSHH
4. Burns, Ventricular fibrillation or Neurological effects.

GENERAL RISK ASSESSMENT PRIORITY RANKING

2.6

CONTROL MEASURES

1. Ensure auto lid is closed, allow the software program to return cell to ambient temperature before handling any sample or reference pans and use instrument tweezers at all times. Do not leave pan unattended.
2. No direct contact with gas (nitrogen), make daily checks to ensure equipment is in good condition.
3. Covered in COSHH.
4. Check electrical connections and wires for any damage and wear regularly.

EMERGENCY PROCEDURES

1. In case of gas leak-Ventilate the laboratory and shut down the experiment. Fire.
2. Evacuate via the nearest safe fire exit, if fire alarms are not sounding operate fire alarm break glass.
3. First aid in the mill
4. Contact Stephen Blatch 64835, Des Doocey 63987, Helen Dutton 62684, Keith James 64359, Shahla Khan 64900, Max Rowe 65959.

LEVEL OF SUPERVISION

C. Those with risks (other than A & B) where care must be observed, but where it is considered that workers are adequately trained and competent in the procedures involved.

LONE WORKING

N/A

REVIEW DATE

29 July 2011

REVIEW PERIOD AFTER FIRST REVIEW

1 Month

FINISH DATE

31 August 2011

1 Associated COSHH Form(s):

CO#4886 Thermogravimetric analysis

COSHH 2 for Control of Substances Hazardous to Health Regulations

COSHH Form for RA#5933 Thermogravimetric analysis using the Q5000IR supplied by TA Instruments

Status: Approved by SSA.

Printed on: 28 October 2011 at 14:36

TITLE OF COSHH FORM

Thermogravimetric analysis

Assessor

Al- Shaikh Ali

Supervisor

Dr Arthur Garforth

PERSONS AFFECTED (AND STATUS)

Anaam(MSc by research), Dr Arthur Garforth, Aaron Akah (Post Doc), Chandni Rallan (PhD) Technical staff, other postgraduate in the same group.

AIM

To determine water/ volatile material content and for coke analysis

SUBSTANCES AND QUANTITIES USED AND STORED

Nitrogen gas (50 ml/min) [Stored in gas cylinder]

Air gas (50 ml/min) [Stored in gas cylinder]

Zeolite samples.

Note: Amount used will vary depending on number of runs required.

HAZARDS IDENTIFIED

1. Asphyxiant at high concentrations
2. LD50 : 4220 mg/kg.
3. Harmful if swallowed and in contact with skin. Eye and skin irritant
4. LD50: 6450 mg/kg .TLV 10 mg/m³. Dust may cause irritation.

IS THERE A LESS HAZARDOUS SUBSTANCE? WHY NOT USE IT?

No

PRECAUTIONS / CONTROL MEASURES TO BE ADOPTED

1. Prior training, supervision and research for equipment use experimental method required.
2. Safety glasses and laboratory coats to be worn at all times. Check equipment piping prior to use.
3. Keep workspace clean and tidy. Sample materials should be placed in trays and stored safely with name and content.
4. Do not inhale or smell material.

CHECKS ON EFFECTIVENESS OF THESE CONTROLS AND FREQUENCY

It should be every time before starting experiments.

INFORMATION SOURCES

EU-OHSA, HSE & <http://msds.chem.ox.ac.uk/>

DISPOSAL PROCEDURES AND ESTIMATED COST

None

ACCOUNT CODE FOR DISPOSAL CHARGES

N/A

EMERGENCY PROCEDURES

SPILLAGE AND UNCONTROLLED RELEASE

Wear personal protective clothing. In case of uncontrolled release, if harmful, trigger alarm and notify safety officers. If not harmful, contact experienced technician.

FIRE

Sound Alarm and call emergency services. If there is no danger to life, turn off the unit and close the cylinder valves before evacuating the building.

FIRST AID FOR AFFECTED PERSONNEL

1. In the case of exposure: call for medical aid and do the following treatments
Eyes: Hold eyelids open and flush with plenty of water for 20 minutes.
2. Skin: Flush affected area with plenty of water.
3. Inhalation: Move victim to fresh air. If breathing has stopped, give artificial respiration only if not chemically contaminated. If breathing is difficult, give oxygen.
4. Ingestion: If swallowed and victim is conscious, let the victim drink water or milk. Do not induce vomiting. Asphyxiation - If victim is in different room, sound alarm, contact emergency service (9999) and notify lab technicians. Do not enter contaminated room. Normal office hours

5. First aid in the mill
6. Contact Stephen Blatch 64835, Des Doocey 63987, Helen Dutton 62684, Keith James 64359, Shahla Khan 64900, Max Rowe 65959.
 1. Emergency contact on (69966)

REVIEW DATE

29 July 2011

REVIEW PERIOD AFTER FIRST REVIEW

1 Month

FINISH DATE

31 August 2011

RISK ASSESSMENT 3 for Management of Health and Safety at Work Regulations 1999

Status: Approved by SSA.

Printed on: 28 October 2011 at 14:46

TITLE OF EXPERIMENT/PROCEDURE

Hydroisomerization of n- C7 over Pt USY and Pt/Ni USY to improve the octane number of the light straight run gasoline

Assessor

Al- Shaikh Ali

Supervisor

Dr Arthur Garforth

PERSONS AFFECTED

Anaam Al ShaikhAli MSc by research All other laboratory users: technicians, other students, academic staff, visitors, estates workers etc..

SITE OF EXPERIMENT

ML/C42

HAZARDS IDENTIFIED

The identified hazards would be:

- 1- Pressure
- 2- Temperature
- 3-Sharps
- 4-Chemical
- 5- Electrical

RISKS ASSOCIATED

Risks associated with hazards are:

- 1- Failure of cylinder, regulator or pipe work(blast type injuries cuts, bruises, eye damage)
- 2- Burns and ignition source (GC oven).
- 3- Cuts needle stick injuries (clean and contaminated)

4- See COSHH.

5- Electrical burns, shock and ignition source.

GENERAL RISK ASSESSMENT PRIORITY RANKING

4.16

CONTROL MEASURES

- 1- All regulators in date and on CEAS system, regulator and pipe work checked before use for wear and damage.
- 2- Trained on moving or changing regulators and cylinders.
- 3- Temperature allows cooling before handling, use heat resistant gloves.
- 4- Auto- sampler has protective barrier around it to prevent inadvertent stick injures by syringe which also retracts within its own housing.
- 5- Safety glasses and lab coat.
- 6- Visual check before use, power supplies protected by RCD.

EMERGENCY PROCEDURES

Fire security contact number is 69966.

First aid occupational health is no longer a first call for first aid

Morton lab first aid contacts are Jim Fearick 64356, Liz Davenport 68869, Brain Hancock 64543, Andrew Evans 64543, Eric Warburton 64364, Tom Szpitter 62678.

LEVEL OF SUPERVISION

C. Those with risks (other than A & B) where care must be observed, but where it is considered that workers are adequately trained and competent in the procedures involved.

LONE WORKING

Not permitted

REVIEW DATE

30 November 2011

REVIEW PERIOD AFTER FIRST REVIEW

1 Month

FINISH DATE

20 January 2012

1 Associated COSHH Form(s):

CO#4863 Hydroisomerization of n-C7 over Pt USY and Pt/Ni USY to improve the octane number of the light straight run gasoline

COSHH3 for Control of Substances Hazardous to Health Regulations

COSHH Form for RA#5912 Hydroisomerization of n- C7 over Pt USY and Pt/Ni USY to improve the octane number of the light straight run gasoline

Status: Approved by SSA.

Printed on: 28 October 2011 at 14:46

TITLE OF COSHH FORM

Hydroisomerization of n-C7 over Pt USY and Pt/Ni USY to Improve the octane number of the light straight run gasoline

Assessor

Al- Shaikh Ali

Supervisor

Dr Arthur Garforth

PERSONS AFFECTED (AND STATUS)

Anaam Al Shaikhali

AIM

To improve the octane number of the light straight run gasoline using

Hydroisomerization over platinum-loaded zeolite catalysts

SUBSTANCES AND QUANTITIES USED AND STORED

1. Liquid organics [nC5-nC10]
(flow rate: 2.5-30 ml/hr) bulk 2.5l stored in metal cabinet, 20l drum
2. Hydrogen (flow rate: 100-1000 ml/min) plus cylinder
3. Nitrogen (flow rate: 100-1000 ml/min) plus cylinder

HAZARDS IDENTIFIED

1. Flammable liquids (nC5-nC10)
2. Hydrogen, Flammability range in air: 4 - 75%
3. Auto ignition temperature: 560 C
4. Asphyxiation displace the oxygen in air

IS THERE A LESS HAZARDOUS SUBSTANCE? WHY NOT USE IT?

No

PRECAUTIONS / CONTROL MEASURES TO BE ADOPTED

1- Training

2- Using fume cupboard

3- Electrical testing

4- Visual check before use

5- Check pipe work before use

CHECKS ON EFFECTIVENESS OF THESE CONTROLS AND FREQUENCY

Check by supervisor weekly

INFORMATION SOURCES

OSHA safety handbook

DISPOSAL PROCEDURES AND ESTIMATED COST

None

ACCOUNT CODE FOR DISPOSAL CHARGES

AA03019

EMERGENCY PROCEDURES

SPILLAGE AND UNCONTROLLED RELEASE

Spillage of normal alkanes:

a. Wear the personal protective clothes (goggle, chemical resistance gloves, and lab coat) before handling dealing with the chemicals

FIRE

Call emergency services. If there is no danger to life, turn off the unit and closed the cylinder valves before evacuating the building.

FIRST AID FOR AFFECTED PERSONNEL

In the case of normal alkanes exposure: call for medical aid and do the following treatments

i. Eyes: Hold eyelids open and flush with plenty of water for 20 minutes.

ii. Skin: Flush affected area with plenty of water.

iii. Inhalation: Move victim to fresh air. If breathing has stopped, give artificial respiration. If breathing is difficult, give oxygen.

iv. Ingestion: If swallowed and victim is conscious, let the victim drink water or milk. Do not induce vomiting.

Asphyxiation - take to fresh air, call for medical assistance 64007.

Normal office hours

1. Dr D Doocey, E63 (63987)
2. Jim Fearick, Morton Lab (64356)
3. Loris doyle, D43a The Mill (62505)
4. Brian Hancock, Morton Lab
5. Andrew Evans, Morton Lab (64345)
6. Shahla Kahn
7. Occupational Health Service, B20 The Mill (64007)

After office hours

1. Contact security at (69966)

REVIEW DATE

30 November 2011

REVIEW PERIOD AFTER FIRST REVIEW

1 Month

FINISH DATE

20 January 2012

RISK ASSESSMENT 4 for Management of Health and Safety at Work Regulations 1999

Status: Approved by SSA.

Printed on: 28 October 2011 at 14:47

TITLE OF EXPERIMENT/PROCEDURE

Gas Chromatography

Assessor

Al- Shaikh Ali

Supervisor

Dr Arthur Garforth

PERSONS AFFECTED

Anaam Al-Shaikhali (Postgraduate student/ MSc by research) Dr. Arthur Garforth
(Supervisor)

SITE OF EXPERIMENT

ML/C4c

HAZARDS IDENTIFIED

1- Pressure

2- Temperature

3- Sharps

4- Chemical

5- Electrical

RISKS ASSOCIATED

Risks associated with hazards are:

1- Failure of cylinder, regulator or pipe work(blast type injuries cuts, bruises, eye damage)

2- Burns and ignition source (GC oven).

3- Cuts needle stick injuries (clean and contaminated)

4- See COSHH.

5- Electrical burns, shock and ignition source.

GENERAL RISK ASSESSMENT PRIORITY RANKING

2.6

CONTROL MEASURES

- 1- Add all regulators in date and on CEAS system, regulator and pipe work checked before use for wear and damage.
- 2- Trained personally on moving or changing regulators and cylinders.
- 3- Walls of Column Oven are insulated to protect against contact burns.
- 4- The injection ports and those of the detectors are behind the protective barrier and should not be touched until after they have cooled (their temperatures are displayed by the system software in real-time).
- 5- Auto- sampler has protective barrier around it to prevent inadvertent stick injuries by syringe which also retracts within its own housing.
- 6- Safety glasses and lab coat.
- 7- Visual check before use, power supplies protected by RCD.

EMERGENCY PROCEDURES

Fire security contact number is 69966.

First aid occupational health is no longer a first call for first aid

Morton lab first aid contacts are Jim Fearick 64356, Liz Davenport 68869, Brian Hancock 64543, Andrew Evans 64543, Eric Warburton 64364, Tom Szpitter 62678

LEVEL OF SUPERVISION

C. Those with risks (other than A & B) where care must be observed, but where it is considered that workers are adequately trained and competent in the procedures involved.

LONE WORKING

Lone work is acceptable. The equipment is designed to be safe unattended.

REVIEW DATE

29 July 2011

REVIEW PERIOD AFTER FIRST REVIEW

1 Month

FINISH DATE

31 August 2011