# DEVELOPMENT OF THE MODIFIED ZEOLITE-A CATALYST FOR THE DIRECT CONVERSION OF METHANE TO LIQUID HYDROCARBONS

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JUDUL: DEVELOPMENT OF THE MODIFIED ZEOLITE-A CATALYST FOR
THE DIRECT CONVERSION OF METHANE TO LIQUID HYDROCARBONS

SESI PENGAJIAN: **2007/2008**

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# DEVELOPMENT OF THE MODIFIED ZEOLITE-A CATALYST FOR THE DIRECT CONVERSION OF METHANE TO LIQUID HYDROCARBONS

## MOHAMMAD AFIFI FAIZ BIN AZHA @ AZAHAR

A thesis submitted in fulfillment of the
requirements for the award of the degree of
Bachelor of Chemical Engineering (Gas Technology)

**Faculty of Chemical and Natural Resources Engineering**

**Universiti Malaysia Pahang**

**MAY 2008**

I declared that this thesis entitled

'Development of the modified Zeolite-A catalyst for the direct conversion of methane to liquid hydrocarbons' is the result of my own research except as cited in the references. The thesis has not been accepted for any degree is not concurrently submitted candidature of any degree.


Signature            : …………………………..

Name of Candidates    : MOHAMMAD AFIFI FAIZ BIN AZHA@AZAHAR

Date                  : 9 MAY 2008

Special dedicated to my beloved mother and father

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**ABSTRACT**

The characteristic of Zeolite-A loaded with iron and zinc on the direct conversion of methane to liquid hydrocarbons is investigated. Zeolite-A is loaded with different mass ratio of zinc and iron. Thermo Gravimetric Analysis (TGA), X-Ray Diffraction (XRD), and Fourier transform spectroscopy (FTIR) are used to analyze the physicochemical properties of the modified zeolite such as functional group, surface area and average diameter of unit cell. The absence of the iron content in the catalyst does not affect the framework and the crystalline of the catalyst but only affect the size of the unit cell and the surface area of the catalyst. As compare to zinc, it has modified the crystalline and framework of the catalyst. The result indicated that Zeolite-A with 8% of zinc and 2% of iron of metal doped is the most suitable catalyst for the methane conversion to liquid hydrocarbons. The catalyst has high thermal stability, high surface area, and high average diameter of unit cell and has low weight loss.

# ABSTRAK

Kajian ciri-ciri Zeolite-A dengan campuran logam besi dan zink terhadap proses penukaran metana secara terus kepada hidrokarbon cecair telah dijalankan. Zeolite-A akan dicampur dengan nisbah jisim zinc dan iron yang berbeza-beza. Thermo Gravimetric Analysis (TGA), X-Ray Diffraction (XRD), dan Fourier transform spectroscopy (FTIR) akan digunakan untuk mengesan fizikal kimia pemangkin yang telah diubahsuai  seperti kumpulan berfungsi, luas permukaan dan diameter purata unit cell. Kehadiran unsur besi dalam pemangkin tidak mengubah rangka dan stuktur kristal tetapi hanya mengubah saiz unit sel dan luas permukaan pemangkin tersebut. Berbanding dengan unsur zink, ia mengubah rangka dan struktur kristal pemangkin tersebut. Keputusan menunjukkan bahawa Zeolite-A dengan campuran 8% zink dan 2% besi merupakan pemangkin yang paling sesuai untuk proses penukaran metana secara terus kepada hidrokarbon cecair. Pemangkin ini mempunyai kestabilan termal yang tinggi, permukaan pemangkin yang luas, saiz unit sel yang besar dan mempunyai kadar pengurangan jisim yang rendah.

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# LIST OF SYMBOLS

TGA             Thermo Gravimetric Analysis

FTIR            Fourier Transform Infrared Spectroscopy

XRD             X-Ray Diffraction

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# CHAPTER 1

# INTRODUCTION

## 1.1    Research Background

Natural gas consists of mixture of hydrocarbon gases. The characteristic of the natural gas is colorless, shapeless, and odorless in its pure form. Natural gas is formed primarily of methane but it also includes ethane, propane, butane and pentane. Table 1.1 show outlines the typical makeup of natural gas before it is refined. Natural gas is considered 'dry' when it is almost pure methane, having had most of the other commonly associated hydrocarbons removed. When other hydrocarbons present, the natural gas is 'wet' (Thomas and Dawe, 2003).

Table 1.1    The typical composition of natural gas before it is refined
(Kvenvolden, 1995)

| Typical Composition of Natural gas | | |
|---|---|---|
| Methane | $CH_4$ | 70-90% |
| Ethane | $C_2H_6$ | 0-20% |
| Propane | $C_3H_8$ | 0-20% |
| Butane | $C_4H_{10}$ | 0-20% |
| Carbon Dioxide | $CO_2$ | 0-8% |
| Oxygen | $O_2$ | 0-0.2% |
| Nitrogen | $N_2$ | 0-5% |
| Hydrogen Sulphide | $H_2S$ | 0-5% |
| Rare Gases | A, He, Ne, Xe | trace |

In the last several decades, methane represents over 90% of the natural gas content and hence it is considered as promising source with high hydrocarbon content (Mat *et. al.,* 1999). However, not all the available and produced methane is utilized. A lot of effort has been considered toward the conversion of methane to value-added products such as transportable liquid hydrocarbons and chemicals. Traditionally, there are two competing demands for natural gas. It is used as a clean fuel in power generation, industrial kilns and furnaces, vehicles, and domestic heating. Natural gas is also demanded as a feedstock for petrochemical and chemical industries (Mat *et. al.,* 1999).

Gas to liquids or GTL is a refinery process to convert natural gas or other gaseous hydrocarbons into longer-chain hydrocarbons (Aguiar *et. al.,* 2005). Methane-rich gases are converted into liquid fuels either via direct conversion or via syngas as an intermediate, using the Fischer Tropsch process (Yagi *et. al.,* 2005). Using such processes, refineries can convert some of their gaseous waste products into valuable fuel oils, which can be sold as or blended only with Diesel fuel (Vosloo, 2001). The process may also be used for the economic extraction of gas deposits in locations where it is not economic to build a pipeline. This process will be increasingly significant as crude oil resources are depleted, while natural gas supplies are projected to last into the 22$^{nd}$ century (Wittcoff *et. al.,* 2004).

The direct conversion of natural gas to liquid hydrocarbons has not yet been successfully economized in an inexpensive process. The conversions of methane to gasoline by direct routes are still at low activity and selectivity (Amin *et al.,* 2006). These processes are possible if the reaction is carried out by controlled oxidation over a suitable catalyst (Mat *et. al.,* 1999). Recent studies have shown that modification of ZSM-5 zeolite by ion exchange, direct synthesis or wet impregnation method with metal oxides of different size and chemical properties are very important to control its acidity and shape selectivity. These modification methods led to an improvement in the catalytic activity and gasoline selectivity. When the acidity is increased by exchanging the zeolite with alkali metal cations, the conversion of methane to hydrocarbons is slightly enhanced. As a result, the metal containing

ZSM-5 can produce higher conversion hydrocarbons in methane oxidation (Amin *et. al.*, 2004).

The performance for direct methane conversion to higher hydrocarbons mainly depends on the physicochemical properties of the catalyst and this process uses zeolite as a catalyst. Physicochemical properties such as surface area and thermal stability are the factors to achieve the higher conversion and quality for this process. Modification by incorporation of elements of different size and different chemical features on zeolite is important to control the acidity and the shape selectivity of a specific zeolite structure.

## 1.2    Problem Statement

Numerous recent researches have demonstrated the feasibility of direct transformation of methane into products of higher added values such as olefins, aromatics and oxygenous derivatives .These processes are possible if the reaction is carried out by controlled oxidation over a suitable catalyst.

In practice, two routes for direct methane conversions to higher hydrocarbons have been identified. There are oxidative coupling and methane aromatization. A lot of efforts have led to a significant increase in the activity and selectivity of the applied catalyst. Unfortunately, the maximum yield obtained is about 20%, which means that the process is economically unfeasible (Huggil *et. al.,* 2005).  In the partial oxidation process, methane reacts with oxygen in the presence of catalyst to produce methanol. Unfortunately, the yield of methanol is too low (below 10%) and beyond industrial interest (Zhang *et. al.,* 2002; Michalkiewicz, 2004, Michalkiewicz, 2006). Direct conversion of methane to mainly ethane and ethene has been observed over fluorinated H-mordenite zeolite at $525^{o}C$, but with very poor methane conversion far below 1% (Kowalak *et. al.,* 1988). These low conversions are quite expected due to an unfavorable thermodynamic equilibrium at temperatures below $1000^{o}C$.

The application of zeolite for plasma catalytic methane conversion (PCMC) to higher hydrocarbons at very low gas temperature (room temperature to 200oC) by using Zeolites NaY, HY, NaX, NaA, Linde Type 5A and Na-ZSM-5 have been tested (Chang-jun Liu, 1999). NaA showed produce higher methane conversion (49%) compare using Na-ZSM-5 (44.6%) (Chang-jun Liu, 1999).

The present study focuses on the direct conversion of methane to liquid hydrocarbons. In order to overcome the current problems, the Zeolite-A will be doped with iron and zinc with different mass ratio in order to change the structure catalyst, thermal stability and other physicochemical to improve the quality of catalyst.

## 1.3    Research Objective

The objectives of this research are to:
1. To synthesis the Fe/Zn-Zeolite-A catalyst.
2. To study the physicochemical properties of the modified catalyst.
3. To relate the physicochemical properties of the catalyst with the conversion of methane to the liquid hydrocarbons.

## 1.4    Scope of Research

The scopes of this study are divided into four stages:
- Preparation and modification of catalysts
- Characterization of the catalyst for its physicochemical properties
- Compare the physicochemical properties of modified zeolite with unmodified zeolite and previous research.
  - Predict the catalyst performance of methane conversion to liquid hydrocarbons based on the physicochemical properties of the catalyst.

**CHAPTER 2**

**LITERATURE REVIEW**

## 2.1 Methane Convert to Higher Hydrocarbon

The first step to convert methane to higher hydrocarbons is methane oxidation that will produce olefin. Higher hydrocarbons will be produced from reaction of olefin through oligomerization, dehydrocyclization and aromatization using zeolite base catalyst according to the reaction scheme below:

$$CH_4 + O_2(cat) \longrightarrow C_2H_6 \longrightarrow C_2H_4 \longrightarrow \text{Higher Hydrocarbons}$$

The combination of the oxidative catalysis of methane with acid catalyst in a single catalytic process over bifunctional oxidative acid catalyst would be possible to convert methane directly to liquid hydrocarbon. This could be done by modifying pentasil zeolite catalyst with a suitable element. One possibility of modifying zeolites is the replacement of some of the silicon and aluminum with transition metal (Mat *et al.,* 2006).

Numerous catalysts have been discovered which possess different activities and selectivities for methane conversion to higher hydrocarbon. Most of them are based on metal or transition metal oxides, which are often supported on silica and alumina.

Direct partial oxidation of methane with $O_2$ to higher liquid hydrocarbons over transition metal containing ZSM-5 catalyst is reported (Han *et al.,* 1994; Amin *et al.,* 2004). Han *et al.* (1994) found that the successful methane conversion to hydrocarbons can be done over metal-containing ZSM-5 catalyst to two effects:

i. Ability of the metal to show some limited activity to generate olefins from methane.

ii. Sufficient low olefin oxidation activity to allow the olefin produced to remain in the system.

Han *et al.* (1994), found that when Zn loaded into ZSM-5 beyond one wt% metal, it potentially to reduce desired catalyst acidity needed for the conversion of methanol produced to $C_{5+}$. During the early days, another synthetic zeolite (HZSM-5 Zeolite) was found to be a suitable catalyst for the conversion of the methane to higher hydrocarbons. The acidic HZSM-5 zeolite catalyst has shown a reasonable good aligomerization performance for olefin products to higher hydrocarbons.

## 2.2    Zeolites

By the conventional definition, zeolites are microporous aluminosilicates. This definition has been modified within the past years and nowadays isomorphously substituted materials, like for example gallosilicates, titanosilicates or aluminophosphates, are also called zeolites or zeolitic materials. Microporosity (pores with diameters below 2 nm) is an intrinsic feature of all these materials and is caused by channels and cavities within the crystal structures of zeolites (Baerlocher *et al.,* 2001).

The structure of zeolite as shown (Figure 2.1) consists the primary building units which cations coordinated tetrahedrally by oxygen. These tetrahedral are connected via corners, thus forming the crystal structure of the specific zeolite.
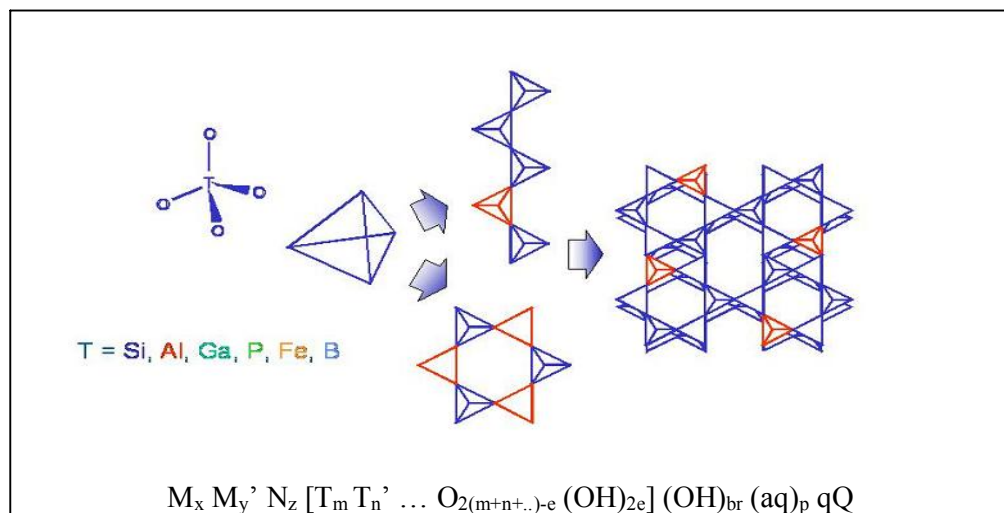
$$M_x M_y' N_z [T_m T_n' \ldots O_{2(m+n+..)-e} (OH)_{2e}] (OH)_{br} (aq)_p qQ$$

**Figure 2.1**     The Structure of Zeolite (Baerlocher *et al.,* 2001)

About 140 different zeolite structures are known of which about 40 are found in natural zeolites. The nomenclature of zeolites is rather confusing since every company is using its own names and abbreviations (Akporiaye *et al.,* 2001). To overcome this problem, a three-letter code system has been developed. These codes are assigned to specific structure type name *L*inde *T*ype A (Meier *et al.,* 1987). This structure type is found in various materials, as for example in aluminosilicates, aluminogermanates, gallophosphates or silicoaluminophosphates. A collection of all known zeolite structures can be found in the atlas of zeolite framework types or on the web page of the international zeolite association (Ch. Baerlocher *et al.,* 2001).

Zeolite-A exhibits the LTA (Linde Type A) structure and has a 3-dimensional pore structure with pores running perpendicular to each other in the x, y, and z planes, and is made of secondary building units 4, 6, 8, and 4-4. The pore diameter is defined by an eight member oxygen ring and is small at 4.2Å. This leads into a larger cavity of minimum free diameter 11.4Å. The cavity is surrounded by eight sodalite cages (truncated octahedra) connected by their square faces in a cubic structure.

The unit cell is cubic (a = 24.61Å) with Fm-3c symmetry. Zeolite-A has a void volume fraction of 0.47, with a Si/Al ratio of 1.0. It thermally decomposes at 700ºC. (Subhash Bhatia, 1990). Zeolite-A is of much interest because its supercage

structure is useful in spacio-specific catalysis. The inner cavity is large enough for structure changing reactions to take place, but the small pore means only a specific structure can get into the cavity for reaction, typically n-paraffins and olefins. One use is in paraffin cracking. The small entry pore is selective towards linear paraffins, and cracking can occur on sites within the supercage (alpha-cage) to produce smaller chain alkanes. Zeolite-A is also widely used in ion exchange separation (Ribeiro *et. al.,* 1984)

## 2.3    Zeolite Acidity

The concept that solid surfaces may be acidic arose from the observation that hydrocarbon reactions such as cracking that are catalyzed by acid treated clays or silica alumina, give rise to a much different product distribution than those obtained by thermal reaction (Knozinger *et al.,* 1997). These solid catalyzed reactions exhibit features similar to reaction catalyzed by mineral acids. By analogy to solution chemistry, it is postulated that the primary requirement for catalyst activity is that the solid be acidic and be capable of forming carbonium ions by reaction with a hydrocarbon (Subhash Bhatia *et al.,* 1990).

An acid site may be of the Bronsted type in which it denotes a proton to an unsaturated hydrocarbon, or of the Lewis type in which it acts as an electron acceptor, removing a hydride ion from a hydrocarbon (Pfeifer *et al.,* 1997). Acid catalysis is important in catalytic reforming, cracking, hydrocracking, isomerization, hydrodewaxing, alkylation and dealkylation (Farcasiu *et al.,* 1998). It is therefore important to be able to measure acidity and to rank solids as possible candidates for improvement of the yields of the processes.

The general definition of an acid is an electron-pair acceptor. The Bronsted acid site is able to transfer a proton from the solid to the absorbed molecule while the Lewis acid site is able to accept an electron pair from the adsorbed molecule and a coordinative bond with the surface is formed is shown in Figure 2.2.
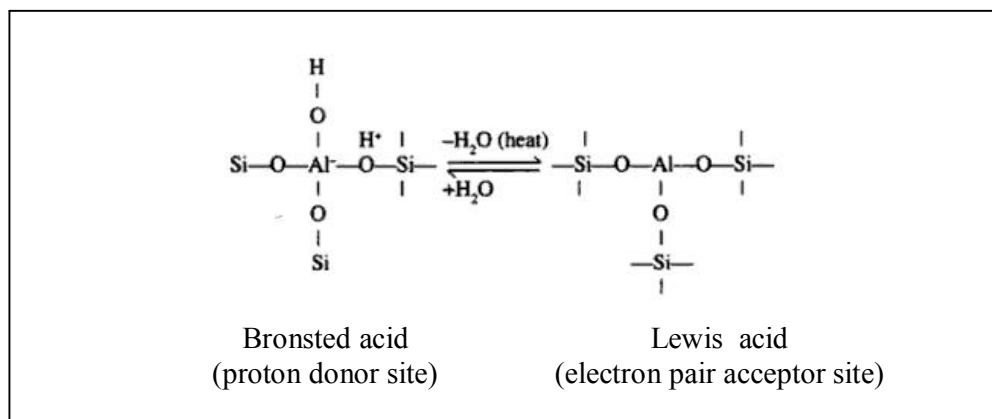
$$Si-O-\underset{\underset{\overset{|}{Si}}{\overset{|}{O}}}{\overset{\overset{\overset{H}{|}}{\overset{O}{|}}}{Al^-}}-O-Si- \quad \overset{-H_2O \text{ (heat)}}{\underset{+H_2O}{\rightleftharpoons}} \quad -Si-O-Al-O-Si-$$

Bronsted acid                    Lewis acid
(proton donor site)        (electron pair acceptor site)

**Figure 2.2**     Acid Site (Subhash Bhatia *et. al.,* 1990)

A description of acidity in general and surface acidity more specifically, requires the determination of the nature, the strength, and the number of acid sites. A solid acid is capable of transforming an adsorbed basic molecule into its conjugated acid form (Artioli *et al.,* 2001).

The catalyst acidity indicated the total amount of acid sites of modified zeolite is higher than ZSM-5. The metal-loaded will increase the acidity of the catalyst and improve the conversion of the process (Amin *et.al.*, 2006).

## 2.4     Ga-HZSM-5

Gallium is one of the potential elements that could modify the properties of zeolites. Over this catalyst, higher quality gasoline yield was obtained in the oxidative methane conversion (Anggoro, D. D. *et al.,* 1998). Ga loaded on HZSM-5 is claimed to be very efficient for the aromatization of light alkenes and alkanes (Vermeiren *et al.,* 1989), and has the potential to convert methane to liquid hydrocarbons with high selectivity (Anggoro, D. D. *et al.,* 1998). HZSM-5 was modified with gallium by ion exchange to create a bifunctional catalyst with sites active in both acid catalysed and oxidation reactions for the conversion of methane to liquid hydrocarbons in a single catalytic step. The prepared catalyst, Ga-HZSM-5,

could act as a better bifunctional catalyst than its parent catalyst, HZSM-5 zeolite (Mat *et al.,* 1999).

## 2.5    W-HZSM-5

The W-HZSM-5 based catalyst was found to be a highly active catalyst for methane dehydroaromatization in the absence of oxygen (Zeng *et al., 2001*). The catalyst showed a high activity and a high heat resistivity under reaction temperature of 1073 K. It was also reported that the addition of a second metal component into the catalyst by sequence impregnation method such as Zn (or Mn, La, Mg, Li) on W/HZSM-5 (Xiong *et al.,* 2001) enhanced the catalytic performance. The work reported by Xiong *et al., (*2001) demonstrated that the catalyst with medium strength acidity could improve the dehydroaromatization of methane.

## 2.6    Zn-ZSM-5

In FT-IR study showed that zinc in the cationic position causes the generation of Lewis acid sites and decrease of the Bronsted. Disproportionation of toluene continuously decreases with increasing amount of Zn indicating the decline of the number of Bronsted acid site by introduction of zinc into zeolites. Aromatization of n-hexane on acid ZSM-5 zeolite is affected by the particle properties of the zeolite. The activity/selectivity of monofunctional acid catalysts is significantly higher on the HZSM-5 sample that has particles of smaller size, probably mainly due to the higher external surface of the zeolite (Agáta Smiešková *et al.,* 2004).

The selectivity of Zn-ZSM-5 catalysts continuously rises with increasing amount of Zn in the zeolite. This indicates the increase of the concentration of olefins precursors of aromatics in the reaction mixture due to the dehydrogenation activity of Zn species. Results showed that at higher Zn concentration the performance of Zn-

ZSM-5 catalysts is very different probably due to the fact that Zn species in the ZSM-5 zeolites in the case of higher Zn concentration are of different types (Agáta Smiešková *et al.,* 2004). The distances between the adjacent Al atoms in the zeolite framework affect the position of the zinc cations and determine if isolated or oxygen-bridged cationic species of Zn are created in the catalyst (A. Hagen *et al.,* 1994).

From the technological point of view it is important that the results call attention to the fact that besides of the composition and the acidity of the Zn-ZSM-5 catalysts, also the particle properties and aluminum distribution in the framework of the zeolite can affect the effectivity of Zn-ZSM-5 catalysts in aromatization of light alkanes (Agáta Smiešková *et al.,* 2004).

## 2.7 Mo-ZSM-5

Many progresses have been achieved since the first report on methane dehydro-aromatization over Mo/ZSM-5 in 1993 (L.Wang *et al.,* 1993). It is now generally accepted that the reaction takes place in two steps (Y.H. Kim *et al.,* 2000). In the early stages of the reaction, the molybdenum oxide is converted to $MoC_x$ that later performs the $CH_4$ dehydrogenation and coupling to ethylene. Then, in a second step, the ethylene is oligomerized to benzene on the Brønsted acid sites of the zeolite (Figure 2.3). The location of the molybdenum plays a major role in this general scheme.
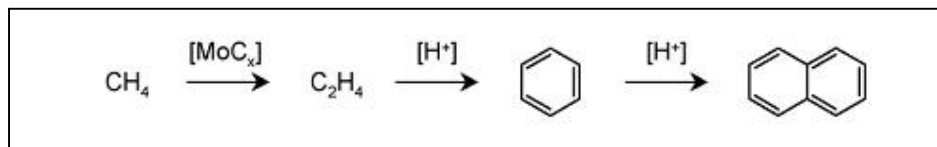


**Figure 2.3**     Formation of benzene and naphthalene from methane on Mo/ZSM-5 (Jean-Philippe Tessonnier *et al.,* 2007)

Molybdenum oxide supported on classical supports like $SiO_2$, $Al_2O_3$ or $TiO_2$ is quickly carburized to $MoC_2$ under the reaction conditions and then only catalyses

the coke formation (F. Solymosi *et al.,* 1995). Different groups have also supported molybdenum oxide on various zeolites and mesoporous materials (Y. Shu *et al., 2001*). Best results were obtained with zeolites ZSM-5 and MCM-22, presenting a two-dimensional porous network, with channels having a diameter of 5–6 Å that corresponds exactly to the kinetic diameter of the benzene molecule.

Tan et al. investigated in details the synthesis of 2 wt. % Mo/ZSM-5 and the consequences on its catalytic activity (P.L. Tan *et al.,* 2002). They found out that both common precursors, ammonium heptamolybdate (AHM) and $MoO_3$, are too large to penetrate the ZSM-5 channels during the impregnation process or during calcinations at temperatures below $600^{\circ}C$, in good agreement with previous work of Agudo et al. (A.L. Agudo *et al.,* 1992). However, at $700^{\circ}C$ the $MoO_3$ vapor pressure becomes high enough (56 Pa) to allow $MoO_x$ species start to diffuse inside the channels of the ZSM-5 (O. Knacke *et al.,* 1991).

Borry et al. further studied the diffusion of these species and their interaction with the Brønsted acid sites of the zeolite (R.W. Borry *et al.,* 1999). They provided clear evidence that $Mo_xO_x$ vapor reacts with the acid sites to form a $(Mo_2O_5)^{2+}$ cluster bridging two Brønsted sites of the zeolite (Figure 2.4a). Until now, this model was generally accepted. However, several groups provided contradictory elements. Mosqueira and Fuentes (2002) studied the spreading of molybdenum oxides on different supports, including ZSM-5 (L. Mosqueira *et al.,* 2002). They found by using diffuse reflectance UV spectroscopy that the molybdenum anchored on the support and exist in two different configurations: $Mo_2O_7$ dimer as predicted by Borry et al., but also as tetrahedral $MoO_4$ monomer. Mosqueira and Fuentes do not make further hypothesis about the anchoring of this monomer. $MoO_2^{2+}$ clusters could bridge two Brønsted acid sites, like for H–Y zeolites (Figure 2.4b) (H. Minming *et al.,* 1987). DFT calculations performed by Zhou et al. demonstrated that grafting could also occur via a $MoO^{2+}$ cluster bridging two neighboring oxygen atoms (Figure 2.4c) (D. Zhou *et al.,* 2001).
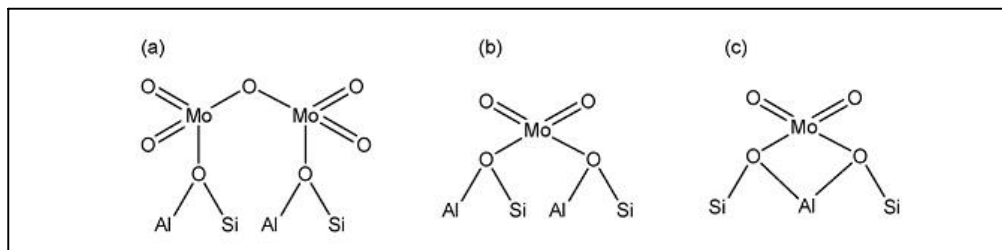
**Figure 2.4**    Different model of Mo anchoring on Brønsted acid sites of the ZSM-5 (R.W. Borry *et al.,* 1999)

## 2.8    Mo-HZSM-5

Recently, it has been shown that supported molybdenum, preferentially Mo supported on H-ZSM-5, is active and selective for benzene aromatic from methane (Y. Xu *et al.,* 1995). It was clearly established that at high temperature under $CH_4$ molybdenum in Mo-HZSM-5 was reduced and formed $Mo_2C$ species (D. Wang *et al.,* 1997) and further during the activation process of Mo-HZSM-5 molybdenum species migrated towards exchangeable sites in the zeolite framework (D. Wang *et al.,* 1997). It is generally reported that the activation of methane occurs on molybdenum active species forming ethylene as primary product $C_2H_4$ being converted into benzene over $H^+$ acid sites of the zeolite (Y. Xu *et al.,* 1995).

In a very recent work it was shown by contrast that acetylene was the primary product of the reaction of methane over Mo-HZSM-5 (P. Meriaudeau *et al.,* 1999), and the authors concluded that a possible route for the formation of benzene is the production of $C_2H_2$ on Mo sites. The aim of this work was to provide an integrated understanding on the nature of active sites operating during the aromatization of methane over Mo-H-ZSM-5 catalyst. The role of the zeolite was examined by comparing H-ZSM-5 and H-MCM-22 having different topology. The role of protons in the zeolite, in which protons apparently improved the catalytic performances, was examined, and a reaction mechanism was proposed.

## 2.9    Characterization of Catalyst Using X-Ray Diffraction

X-ray diffraction provides information on the structure and unit cell parameter of zeolites, XRD analyses of gallium loaded zeolites was typical of crystalline HZSM-5 and did not reveal clear XRD lines attributable neither to oxide phases nor to metal oxide clusters (Figure 2.5) and The unit cell parameters and unit cell volume of the zeolite catalysts are presented in Table 2.1. The unit cell volume of Ga-HZSM-5 is smaller than that of HZSM-5, due to the removal of some of the aluminium from the zeolite framework (Amin *et. al.,* 2001). It because of the ionic radii of tetrahedral structure of $Si^{4+}$ is lower than $Al^{3+}$ , 0.40Å and 0.53Å, respectively (Szostak, *et al.,*1989). So, as the aluminium framework decrease, the unit cell parameters decrease, and the unit cell volume also decrease.
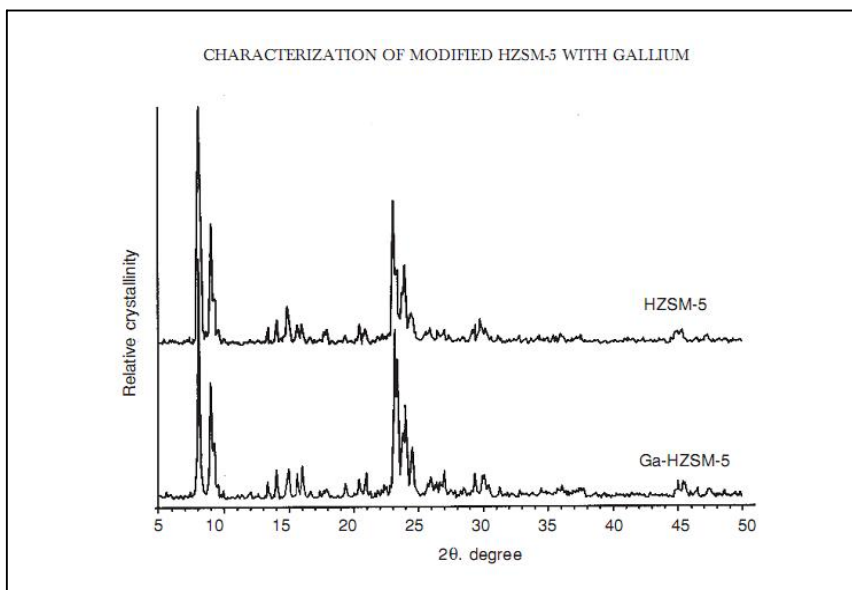


**Figure 2.5**    XRD diffractogram of HZSM-5 and Ga-HZSM-5 zeolite catalyst (Amin *et al.,* 2001)

**Table 2.1**      The Si/Al ratio and unit cell parameters of zeolites (Amin *et al.,* 2001)

| Sample | The Si/Al ratio (*) | | | |
|---|---|---|---|---|
| | a (Å) | b(Å) | c(Å) | V(Å$^3$) |
| HZSM-5 | 19.674 | 20.725 | 14.665 | 5979.56 |
| Ga-HZSM-5 | 19.505 | 20.627 | 13.825 | 5562.21 |

## 2.10    Characterization of Catalyst Using TPD

The acidity of the catalysts was examined by using temperature programmed desorption of ammonia. The amount of acid or acidity on a solid is expressed as moles of acid sites per unit weight of the solid. The amount of chemisorbed $NH_3$ on the HZSM-5 zeolite catalyst is much higher than Ga-HZSM-5. It indicates that the parent zeolite has more acid sites than the gallium zeolite. However, both low temperature (LT) and high temperature (HT) of Ga-HZSM-5 are lower than that of HZSM-5. Koval et al. (1996) reported that the desorption of $NH_3$ at the LT and HT is related to the acid strength of the zeolites. The result of the TPD is show in Table 2.2.

Both the zeolite catalyst contain LT and HT that suggest there is no significant changes in the acid strength, but Ga-HZSM-5 zeolite contains less number of acid sites than HZSM-5 zeolite. Topsoe et al. (1981) have postulated that the number of acid sites decreases as aluminium is removed from the crystal lattice and increases as aluminium is inserted into the framework of HZSM-5. The acidity also decreased with a decreasing micropore volume of HZSM-5, which caused a reduction in ammonia adsorption (Koval *et al.,* 1996). Based on the XRD, Si MAS NMR, and nitrogen adsorption data, the decrease in acidity is due to the effects of the removal of aluminium from the framework and metal oxide trapped inside the channels of modified zeolite.

**Table 2.2**      Nitrogen adsorption data (Amin *et al,* 2001)

| Sample | Amount of chemisorbed (moles/kg) | Low temperature ($^{o}$C) | High temperature ($^{o}$C) |
|--------|-------|-------|-------|
| HZSM-5 | 0.5424 | 214 | 415 |
| Ga-HZSM-5 | 0.1418 | 209 | 414 |

## 2.11    Characterization of Catalyst Using TGA

TGA can be used to accurately detect the desorption of basic molecules from a zeolite as a function of temperature and the resulting data can be used to calculate the acid site strength and distribution of various zeolites (Bhatia *et.al.,* 1990).

## 2.12    Characterization of Catalyst Using FTIR

The infrared spectra for ZSM-5 and metal-loaded ZSM-5 samples are shown in figure 2.6. The structure sensitive absorption around 1200 and 550 cm$^{-1}$ is of special interest to distinguish the zeolite types (Jansen *et al., 1984)*. In Table 2.2 the positions of some characteristic vibration bands are summarized. All samples have vibration bands between 546 and 1223 cm$^{-1}$. The frequency band at 1099 cm$^{-1}$ is assigned to the asymmetric stretching of framework Si–O–Si or Si–O–Al bonds (Le Van Mao R *et al.*, 1999*)*. The bands of Cr-ZSM-5 and Ga-ZSM-5 demonstrated a significant change in the frequency shift or a reduction in the intensity framework. This indicates that Cr-ZSM-5 and Ga-ZSM-5 catalysts experienced a significant change in the number of those forming framework bonds.
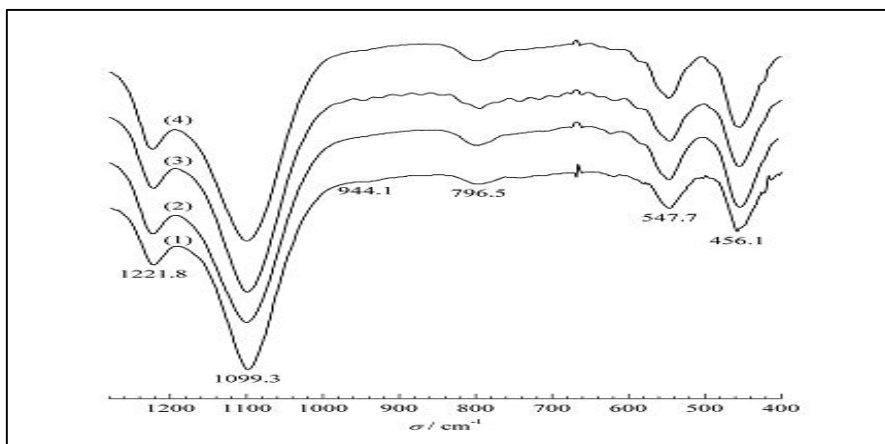
**Figure 2.6**     Infrared spectra (Amin *et al.,* 2003) (1) ZSM-5, (2) Cr-ZSM-5, (3) Cu-ZSM-5, (4) Ga-ZSM-5

**Table 2.3**     Infrared band positions of ZSM-5 and metal loaded ZSM-5 (Amin *et al.,* 2003)

| Sample | Wavenumber ($cm^{-1}$) | | | | |
| | Asymmetric strech | | Symmetric strech | Double ring | To bending |
| | External | Internal | External | | |
| ZSM-5 | 1221.8 | 1099.3 | 796.5 | 547.7 | 456.1 |
| Cr-ZSM-5 | 1223.7 | 1101.3 | 798.5 | 546.8 | 455.2 |
| Cu-ZSM-5 | 1222.8 | 1100.3 | 795.6 | 545.8 | 457.1 |
| Ga-ZSM-5 | 1223.7 | 1100.3 | 798.5 | 545.8 | 458.1 |

# CHAPTER 3

# METHODOLOGY

## 3.1 List of Materials

The Table 3.1 shows the list of materials that were used during the experiment of the studies.

**Table 3.1** List of materials

| No. | Materials | Purpose | Supplier |
|-----|-----------|---------|----------|
| 1 | Zeolite A | Synthesis catalyst | Sigma-Aldrich Chemie |
| 2 | Iron sulfate | | |
| 3 | Zinc sulfate | | |

## 3.2 Overall Methodology

Figure 3.1 shows the experimental work flow
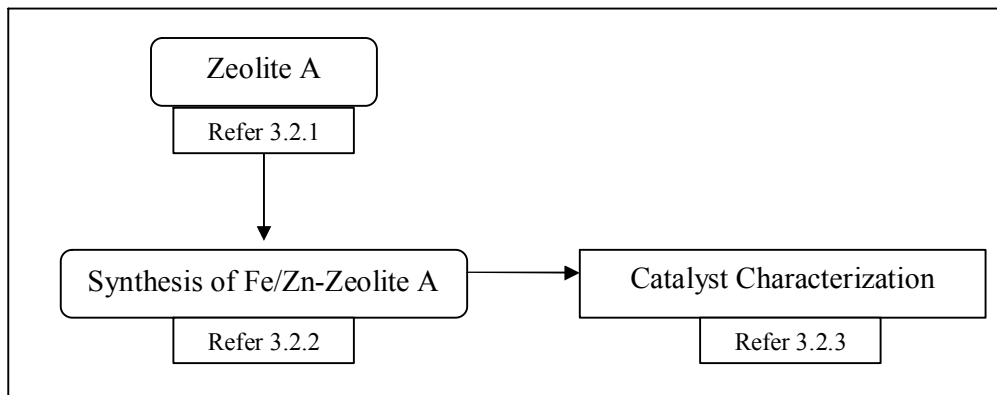


**Figure 3.1**     Experimental Work Flow

### 3.2.1 Zeolite A

Zeolite A was supplied by Sigma-Aldrich Chemie. The surface area of the zeolite is less than 45 micrometer.

### 3.2.2 Synthesis of Fe/Zn-Zeolite A

Iron nitrate, zinc nitrate, Zeolite-A and some water were mixed together with different mass ratio, this method called ion exchange method (Amin *et al.,* 2003). Table 3.2 shows the detail of the mass for each sample. Then the sample was dried at $100^{\circ}C$ overnight and calcined at $550^{\circ}C$ for 3 hours in an air flow.

**Table 3.2**    Ma**ss** of zinc, iron and zeolite for each sample

| Component | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 |
|-----------|----------|----------|----------|----------|----------|
| Iron | 0 | 0.2 gram | 0.5 gram | 0.8 gram | 1 gram |
| Zinc | 1 gram | 0.8 gram | 0.5 gram | 0.2 gram | 0 |
| Zeolite | 10 gram | 10 gram | 10 gram | 10 gram | 10 gram |
| Water | 10 ml | 10 ml | 10 ml | 10 ml | 10 ml |

### 3.2.3    Catalyst Characterization

The acid site, acid strength, thermal stability, structural and other physicochemical of the modified were measured using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and thermo gravimetric analysis (TGA).

### 3.2.3.1 X-Ray Diffraction (XRD)

The XRD analysis was used to check the structure of the catalyst and presence of the crystalline phase. The XRD analysis was carried out at the Ibnu Sina Laboratory, Universiti Teknologi Malaysia. XRD measurements were performed in the range of $2\Theta = 5^{o}$ to $50^{o}$ using a siemen 5000 diffractometer with vertical goniometer and CuK$\alpha$ radiation ($\lambda = 1.542$Å) at 35 kV and 35 mA (scanning speed: $4^{o}$/minute).

### 3.2.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

FT-IR spectra were recorded on a Perkin Elmer Series II IR spectrometer at room temperature using KBr pellet technique. The sample was ground with the spectra grade KBr to form a pellet under hydraulic pressure. The pellet was used to

record the IR spectrum in the range of 400-1200 cm$^{-1}$ under the atmospheric conditions with a resolution of 1 cm$^{-1}$.

### 3.2.3.3 Thermo Gravimetric Analysis (TGA)

The thermal stability of the catalysts was determined using a thermogravimetric analyzer (Perkin-Elmer TGA 7). The samples were placed in a pan that was heated under flow of air (25 ml/min) from room temperature to 1000˚C at the heating rate of 10$^{o}$C min$^{-1}$.

# CHAPTER 4

# RESULTS & DISCUSSION

## 4.1     XRD Characterization

Most of the structural information about Zeolite-A was obtained from X-ray diffraction (XRD). X-ray diffraction provides information about the average diameter of unit cell and the crystallinity of the zeolites, as shown in Table 4.1 based on the XRD diffractograms (Figure 4.1, Figure 4.2, Figure 4.3, Figure 4.4 and Figure 4.5). The diffactograms revealed that there is no change in the Zeolite-A crystalline structure after loaded with iron. The crystalline structure changes after zinc loaded on Zeolite-A as shown by the peaks at $2\theta$ values of 16 and 24 appeared in sample 1, sample 2, sample 3 and sample 4.

**Table 4.1**     Crystallinity, average diameter of unit cell and rank average diameter of unit cell

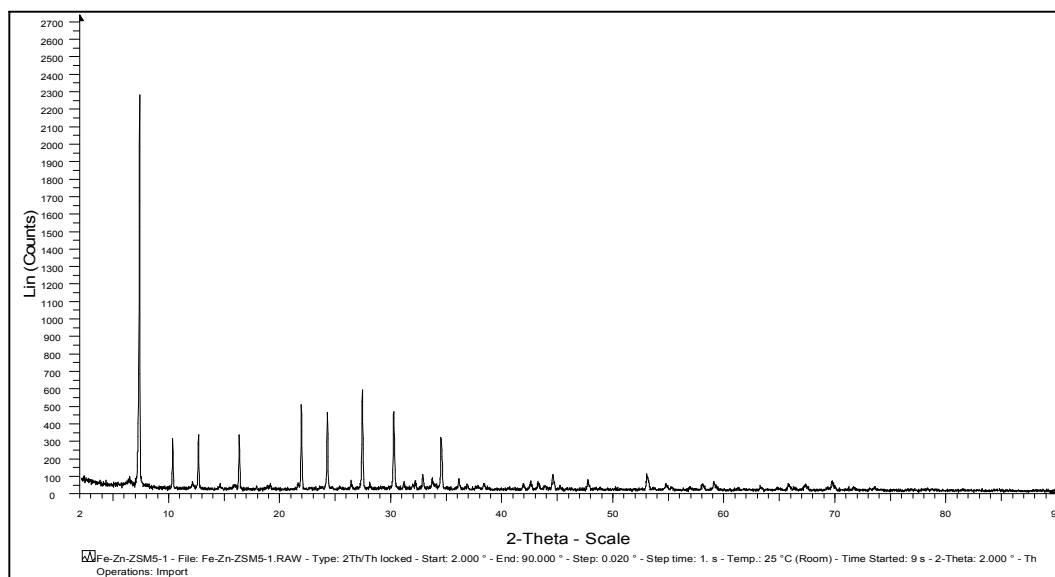| Samples | Crystallinity (%) | Average diameter of unit cell (Å) | Rank average diameter of unit cell |
|---------|-------------------|-----------------------------------|-------------------------------------|
| Sample 1 | 23.2 | 3.67204 | 5 |
| Sample 2 | 24.8 | 3.67621 | 3 |
| Sample 3 | 38.3 | 3.67576 | 4 |
| Sample 4 | 41.6 | 3.68064 | 2 |
| Sample 5 | 53.5 | 3.6878 | 1 |

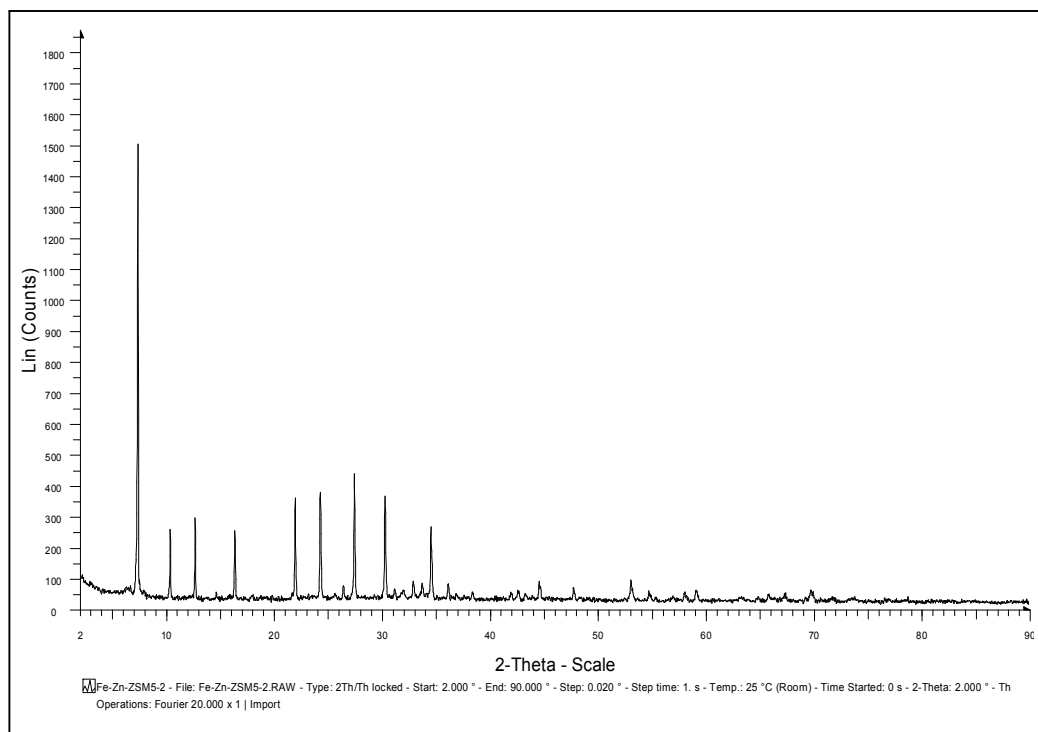**Figure 4.1**     X-ray diffractogram of sample 1



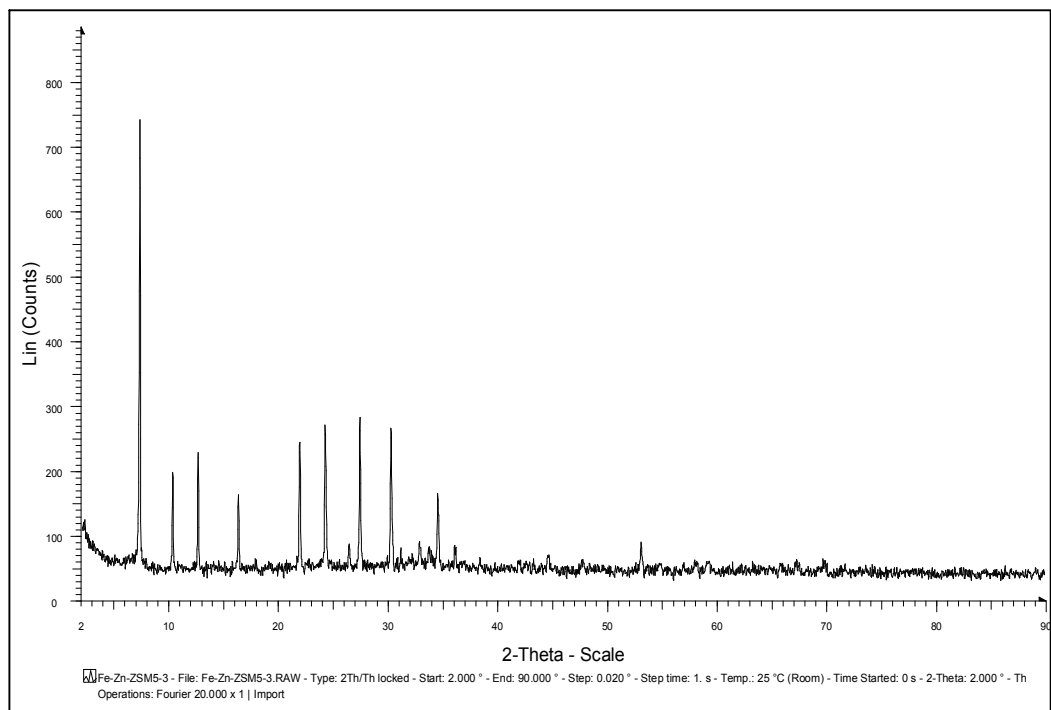**Figure 4.2**     X-ray diffractogram of sample 2

**Figure 4.3**    X-ray diffractogram of sample 3
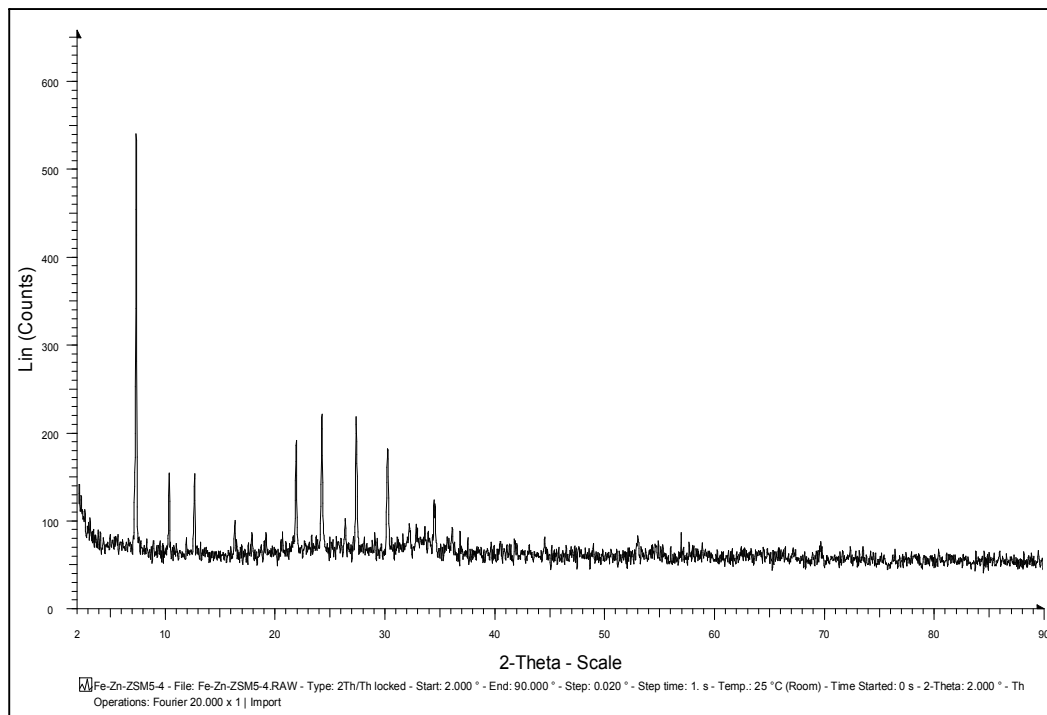


**Figure 4.4**    X-ray diffractogram of sample 4

Fe-Zn-ZSM5-5 - File: Fe-Zn-ZSM5-5.RAW - Type: 2Th/Th locked - Start: 2.000 ° - End: 90.000 ° - Step: 0.020 ° - Step time: 1. s - Temp.: 25 °C (Room) - Time Started: 0 s - 2-Theta: 2.000 ° - Th
Operations: Smooth 0.150 | Import
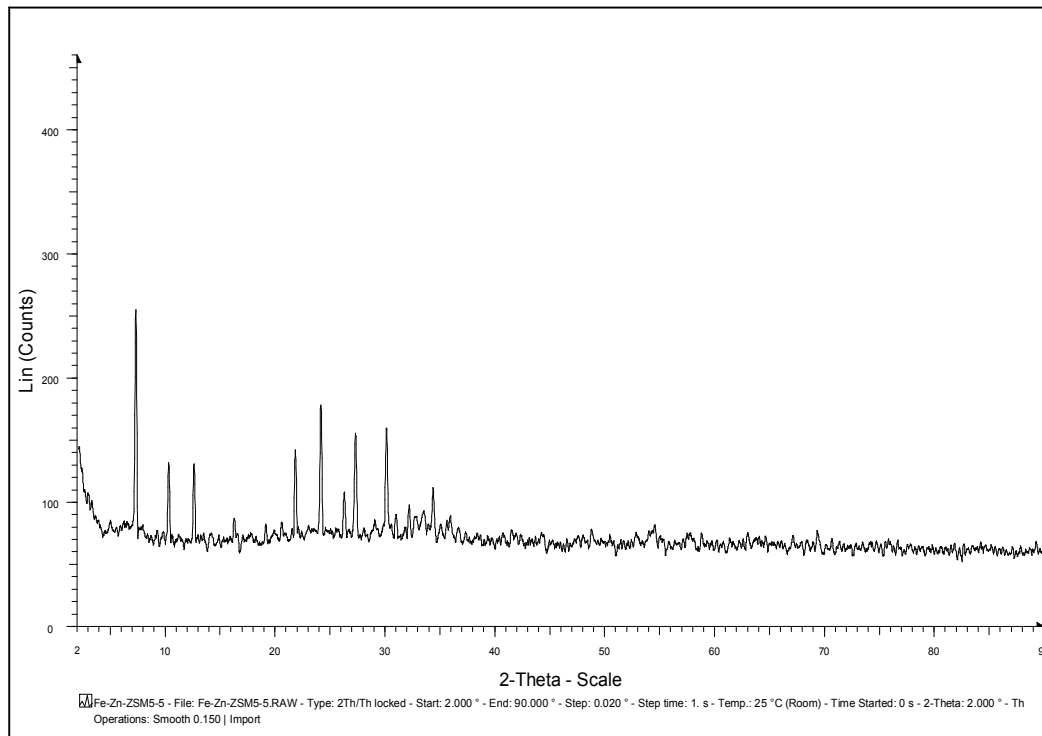
**Figure 4.5**     X-ray diffractogram of sample 5

The crystallinity of the zeolite can be calculated from the diffractograms. The crystallinity of the zeolite is expressed as the percentage of crystallinity using the intensity of the main peak at $2\theta=22.5 -24.4$ in the XRD pattern (Amin *et. al.,* 2003). The crystallinities of Sample 1, Sample 2, Sample 3, Sample 4 and Sample 5 are 23.2, 24.8, 38.3, 41.6 and 53.5, respectively.

The results indicate that the crystallinity of the iron loaded Zeolite-A has increased the crystallinity. The change in crystalline structures were observed in the zinc and iron metal-loaded into Zeolite-A. The average diameter of unit cell of sample 1, sample 2, sample 3, sample 4 and sample 5 are 3.67204Å, 3.67621Å, 3.67576Å, 3.68064Å and 3.6878Å, respectively and have been summarized in Table 4.1.

From the result, it shows that sample 5 has highest volume of unit cell and followed by sample 4, sample 2, sample 3 and sample 1. The removal of some of the aluminium from the zeolite framework could affect the average of unit cell (Amin *et.*

*al.,* 2001). Iron content has increased the diameter of the Zeolite-A by replacing some of the aluminium from the zeolite framework.

Figure 4.1, Figure 4.2, Figure 4.3, Figure 4.4 and Figure 4.5 show the intensity of the diffractograms for each samples decrease from sample 1 until sample 5. The peak at $2\theta = 6.5$-$7.5$ for sample 1, sample 2, sample 3, sample 4 and sample 5 are 1990, 1560, 738, 548 and 383, respectively and have been summarize in Table 4.2.

Reported that the band intensities could be influenced by various factors such as the size of particles, the surface effect, and the dispersity of the metal, which resulted in a little change of the band intensity (Jia *et al.,* 1993). There is a gradual decrease in surface area with increasing iron content. The drop in surface areas may be attributed to micropore blockage by highly dispersed iron oxide particles (Debasish Das *et al,* 1993).

**Table 4.2**     Intensity of the highest peak in x-ray diffractogram

| Sample | Intensity of the highest peak |
|--------|-------------------------------|
| Sample 1 | 1990 |
| Sample 2 | 1560 |
| Sample 3 | 738 |
| Sample 4 | 548 |
| Sample 5 | 383 |

## 4.2     FTIR Characterization

Figure 4.6 shows the infrared spectra for sample 1, sample 2, sample 3, sample 4 and sample 5. The structure sensitive absorption around 1200 and 550 cm$^{-1}$ is of special interest to distinguish the zeolite types (Jansen *et al,* 1984). All samples have vibration band between 600 and 2400 cm$^{-1}$. The frequency band a 1099 cm$^{-1}$ is

assigned to the asymmetric stretching of framework Si–O–Si or Si–O–Al bonds (Le Van Mao R *et al,* 1999).

The bands of sample 1, sample 2, sample 3 and sample 4 demonstrated significant changes in the frequency shift or a reduction in the intensity framework. This indicates that zinc content in the catalysts experienced a significant change in the number of those forming framework bonds. Except sample 5, there has a new intensity appear around $900 - 910$ cm$^{-1}$.

In sample 4, wavenumber 1100cm$^{-1}$ shows the catalyst form a new framework with the present of 8 percent of iron and 2 percent of zinc. Combination Zeolite-A with ratio 4:1 of iron and zinc affects the framework of catalyst. Beside that, sample 3 with ratio 1:1 of iron and zinc increases the intensity of the framework at wavenumber 729 and 692cm$^{-1}$.
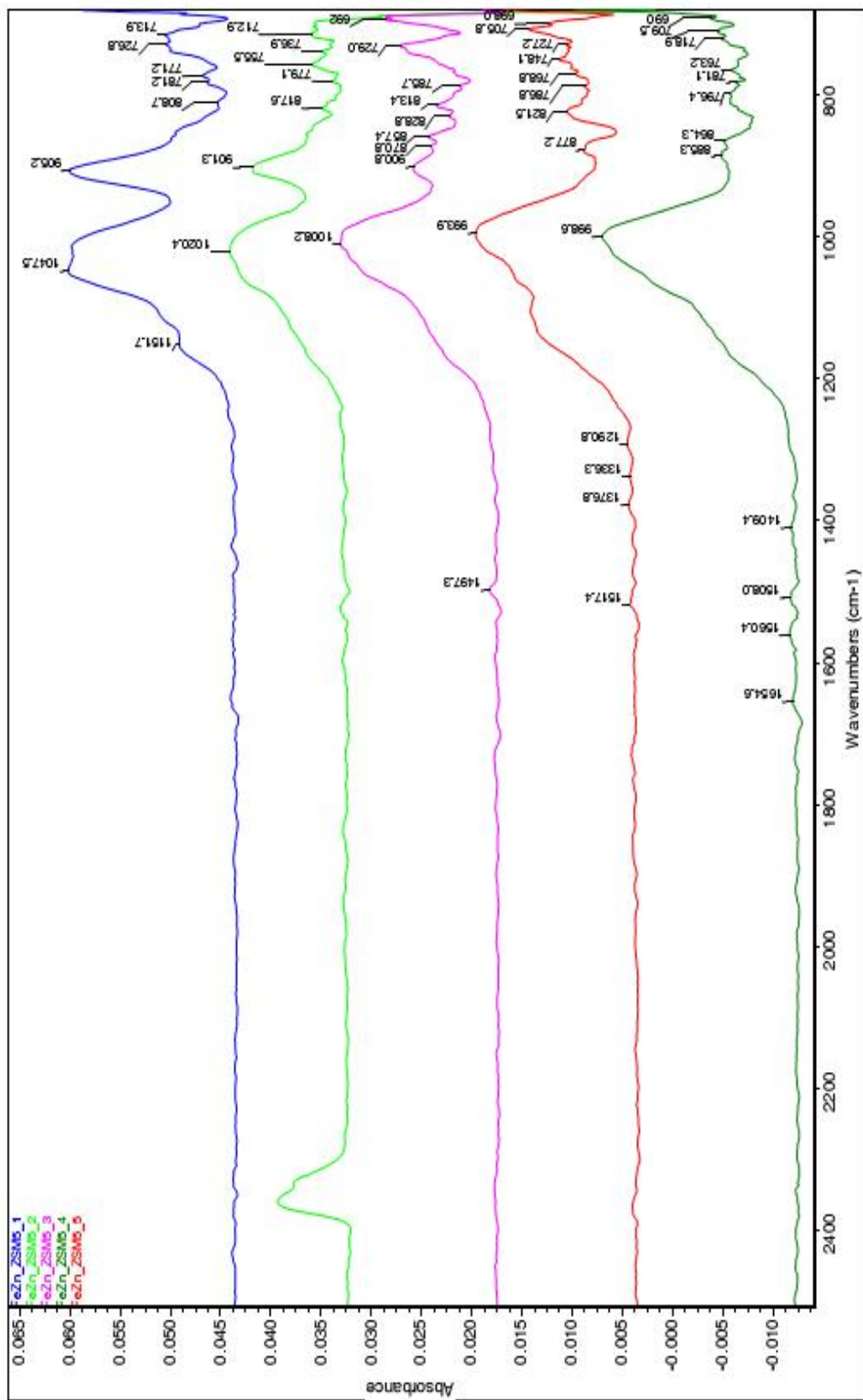
**Figure 4.6**     Wavenumber vs absorbance using FTIR

## 4.3    TGA Characterization

Thermo Gravimetric Analysis (TGA) characterization was done by using thermogravimetric analyzer (Perkin-Elmer TGA 7).. TGA analysis was done for each sample in order to identify the thermal stability of the modified Zeolite-A. Figure 4.7 for sample 1, Figure 4.8 for sample 2, Figure 4.9 for sample 3, Figure 4.10 for sample 4 and Figure 4.11 for sample 5.
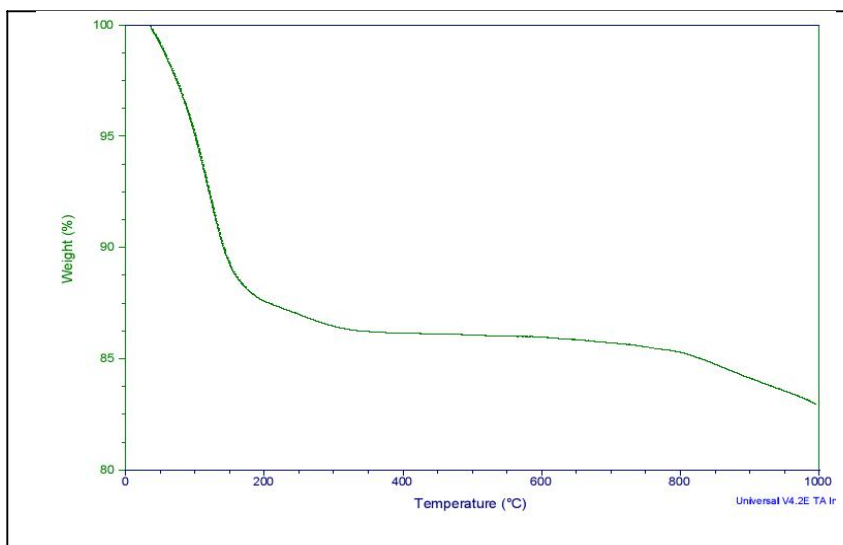


**Figure 4.7**    Weight Loss (%) vs Temperature for sample 1
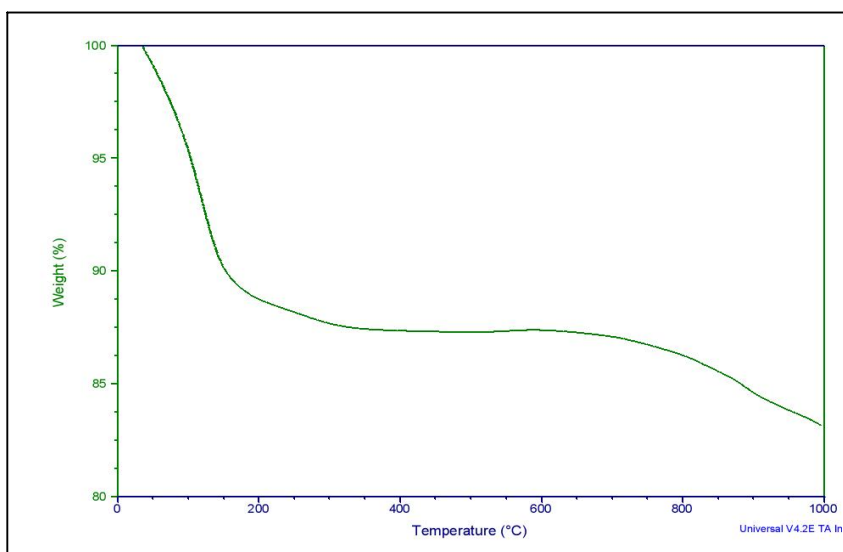


**Figure 4.8**    Weight Loss (%) vs Temperature for sample 2
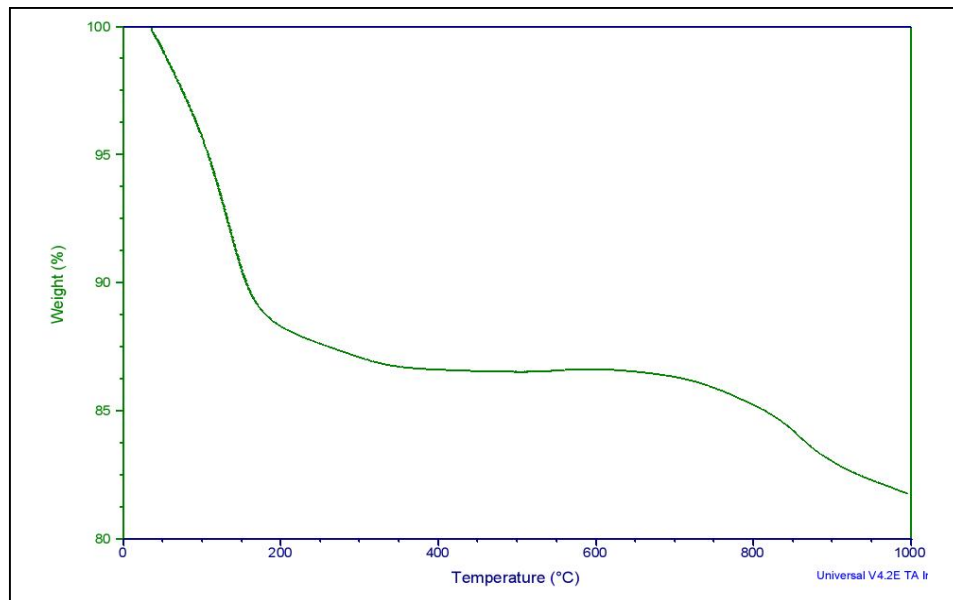
**Figure 4.9**     Weight Loss (%) vs Temperature for sample 3
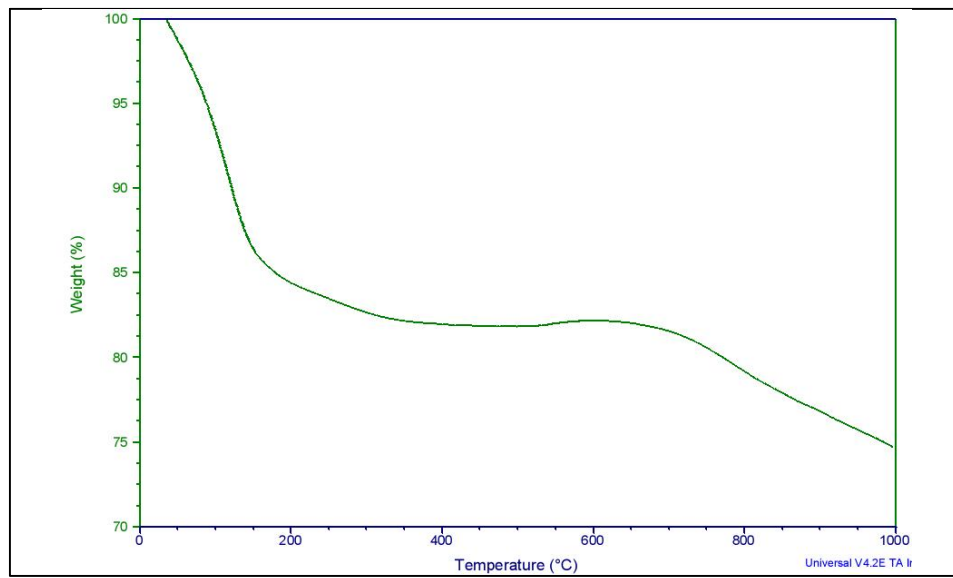


**Figure 4.10**    : Weight Loss (%) vs Temperature for sample 4
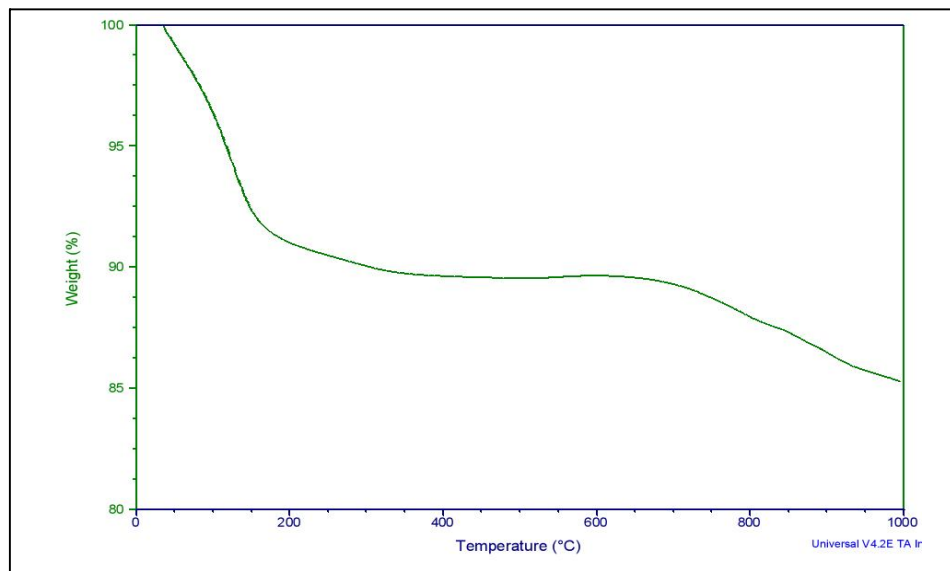
**Figure 4.11** : Weight Loss (%) vs Temperature for sample 5

These figures are plotted by of weight loss versus temperature. The catalyst was heating from room temperature until 1000$^{o}$C with the heating rate of 10$^{o}$C per minute. Figure 4.7 was prepared with 10% of zinc content loaded into the catalyst. There are four situations occur on the catalyst during the heating. A weight loss of 11% has occured in a short time starting from room temperature until 150$^{o}$C. At this stage, all the moisture that attached on the catalyst has been removed.

The second stage occurs around 150$^{o}$C until 350$^{o}$C, the catalyst only has a small weight loss and the catalyst is stable with the increasing of the temperature. At the third stage from 350$^{o}$C until 800$^{o}$C, the weight loss of the catalyst seems does not occur. This stage is good to perform the methane conversion to liquid hydrocarbons. This is in line with the performance studies done by Amin *et. al.,* (2003). The final stage starts from 800$^{o}$C until the highest temperature at 1000$^{o}$C, at this stage the catalyst starts to decompose.

Result of TGA study for sample 2 is shown in Figure 4.8. The existent of zinc content at 2% of catalyst does not affect the thermal stability but affect the weight loss of the catalyst. Sample 2 has decreased the percentage of the weight loss of the catalyst as compared to the sample 1. The total weight loss for the sample 2 and

sample 1 at third stage are 12.5% and 13.75%, respectively. Since all the samples were prepared at the same condition, the content of all the catalyst's moisture were the same. The iron content in the sample 2 has supported the catalyst to decrease the total weight.

Figure 4.9 shows the result of sample 3. In this sample, the content of zinc and iron are 5% of the weight of catalyst. Combination of zinc and iron at same ratio has decreased the thermal stability of catalyst. The third stage of this sample starts at $350^{o}C$ and end earlier as compared to sample 1 and 2 at $750^{o}C$. The increasing of iron content and decreasing of zinc content has affected the thermal stability. The total weight loss of sample 3 remains unchanged as compared to the sample 2 at 12.5%.

Sample 4 (Figure 4.10) has the highest weight loss of 17.5% until third stage, beside. The third stage of this sample occurs at $400^{o}C$ until $650^{o}C$. The catalyst has started the third stage at higher temperature and ended at lower temperature. This sample was prepared with 2% of zinc content and 8% of iron content. This ratio of zinc and iron decreases the thermal stability and increases the percentage of weight loss. It can be concluded that the iron content should not higher than the zinc content in the same catalyst.

Sample 5 was prepared with 10% of iron content into Zeolite-A without zinc content. With existent of 10% of iron content without zinc content, this catalyst produces the lowest weight loss. The thermal stability of this sample is higher than the sampel 4 but it is lower than sampel 1 and sample 2. As compared to sample 3, sample 5 is better because sample 3 and sample 5 have same thermal stability but different weight loss. Result for sample 5 is shown in Figure 4.11.

**4.4    General discussion**

Table 4.3, Table 4.4 and Table 4.5 show the summary of the result of XRD, FTIR and TGA. Sample 1 shows the lowest percentage of crystallinity with the lowest average diameter of the unit cell but produces the highest surface area. It shows that the zinc content does not support the volume of the unit cell but increase the mircopore volume and it also has low weight loss of the catalyst.

**Table 4.3**    Crystallinity, average diameter of unit cell and Intensity of the highest peak in x-ray diffractogram

| Samples | Crystallinity (%) | Average diameter of unit cell (Å) | Intensity of the highest peak |
|---|---|---|---|
| Sample  1 | 23.2 | 3.67204 | 1990 |
| Sample 2 | 24.8 | 3.67621 | 1560 |
| Sample 3 | 38.3 | 3.67576 | 738 |
| Sample 4 | 41.6 | 3.68064 | 548 |
| Sample 5 | 53.5 | 3.6878 | 383 |

**Table 4.4**    Peak at $900 - 910$ cm$^{-1}$ and changing of the samples in FTIR characterization

| Samples | Peak at $900 - 910$ cm$^{-1}$ | Changing |
|---|---|---|
| Sample  1 | **yes** | - |
| Sample 2 | **yes** | - |
| Sample 3 | **yes** | Increase intensity at 729 and 692 cm$^{-1}$ |
| Sample 4 | **yes** | New peak at 1100 cm$^{-1}$ |
| Sample 5 | **no** | - |

**Table 4.5**     Result of TGA characterization

| | First stage | Second stage | Third stage | Weight Loss |
|---|---|---|---|---|
| **Sample 1** | Room temperature until 150$^{\circ}$C. | 150$^{\circ}$C to350$^{\circ}$C | 350$^{\circ}$C to800$^{\circ}$C | 13.75% |
| **Sample 2** | | | | 12.5% |
| **Sample 3** | | | 350$^{\circ}$C to 750$^{\circ}$C | |
| **Sample 4** | | 150$^{\circ}$C to400$^{\circ}$C | 400$^{\circ}$C to750$^{\circ}$C | 17.5% |
| **Sample 5** | | 150$^{\circ}$C to350$^{\circ}$C | 350$^{\circ}$C to750$^{\circ}$C | 10% |

Sample 2 has higher percentage of crystallinity, average diameter of unit cell and weight loss of the catalyst with existent of two percent of iron content in the catalyst but surface area of the catalyst is decreased. Sample 3 has increased the intensity of wavenumber at 729 and 692 cm$^{-1}$ and this results a decrease in the size of the unit cell and the thermal stability of the catalyst.

Sample 4 has higher percentage of crystallinity and average diameter of unit cell but lower surface area and thermal stability. It also has highest weight loss of the catalyst. Sample 4 also produces a new peak at wavenumber 1100 cm$^{-1}$ as compared to the other samples.

Sample 5 with 10% of iron content has the highest percentage of crystallinity and average diameter of the unit cell but lowest surface area. It also has lowest percentage of weight loss.

The absence of the iron content in the catalyst does not affect the framework and the crystalline of the catalyst but only affect the size of the unit cell and the surface area of the catalyst. As compare to zinc, it has modified the crystalline and framework of the catalyst. The results of the XRD, TGA and FTIR have shown effects these two metals in Zeolite-A.

Sample 2 with 8% of zinc and 2% of iron on Zeolite-A produces the most suitable catalyst for the methane conversion to liquid hydrocarbons. This sample has

high thermal stability, high surface area, and high average diameter of unit cell and has low weight loss. The higher performance of the methane conversion to liquid hydrocarbons is based on the surface area and the metal oxide that doped into the catalyst (Amin *et al,* 2003).

Zeolite doped with zinc is better than the parent zeolite and this indicates the increase of the concentration of olefins—precursors of aromatics in the reaction mixture due to the dehydrogenation activity of Zn species (Agáta Smiešková *et al.,* 2004). Iron content also increases the performance of methane to liquid hydrocarbons (Ammasi, S. *et al,* 2005*).*

# CHAPTER 5

## CONCLUSION & RECOMMENDATION

### 5.1    Conclusion

Results of this experiment show that zinc content improves the surface area of the catalyst and the iron content improve the thermal stability. Both of this metal needed in order to have higher conversion and selectivity of methane conversion. The iron content should not more than the zinc content because it will decrease the thermal stability

Iron content increases the thermal stability but decreases the surface area of the catalyst. However, zinc content increases the surface area. Sample 2 shows the suitable and perfect combination of zinc content and iron content because has high thermal stability, surface area and also has low percentage of weight loss.

**5.2    Recommendation**

The characterization study should including the characterization using $NH_3$-TPD. $NH_3$-TPD is used to identify the acid site of the catalyst such as bronsted and lewis acid site. The main physicochemical of catalyst for higher methane conversion is mainly base on the acid site (Amin *et al,* 2003). The higher acid site catalyst will produce the higher conversion of products. After the characterization, performance study should be continued in order to prove the result of the characterization.

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# APPENDIX A

# RESULT OF XRD CHARACTERIZATION

**Table A1** : Result XRD Sample 1

| Angle 2-Theta ° | Average diameter Angstrom | Intensity Count | Intensity % |
|---|---|---|---|
| 6.349 | 13.90912 | 72 | 3.6 |
| 7.221 | 12.23286 | 1990 | 100 |
| 10.263 | 8.61244 | 309 | 15.5 |
| 12.045 | 7.3421 | 64 | 3.2 |
| 12.581 | 7.03023 | 330 | 16.6 |
| 14.524 | 6.09388 | 53 | 2.7 |
| 15.845 | 5.58876 | 44 | 2.2 |
| 16.244 | 5.45238 | 331 | 16.6 |
| 19 | 4.66714 | 38 | 1.9 |
| 21.877 | 4.05946 | 505 | 25.4 |
| 24.218 | 3.67204 | 461 | 23.2 |
| 26.356 | 3.37885 | 71 | 3.6 |
| 27.367 | 3.25623 | 589 | 29.6 |
| 28.05 | 3.17847 | 60 | 3 |
| 30.204 | 2.95653 | 465 | 23.4 |
| 31.12 | 2.8716 | 65 | 3.3 |
| 32.103 | 2.78591 | 59 | 3 |
| 32.821 | 2.72659 | 103 | 5.2 |
| 33.712 | 2.65652 | 73 | 3.7 |
| 34.485 | 2.59871 | 317 | 15.9 |
| 36.08 | 2.4874 | 79 | 4 |
| 36.804 | 2.44009 | 47 | 2.4 |
| 38.364 | 2.34439 | 49 | 2.5 |
| 41.927 | 2.15305 | 48 | 2.4 |
| 42.579 | 2.12156 | 68 | 3.4 |
| 43.249 | 2.09023 | 64 | 3.2 |
| 43.885 | 2.0614 | 41 | 2.1 |
| 44.573 | 2.03118 | 102 | 5.1 |
| 45.243 | 2.00266 | 40 | 2 |
| 47.749 | 1.90323 | 67 | 3.4 |
| 53.081 | 1.72392 | 96 | 4.8 |
| 54.784 | 1.6743 | 54 | 2.7 |
| 58.091 | 1.58661 | 49 | 2.5 |

**Table A2** : Result XRD Sample 2

| Angle 2-Theta ° | Average diameter Angstrom | Intensity Count | Intensity % |
|---|---|---|---|
| 7.224 | 12.227 | 1560 | 100 |
| 10.218 | 8.65012 | 258 | 16.5 |
| 12.538 | 7.05434 | 312 | 20 |
| 14.518 | 6.09636 | 64 | 4.1 |
| 16.223 | 5.45933 | 274 | 17.6 |
| 17.851 | 4.96487 | 48 | 3.1 |
| 21.854 | 4.06363 | 369 | 23.7 |
| 24.19 | 3.67621 | 387 | 24.8 |
| 26.316 | 3.38389 | 86 | 5.5 |
| 27.347 | 3.25859 | 456 | 29.2 |
| 30.187 | 2.95823 | 404 | 25.9 |
| 31.097 | 2.87371 | 65 | 4.2 |
| 31.889 | 2.80406 | 68 | 4.4 |
| 32.822 | 2.7265 | 94 | 6 |
| 33.66 | 2.6605 | 80 | 5.1 |
| 34.461 | 2.60047 | 279 | 17.9 |
| 36.065 | 2.48843 | 80 | 5.1 |
| 38.312 | 2.34745 | 58 | 3.7 |
| 41.931 | 2.15283 | 59 | 3.8 |
| 42.542 | 2.12331 | 59 | 3.8 |
| 43.224 | 2.09139 | 58 | 3.7 |
| 44.549 | 2.03222 | 92 | 5.9 |
| 47.705 | 1.90489 | 71 | 4.6 |
| 53.038 | 1.72521 | 94 | 6 |
| 54.718 | 1.67617 | 60 | 3.8 |
| 55.335 | 1.65893 | 35 | 2.2 |
| 56.94 | 1.6159 | 44 | 2.8 |
| 58.022 | 1.58833 | 59 | 3.8 |
| 59.084 | 1.56229 | 69 | 4.4 |
| 65.817 | 1.41782 | 53 | 3.4 |
| 67.345 | 1.38932 | 40 | 2.6 |
| 69.757 | 1.34705 | 65 | 4.2 |

**Table A3** : Result XRD Sample 3

| Angle 2-Theta ° | Average diameter Angstrom | Intensity Count | Intensity % |
|---|---|---|---|
| 7.235 | 12.2079 | 738 | 100 |
| 10.25 | 8.6233 | 198 | 26.8 |
| 12.574 | 7.03404 | 241 | 32.7 |
| 13.983 | 6.32824 | 71 | 9.6 |
| 16.253 | 5.44933 | 165 | 22.4 |
| 17.84 | 4.96791 | 56 | 7.6 |
| 21.849 | 4.06456 | 247 | 33.5 |
| 24.193 | 3.67576 | 283 | 38.3 |
| 26.359 | 3.37844 | 90 | 12.2 |
| 27.35 | 3.25829 | 282 | 38.2 |
| 30.206 | 2.95642 | 268 | 36.3 |
| 31.098 | 2.87362 | 95 | 12.9 |
| 32.803 | 2.72799 | 93 | 12.6 |
| 33.663 | 2.66026 | 75 | 10.2 |
| 34.471 | 2.59976 | 180 | 24.4 |
| 36.105 | 2.48576 | 89 | 12.1 |
| 38.32 | 2.34699 | 73 | 9.9 |
| 43.2 | 2.0925 | 64 | 8.7 |
| 44.562 | 2.03165 | 79 | 10.7 |
| 46.39 | 1.95577 | 57 | 7.7 |
| 48.341 | 1.88129 | 66 | 8.9 |
| 51.893 | 1.76055 | 56 | 7.6 |
| 53.051 | 1.72482 | 93 | 12.6 |
| 53.654 | 1.70686 | 54 | 7.3 |
| 58.189 | 1.58415 | 60 | 8.1 |
| 59.265 | 1.55793 | 57 | 7.7 |
| 62.588 | 1.48298 | 53 | 7.2 |
| 65.816 | 1.41784 | 64 | 8.7 |
| 65.88 | 1.41662 | 63 | 8.5 |
| 67.494 | 1.38661 | 63 | 8.5 |
| 69.866 | 1.34523 | 67 | 9.1 |
| 71.322 | 1.3213 | 51 | 6.9 |
| 82.544 | 1.16777 | 52 | 7 |
| 82.775 | 1.16509 | 55 | 7.5 |
| 86.316 | 1.12615 | 54 | 7.3 |

**Table A4** : Result XRD Sample 4

| Angle 2-Theta ° | Average diameter Angstrom | Intensity Count | Intensity % |
|---|---|---|---|
| 7.241 | 12.19824 | 548 | 100 |
| 10.239 | 8.63235 | 160 | 29.2 |
| 12.557 | 7.04374 | 149 | 27.2 |
| 16.234 | 5.45557 | 112 | 20.4 |
| 17.83 | 4.97075 | 85 | 15.5 |
| 19.04 | 4.65742 | 87 | 15.9 |
| 20.555 | 4.31751 | 94 | 17.2 |
| 21.826 | 4.0688 | 184 | 33.6 |
| 24.161 | 3.68064 | 228 | 41.6 |
| 26.299 | 3.386 | 110 | 20.1 |
| 27.324 | 3.26126 | 220 | 40.1 |
| 30.177 | 2.95913 | 196 | 35.8 |
| 32.16 | 2.78107 | 97 | 17.7 |
| 32.821 | 2.72655 | 95 | 17.3 |
| 34.465 | 2.60017 | 110 | 20.1 |
| 36.065 | 2.48841 | 103 | 18.8 |
| 36.84 | 2.43781 | 78 | 14.2 |
| 52.999 | 1.72639 | 85 | 15.5 |

**Table A5** : Result XRD Sample 5

| Angle 2-Theta ° | Average diameter Angstrom | Intensity Count | Intensity % |
|---|---|---|---|
| 7.204 | 12.26022 | 383 | 100 |
| 10.202 | 8.66372 | 162 | 42.3 |
| 12.536 | 7.05533 | 183 | 47.8 |
| 16.215 | 5.462 | 93 | 24.3 |
| 19.074 | 4.64918 | 92 | 24 |
| 21.779 | 4.07754 | 173 | 45.2 |
| 24.113 | 3.6878 | 205 | 53.5 |
| 26.242 | 3.39329 | 109 | 28.5 |
| 27.274 | 3.26719 | 165 | 43.1 |
| 30.096 | 2.96693 | 203 | 53 |
| 30.963 | 2.88582 | 109 | 28.5 |
| 32.164 | 2.78077 | 97 | 25.3 |
| 34.353 | 2.60839 | 125 | 32.6 |
| 58.858 | 1.56775 | 84 | 21.9 |