

**SYNTHESIS AND CHARACTERIZATION OF Cu/Ni-Zeolite-A FOR THE DIRECT  
CONVERSION OF METHANE TO LIQUID HYDROCARBON**

**DONNY GASAH**

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requirement for the award of the degree of  
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**Faculty of Chemical and Natural Resources Engineering  
Universiti Malaysia Pahang**

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I declare that this thesis entitled '*Synthesis and Characterization of Zeolite-A and Cu/Ni-Zeolite-A for the Direct Conversion of Methane to Liquid Hydrocarbon*' is the results of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted candidature of any degree.

Signature : .....

Name : Donny Gasah

Date : 10 May 2008

Specially dedicated to my beloved mother, father and my family...

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## ABSTRACT

The direct conversion of methane to liquid hydrocarbon has not yet been successfully implemented in an economical process. Bimetallic zeolites were shown to have reasonable activities for the formation of higher hydrocarbons from methane. The presence of combine metal, Ni and Cu leads to improved methane conversion and hydrocarbon selectivity and yield of liquid hydrocarbon. The purpose of this study is to modify zeolite with combine metal, copper and nickel for methane conversion into liquid hydrocarbon C<sub>5+</sub>. The yield of C<sub>5+</sub> production is expected to be high when zeolite is introduced with nickel. The presence of Cu species at the surface of zeolite catalyst can enhance the oxidation reaction, thus improved the methane conversion and hydrocarbon selectivity. The catalysts are characterized for their physicochemical properties using the Fourier Transmitter IR Analysis (FTIR), Thermogravimetric Analysis (TGA), and X-ray Diffraction (XRD). The characterize result reveals that IR spectra of Cu/Ni-Zeolite-A sample and other modified zeolite sample match quite closely, indicating the presence of similar structural units and formation of identical chemical moieties of the modified zeolite samples. From XRD analysis, it is found that the synthesized modified zeolite posses a high crystallinite structure and have small particle size, around 3.7 Å. TGA analysis find that the modified zeolite catalyst is suitable for reaction in the temperature range 200<sup>0</sup>C to 700<sup>0</sup>C due to its high thermal stability. Methane conversion to liquid hydrocarbon is predicted to increase due to loading of bi-metal Copper and Nickel. This research suggest that further studies on the concept of bi-metal and catalytic performance for direct conversion of methane to liquid hydrocarbon should be done to make this research more complete.

## ABSTRAK

Proses penukaran metana kepada hidrokarbon cecair masih belum diimplementasikan dengan jayanya dalam proses yang lebih ekonomik. Zeolit bimetal telah menunjukkan aktiviti yang menggalakkan dalam pembentukan rantaian hidrokarbon yang lebih panjang daripada metana. Dengan kehadiran gabungan logam, Ni dan Cu boleh meningkatkan penukaran metana dan kememilihan hidrokarbon dan hasil daripada hidrokarbon cecair. Tujuan kajian ini ialah memodifikasi zeolit dengan logam gabungan, kuprum dan nikel untuk penukaran metana kepada hidrokarbon cecair  $C_{5+}$ . Hasil produk  $C_{5+}$  lebih tinggi apabila zeolit ditambahkan dengan logam nikel. Kehadiran spesies Cu di permukaan zeolit boleh menggalakkan tindakbalas pengoksidaan, seterusnya meningkatkan penukaran metana dan kememilihan hidrokarbon. Pencirian mangkin dilakukan berdasarkan ciri-ciri fizikokemikal dengan menggunakan Fourier Transmitter IR Analysis (FTIR), Thermogravimetric Analysis (TGA), and X-ray Diffraction (XRD). Keputusan daripada pencirian yang telah dilakukan menunjukkan spektra IR sample Cu/Ni-Zeolite-A dan lain sampel zeolit yang diubah mempunyai struktur yang hampir sama dan bentuk formasi kemikel yang serupa. Daripada analisis XRD, didapati zeolit yang dihasilkan mempunyai struktur kristalit yang tinggi dan mempunyai saiz partikel yang kecil, sekitar 3.7 Å. Daripada analisa TGA menunjukkan pemangkin zeolit yang diubah sesuai untuk tindakbalas dalam suhu 200<sup>0</sup>C to 700<sup>0</sup>C kerana sifat ketahanan termal yang tinggi. Penukaran metana kepada hidrokarbon cecair dijangka meningkat dengan penambahan bi-metal kuprum dan nikel. Kajian ini mencadangkan kajian lanjut dalam konsep bi-metal dan kajian mangkin untuk proses penukaran metana kepada hidrokarbon cecair harus dilakukan bagi memastikan kajian tentang mangkin zeolit ini lengkap.

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## NOMENCLATURES

C <sub>2+</sub>	Higher hydrocarbon with carbon number equal to two and above but below five, such as ethane, ethylene, propane and butane.
C <sub>5+</sub>	Higher hydrocarbon with carbon number equal to five and above such as pentane, hexane, and pentene.
FTIR	Fourier Transform Infrared Spectra
GC	Gas Chromatography
IR	Infrared
ZSM-5	Zeolite Socony Mobil Number 5
NH <sub>3</sub> -TPD	Ammonia Temperature-Program Desorption
TGA	Thermogravimetric Analyzer
XRD	X-ray Diffraction

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Introduction

There is abundant of natural gas reserves in all over the world today. Natural gas which contains 60-90% methane, depends on its source, is gaining a great interest from many researchers to find the way to produce liquid hydrocarbons from natural gas, especially in the gasoline range fuel in more economical process. Methane, principal component of most natural gas, is currently used for home (in cold regions) and industrial heating, also use in electrical power generations. Methane is an ideal fuel for these purposes for its availability in most populated centers. Methane also easy to purify to remove sulfur compounds (Jack H. Lunsford, 2000). It also has the largest heat of combustion relatives to the amount of CO<sub>2</sub> formed. The conversion of methane to useful products especially into gasoline range has been studied over the past decade. There are two routes for converting methane to gasoline; direct or/and indirect method. Direct methods have a distinct economic advantage over indirect methods, but up to date, no direct processes have progressed into a commercial stage due to its low conversion and selectivity. These processes are possible if carried out under controlled oxidation over a suitable catalyst (Sriraj Ammasi, 2005).

### **1.1.1 Natural Gas**

Natural gas is a mixture of hydrocarbon gaseous. It is colorless, shapeless and odorless in its pure form. While natural gas is formed primarily of methane, it can also include ethane, propane, butane and pentane. Like oil and coal, natural gas is a fossil fuel, meaning that it is the remains of plants, animal, and microorganisms that lived millions years ago. It is said that fossil fuels are formed when organic matter such as remains of plant or animal is compressed under the earth at very high pressure. This compression plus with high temperature of deep underneath earth break down the carbon bound in organic matter into oil and natural gas. As it gets deeper in earth, the temperature gets higher (Jack H. Lunsford, 2000).

### **1.1.2 Gas to Liquids (GTL) Technology**

GTL is a technology that converts the gas in liquid fuel for easy transportation (Wilhelm et al., 2001). The conversion of natural gas to liquid fuels in GTL technology consists of three stages: synthesis gas generation, production of heavy-chain hydrocarbons by Fischer-Tropsch synthesis and heavy fraction hydrocracking for production of useful products such as naphtha, lubricants and diesel (Aguilar et al., 2005 and Yagi et al., 2005). Although the stages have been well studied and commercially available, it is still costly for commercial production plant. Plus, the synthesis gas generation stage has the greatest costs in investments and operation (Vosloo, 2001). Consequently, many companies are seeking to find a way to optimize the synthesis gas generation stage, in order to make the GTL technology commercially viable (Wittcoff et al., 2004).

### 1.1.3 Natural Gas Conversion

Often, in remote location of oil fields, a considerable amount of natural gas can be found, where the pipelines to transport the gas is not economically available. This condition has led natural gas to be flared, vented, or pumped undergrounds (Thomas and Dave, 2003). Therefore, the need to find an efficient process for utilizing natural gas receives considerable attention. The conversion of methane, a main component of natural gas, into valuable hydrocarbons has gained great interest. Until now, indirect processes involving partial oxidation and Fischer-Tropsch synthesis are being used for conversion of methane into other hydrocarbon.

Direct process for converting methane and the effective chemical activation of methane molecule remains the most challenging step in such a process (Sriraj Ammasi, 2005). The direct conversion processes utilize catalysts and specific synthesis routes to chemically transform the molecules of methane into more complex chained substances with heavier molecules. But the problem is that the high stability of methane molecule creates a series of technical problems to make the chemical reactions involved viable. Thus the research and development efforts for direct conversion process are focused on the improvement of the catalyst for the reaction and the development of new equipment. Another area that is being developed to fulfill the future demand is GTL (gas-to-liquid) technology.

Up to now, indirect processes are being used for the conversion of methane into more valuable hydrocarbons. The indirect route is technically easier than that of the direct conversion processes. The technologies of the processes involved have been better studied and several pilot and commercial plants are already in operation (Wilhelm, 2001). The processes of indirect conversion are characterized by a preliminary stage of transformation of natural gas into synthesis gas - syngas - (a mixture of carbon monoxide - CO and hydrogen - H<sub>2</sub>). Synthesis gas production requires either steam (steam reforming) or oxygen (partial oxidation) as a co-reactant. In either case, generation of these reactants is extremely energy and capital intensive and, as a result, the major cost of converting natural gas to liquid fuels lies in the initial synthesis gas



production step. After being produced, the syngas is converted into liquid hydrocarbons through the Fischer-Tropsch Process (FT) (Gradassi and Green, 1995; and Vosloo, 2001).

## 1.2 Problem Statement

In direct conversion of methane to hydrocarbon, many processes have been reported. One of the processes is Partial Oxidation Process which is used to produce methanol. Unfortunately, the yield of methanol is too low (below 10%) and beyond industrial interest

Another method is called Oxidative Coupling Process. Oxidative Coupling of methane is used to produce  $C_{2+}$  hydrocarbons. Until now, the maximum yield obtained from this process is about 20%, which means that the process is not economically viable.

Zeolite based catalysts are employed in variety of commercial processes in petroleum and petrochemical industries. Some researchers have investigated on the potentials and usefulness of modified zeolite as catalyst for the conversion of methane to higher hydrocarbons.

The study of direct partial oxidation of methane with  $O_2$  to higher hydrocarbons and in particularly  $C_{5+}$  liquid over transition metal containing zeolite catalyst found that the conversion of methane to liquid hydrocarbons is due to two factors: (a) limited activity to generate olefins from methane, (b) low olefin oxidation activity to allow the olefin produced remain in the system.

In this study, zeolite will be modified by combining copper and nickel via impregnation method. The prepared catalyst, Cu/Ni-zeolite would act as a better bimetallic catalyst than its parent catalyst, zeolite, and it will be characterized. The development of catalyst consists of three steps; preparation, characterization and performance prediction. Therefore, the scopes of this study are divided into three stages:

- Preparation and modification of catalysts
- The characterization of catalysts
- To predict the catalyst's performance of methane conversion to liquid hydrocarbons by study the physicochemical properties of the modified catalyst.

### **1.3 Objectives of Study**

The objectives of this work are:

1. To synthesis the Cu/Ni-zeolite.
2. To investigate the physicochemical properties of the modified catalyst.
3. To relate the physicochemical properties of the modified catalyst with conversion of methane to the liquid hydrocarbons reaction

## CHAPTER 2

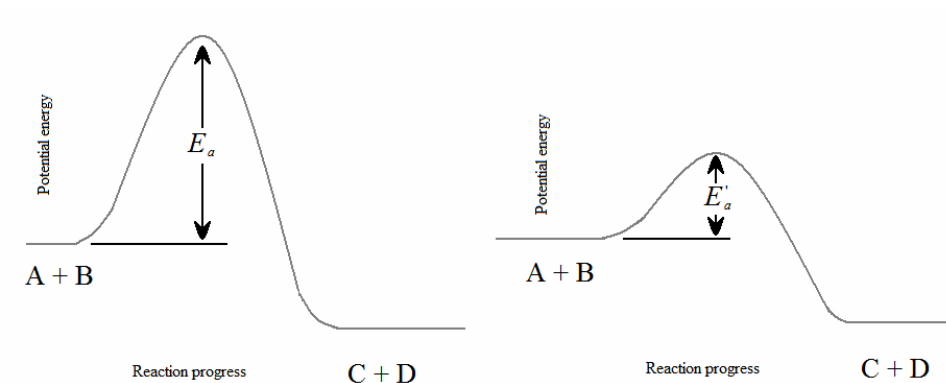
### LITERATURE REVIEW

#### 2.1 Catalyst and Catalysis

A catalyst is a substance that increases rate of a chemical reaction without itself being consumed. Chemical reactions that use catalyst in its process called catalysis. A more comprehensive definition of catalysis is also defined by Berzelius as follow: “Catalysis is a process whereby a reaction occurs faster than the uncatalyzed reaction, the reaction being accelerated by the presence of a catalyst” (Krische, 2005; Somorjai and McCrea, 2000; Haller, 2003; and Ponec, 1998).

There are three types of catalysis, depending on the nature of the rate-increasing substance: heterogeneous catalysis, homogenous catalysis, and enzyme catalysis. In heterogeneous catalysis, the reactants and the catalyst are in different phases. Usually the catalyst is a solid and the reactants are either gases or liquids. Heterogeneous catalysis is by far the most important type of catalysis in industrial chemistry. Heterogeneous catalysts are commonly use for the production of bulk chemicals because it is unmixable with products. This makes the separation of products and catalyst material easier, especially when gaseous products are involved. Thus the reaction can be performed under continuous flow conditions, allowing the scaling up of the production processes to attain high rates. It also reported that heterogeneous catalysis is important because it allows the production of fuel oil, gasoline and other bulk chemicals on a large

scale to provide sufficient bulk chemicals to satisfy high demand of the world market (Holzwarth et al., 2001; Blaser, 2000; and Kerby et al., 2005). Figure 2.1 show a comparison between catalyzed and uncatalyzed reaction and its activation energy.



**Figure 2.1** Comparison of activation energy barriers of an uncatalyzed reaction with the catalyzed reaction.

## 2.2 Zeolite

Zeolite base catalyst is one of the most popular heterogeneous catalyst and was discovered by Axel Cronstedt, a Swedish mineralogist in 1756. Zeolites are hydrated aluminosilicates of the alkaline and alkaline-earth metals. About 40 natural zeolites have been identified during the past 200 years. The most common are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite. More than 150 zeolites have been synthesized; the most common are zeolites A, X, Y, and ZSM-5. Natural and synthetic zeolites are used commercially because of their unique adsorption, ion-exchange, molecular sieve, and catalytic properties (Virta, 2000).

Zeolite is a crystalline material of aluminosilicate featured by a three-dimensional microporous framework structure built of the primary  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra, and ion-exchange capability. Because the widespread use of crystalline

aluminosilicate zeolites in industry today, zeolite is now fairly well known (Subhash Bhatia, 1995).

Kerby et al. 2005 stated that ZSM-5 catalyst are mostly used in oil refining and gas conversion processes such as the conversion and upgrading of the various fractions into transportation fuels, conversion of syngas, light paraffins, methanol-to-gasoline, and olefins into gasoline and gasoil. ZSM-5 attracts a huge interest due to its unique properties that make ZSM-5 catalyst used widely in the industry:

- High thermal and hydrothermal stability in the industrial environment
- High internal surface area
- Ion exchange ability to allow the formation of highly dispersed catalytically active sites
- Pores structure provides shape selectivity
- High acidity promotes the oligomerisation, isomerisation, cracking and aromatization reactions

Zeolite based catalysts have successfully employed in variety of commercial process in petroleum and petrochemical industries. But, there is not many have investigated the potentials and usefulness of modified zeolite as catalyst for the formation of higher hydrocarbon from methane (Nor Aishah et al., 2000). Recent studies 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 is important to control its acidity and shape selectivity. These modification methods led to an improvement in the catalytic activity and gasoline selectivity (Han et al, 1994). Acid zeolites were shown to have reasonable activity but low selectivity towards hydrocarbons as carbon monoxides were formed (Ramli Mat 2003). It is also reported that the presence of acid sites was unfavorable to obtain reasonable selectivity of C<sub>5+</sub> hydrocarbons. The selectivity to C<sub>5+</sub> hydrocarbons was slightly enhanced when the acidity was reduced by exchanging the zeolite with alkali metal cations. The activity of catalyst was strongly dependent on the type of transition metal and acidity. According to Nor Aishah et al, the modification of ZSM-5 with transition metal has resulted lower acidity and improved methane conversion.

### 2.3 Zeolite A

Zeolite A exhibits the LTA (Linde Type A) structure. It 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 ( $a = 24.61\text{Å}$ ) 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 700°C (Subhash Bahtia, 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, F. R., et al, 2000).

### 2.4 Effect of Metal Loaded in ZSM-5

The conversions of methane to gasoline by direct routes are still at low activity and selectivity. These processes are possible if the reaction is carried out by controlled oxidation over a suitable catalyst (Ramli Mat et al. 1999). The main concern is to modify the ZSM-5 zeolite catalyst framework with suitable oxidative elements to develop highly active bifunctional oxidative-acid catalysts could be developed.).

Ernst and Weitkamp (1989) reported that the presence of strong acid sites in the zeolite catalyst is detrimental for the selective oxidation of methane to higher hydrocarbons; otherwise oxidized products, CO<sub>x</sub> (CO, CO<sub>2</sub>) predominate. When the

acidity is reduced by exchanging the zeolite with alkali metal cations, the selectivity to higher hydrocarbons is slightly enhanced. Han *et al.* (1994) demonstrated the successful production of higher hydrocarbons from methane oxidation using a ZSM-5 zeolite catalyst containing metal oxides. The metal oxides with sufficiently high dehydrogenation and low olefin oxidation activities reduce acidity of ZSM-5. As a result, the metal containing ZSM-5 can produce higher hydrocarbons in methane oxidation.

## 2.5 HZSM-5 Zeolite

HZSM-5 which is one of the synthetic zeolite, in its early days, was found to be a suitable catalyst for the conversion of methane to higher hydrocarbon. Later, some studies showed that acidic HZSM-5 zeolite catalyst has shown a good oligomerization performance for olefin products to higher hydrocarbons. Furthermore, the HZSM-5 catalyst is more tolerant to promote the formation of C<sub>5+</sub> products. In spite of its strong acidity, some researchers found a drastic increase in the catalytic activity of HZSM-5 zeolite which consisting of metal functions in addition to their acid function. It is also stated that the oligomerisation, cyclization and aromatization of hydrocarbon species are catalyzed by Brønsted acid sites of the HZSM-5 zeolite (Ramli Mat, 2006). HZSM-5 also provides shape selectivity (which is shown to limit chain length growth to gasoline range hydrocarbons) and its high acidity is effective to promote oligomerization, isomerization and aromatization reactions. It is also found from the recent research, metal loaded HZSM-5 catalyst is suggested to be potential catalysts for direct conversion of methane to liquid hydrocarbons (Sriraj Amasi, 2005).

## 2.6 Effect of Metal Loaded in HZSM-5

Catalysis by metal loaded HZSM-5 is used extensively. The presence of a metal on zeolite is one of the research interest providing new means to design catalytic performance by altering the exposure of the metal sites and it opens the way for creation of new types of catalysts (Sriraj Ammasi, 2005). Baba and Abe's (2003) found that, the catalytic activity and the selectivity for hydrocarbons depended on the kind of metal cations loaded on HZSM-5. They concluded that the bifunctionality of acidic protons and metal cations is essential for the activation of methane.

A reaction between mixture of methane and ethylene over HZSM-5 and metal loaded HZSM-5 catalysts produced high molecular weight hydrocarbons with a carbon number of five and more (Alkhaldeh et al., 2003). It is also reported that the reaction over nickel or cobalt-containing zeolite catalyst in the presence of hydrogen donor co-reactant produced high molecular weight hydrocarbons and the catalyst/reactant feed eliminates rapid catalyst deactivation (Timmons et al., 1992).

Hulea and Fajula (2004) found that both nickel and acid sites are required for the activation of the reaction. Moreover, the acid density plays a significant role in determining the activity, stability and selectivity. They showed its possibility to achieve a desired balance between acid and nickel ion sites so that high catalyst stabilities and high selectivity to suitable products could be achieved.

Chang et al. (1995) reported that the activity of catalysts in facilitating the reaction of ethane with oxygen decreases in order:  $\text{Ru}^{\text{II}}\text{-Na-ZSM-5} > \text{Cu}^{\text{II}}\text{-Na-ZSM-5} > \text{Cu}^{\text{I}}\text{-Na-ZSM-5} > \text{Co}^{\text{II}}\text{-Na-ZSM-5} > \text{V}^{\text{V}}\text{-Na-ZSM-5} > \text{HZSM-5} > \text{Co}^{\text{II}}\text{-HZSM-5} > \text{Cr}^{\text{III}}\text{-HZSM-5} > \text{Fe}^{\text{III}}\text{-HZSM-5} > \text{Na-ZSM-5}$ . The performance of the catalysts is determined by the nature of the metal cations and the acidity of the parent zeolite precursor. Both  $\text{Cu}^{\text{I}}\text{-HZSM-5}$  and  $\text{Cu}^{\text{II}}\text{-HZSM-5}$  catalysts are found to be very active for the reaction of ethane with oxygen, but the selectivity to hydrocarbon are low. They are excellent oxidation catalysts but not for the oxydehydrogenation of ethane.



Sriraj Ammasi, (2005), reported that the yield of  $C_{5+}$  products is affected by the nature of the metal type over HZSM-5. The yield of  $C_{5+}$  production is highest when HZSM-5 is introduced with nickel. The yield of  $C_{5+}$  is about 6.2% when using only HZSM catalyst. The yield increases to 7.5% once Ni is introduced.

## 2.7 Cu Loaded on ZSM-5

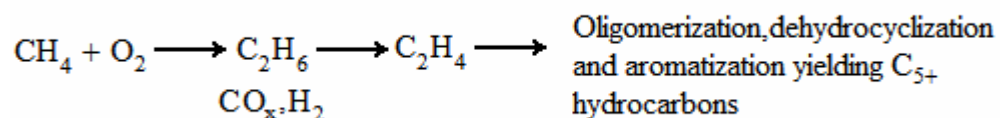
Cu loaded ZSM-5 catalyst prepared by acidic ion exchange method showed a promising performance in the conversion of methane to liquid hydrocarbons where the methane conversion and the composition of gasoline range ( $C_{5-10}$ ) in liquid hydrocarbons were 15.6 and 80.2%, respectively. It had been shown that HZSM-5 zeolite can be modified by adding metal or metal oxides to obtain catalysts for selective hydrocarbon conversions. Since copper-based catalysts are active in oxidation processes, it is possible that the presence of Cu species at the surface of HZSM-5 catalyst can enhance the oxidation reaction (Ramli Mat et al, 2000). It is also reported that introduction of copper species in catalyst (Cu 1wt%BZSM-5) improved the methane conversion and hydrocarbon selectivity (Ramli Mat, 2006).

## 2.8 Nickel Loaded on ZSM-5

Nickel on ZSM-5 is found to be active in the aromatization, hydrocracking and isomerization of hydrocarbon (Changlong Yin, 2005). It is shown that incorporating nickel into ZSM-5 significantly enhances the yield of liquid hydrocarbon (Sriraj Ammasi, 2005). Nickel also can be used as catalyst due to its surface oxidation properties (M.A. Abdel Rahim et al., 2004).

## 2.9 Conversion of Methane to Gasoline Ranged Hydrocarbon Chain

Gasoline ranged hydrocarbon ( $C_{5+}$ ) is produced from reaction olefin through oligomerization, dehydrocyclization, and aromatization using zeolite based catalyst according to the reaction scheme below (Ramli Mat, 2006). The methane oxidation coupling step is thought to be the first step in methane oxidation to produce olefin. Figure 2.2 shows the reaction scheme for the conversion of methane to gasoline ranged hydrocarbon.



**Figure 2.2** Reaction scheme for methane conversion to gasoline range hydrocarbon (Ramli Mat, 2006)

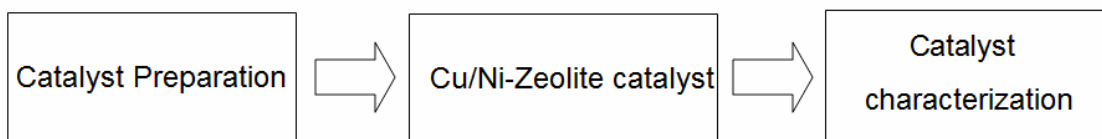
## CHAPTER 3

### MATERIAL & METHODOLOGY

#### 3.1 Introduction

The experiment techniques used for the preparation and characterization of the catalyst through this research are summarized and presented in this chapter.

The flow chart of the experimental work is shown in the Figure 3.1. The first stage of this experimental work is the synthesis of catalyst. Both catalysts were characterized using Fourier Transmitter IR Analysis (FTIR), Thermogravimetric Analysis (TGA) and X-ray Diffraction (XRD) in order to obtain their physiochemical properties. The results obtained were compared with other previous researches. Finally, conclusions were drawn based on the findings obtained from this study. The overall experimental work are summarized in the figure 3.1 below.



**Figure 3.1** Flow chart of overall experimental work

### 3.2 Materials and Chemicals

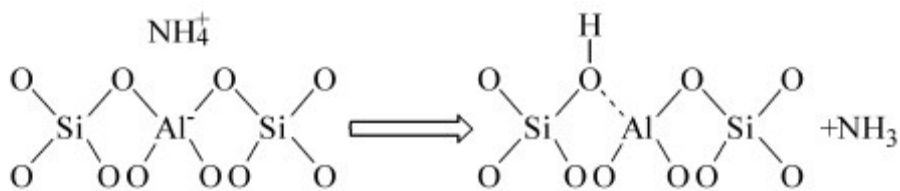
All chemicals and materials used in the present study are listed as Table 3.1 below:

**Table 3.1** List of Chemicals

	Molecular Formula	Supplier	Molecular Weight (g/mol)	Purity (%)
Deionized Water	H <sub>2</sub> O	UMP source	18.00	99.9
Copper Nitrate	Cu(NO <sub>3</sub> ) <sub>2</sub> .3H <sub>2</sub> O	R&M Chemicals	242.55	98.5
Nickel Sulphate	NiSO <sub>4</sub> .6H <sub>2</sub> O	R&M Chemicals	258.78	99.0

### 3.3 Catalysts Preparation

Zeolite was bought and supplied by Fluka. The surface area of the zeolite is 400 m<sup>2</sup>/g. A schematic diagram of the process is illustrated in Figure 3.2.



**Figure 3.2** Schematic diagrams of ammonium ions replaced by hydrogen ions (Amin and Anggoro, 2002)

### 3.3.1 Cu/Ni-Zeolite Synthesis

Zeolite catalysts were bought commercially from Fluka. Then Cu/Ni-Zeolite will be prepared by ion-exchange. 10 g of the zeolite with nickel sulphate ( $\text{NiSO}_4$ ) followed by copper nitrate ( $\text{Cu}(\text{NO}_3)_2$ ) were mixed in the deionized water. The amount of nickel sulphate and copper nitrate doped was differentiating by mass ratio. Then the samples were dried at  $120^\circ\text{C}$  overnight and calcined at  $550^\circ\text{C}$  in air for 5 hours. The sample is designated as Cu/Ni-Zeolite. Table 3.2 shows the percentage of metal loading in the modified zeolite.

**Table 3.2** Percentage of Metal Loading in the Modified Zeolite

Sample	% of Nickel (Ni)	Weight $\text{NiSO}_4$ (g)	% of Copper (Cu)	Weight $\text{Cu}(\text{NO}_3)_2$ (g)
1	10	4.500	0	3.750
2	8	3.585	2	3.000
3	5	2.240	5	1.875
4	2	0.595	8	0.750
5	0	0.000	10	0.000

### 3.4 Catalysts Characterization

The catalysts were characterized using Fourier Transmitter IR Analysis (FTIR), Thermogravimetric Analyzer (TGA), and X-ray Diffraction (XRD) in order to obtain their physiochemical properties. The data that collected was used as references between modified zeolite and unmodified zeolite.

### **3.4.1 Fourier Transform IR Analysis (FTIR)**

FTIR Analysis is a analysis technique that provides information about the functional group of materials, whether organic or inorganic. The resulting FTIR spectral pattern was then analyzed and matched with known signatures of identified materials in the FTIR library. The FTIR analysis was conducted at Membrane Research Unit, Universiti Teknologi Malaysia Skudai.

### **3.4.2 Thermogravimetric Analyzer (TGA)**

The thermal stability of the catalysts was determined using a thermogravimetric analyzer (TA Instruments Model Q 500 TGA with TA 5000 Contoller). The samples were placed in a pan that was heated under flow of air ( $25 \text{ ml min}^{-1}$ ) from room temperature to  $1000 \text{ }^{\circ}\text{C}$  at the heating rate of  $10 \text{ }^{\circ}\text{C min}^{-1}$ . The TGA analysis was conducted at FKKSA Lab, Universiti Malaysia Pahang Gambang.

### **3.4.3 X-ray Diffraction (XRD)**

XRD analysis was used to check the structure of catalyst and presence of the crystalline phases. The XRD analysis was carried out at the Ibnu Sina Institute, Universiti Teknologi Malaysia Skudai. XRD measurements were performed in the range of  $2\theta = 5^{\circ}$  to  $50^{\circ}$  using a Siemens 5000 diffractometer with vertical goniometer and  $\text{CuK}\alpha$  radiataion ( $\lambda = 1.542 \text{ \AA}$ ) at 35 kV and 35 mA (scanning speed:  $4^{\circ}/\text{minute}$ ).

## CHAPTER 4

### RESULTS & DISCUSSION

#### 4.1 Fourier Transform IR Analysis (FTIR)

The Fourier Transform IR (FTIR) spectra of the metal loaded zeolite catalysts are depicted in Figure 4.1. The samples are sensitive absorption around region  $700 - 1200 \text{ cm}^{-1}$  is of special interest to distinguish zeolite types (Nor Aishah et al, 2003). This intense vibration in the region indicates the existing of zeolite. All samples have the highest peak at  $985 - 1001 \text{ cm}^{-1}$ . This also indicates the existing of zeolites (Rayalu et al, 2003). For sample 1, which is 10% weight Ni loaded with zeolite has the highest peak at  $989.6 \text{ cm}^{-1}$ . This strong vibration is assigned to Si-Al-O asymmetric stretching vibration. Other samples, sample 2 until sample 5 also have the quite similar peak with almost the same intensity which is around  $985$  to  $1000 \text{ cm}^{-1}$ . In Table 4.1, the position of some characteristic vibration bands are summarized.

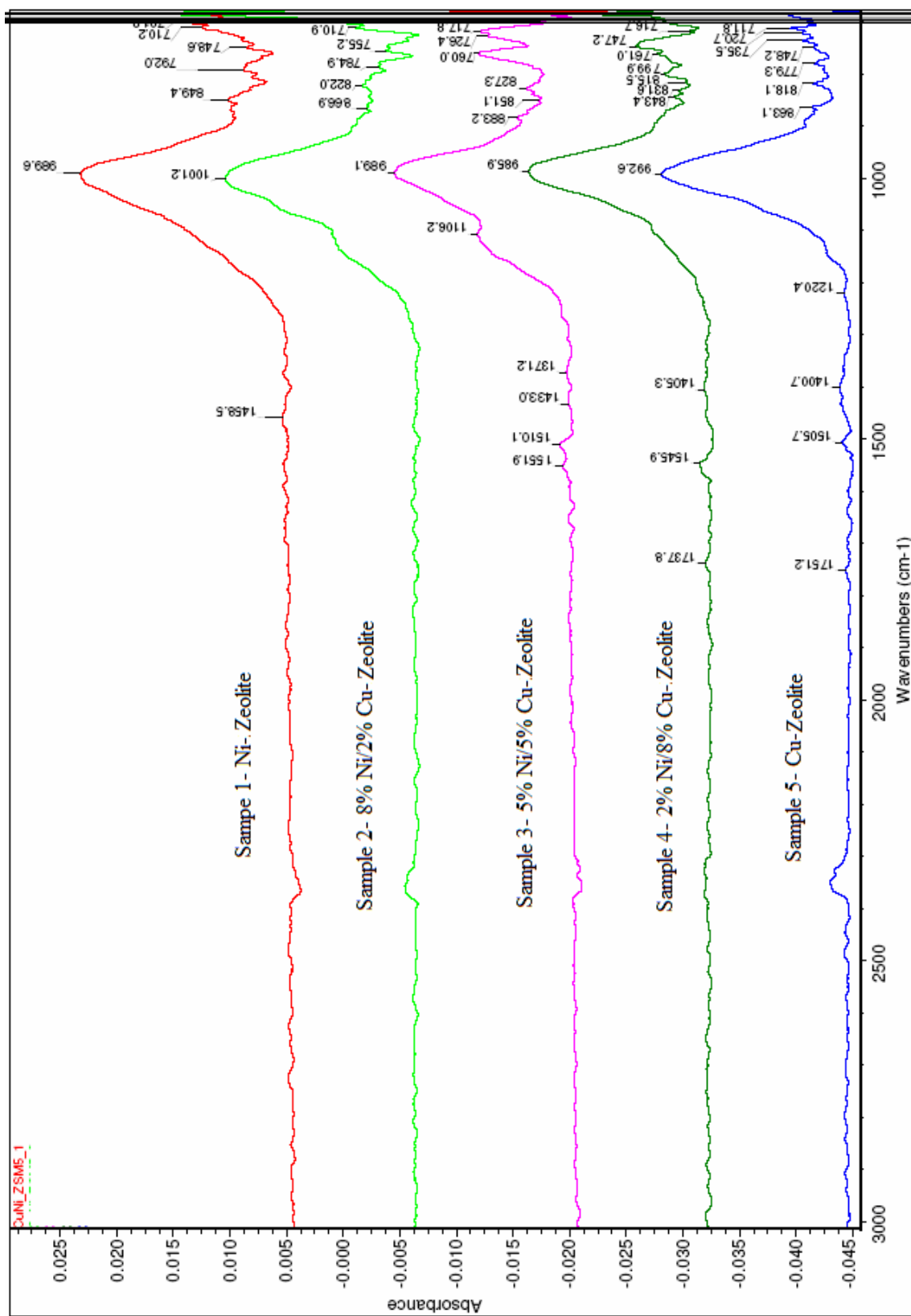


Figure 4.1 Infrared Spectra of Metal Loaded Zeolite



**Table 4.1** Summary of some characteristic vibration band

Sample	Wavelength (cm <sup>-1</sup> )			
	Asymmetric	Symmetric	Double Ring	T-O Bending
1	989.6	849.4	792.0	701.0
2	1001.2	866.9	822.0	710.9
3	989.1	883.2	760.0	717.8
4	985.9	843.4	761.5	747.2
5	992.6	863.1	735.5	711.8

From Table 4.1, the characteristic vibration band starts from 700 - 1000 cm<sup>-1</sup> with the highest peak intensity at 1001.2 cm<sup>-1</sup> and the lowest peak intensity at 701 cm<sup>-1</sup>. It is observed that the band recorded at 849.4 cm<sup>-1</sup> of sample 1 can be assigned to Si-Al-O symmetric stretching has less intensity compared to asymmetric stretching of Si-Al-O bond. This is likely as the probability of symmetric stretching of Si-Al-O bond is less compare to asymmetric stretching and bending (Rayalu et al, 2003). Another intense and sharp bend happened at 792 cm<sup>-1</sup> which indicates the presence of double ring in the framework structure of the sample 1, modified zeolite.

From Table 4.1, it can be observed that other modified zeolite sample also show the characteristic IR bands, in the range of the discussed sample 1. IR spectra of sample 1 show characteristic IR band at frequencies similar to those other sample 2, 3, 4 and 5.

There are some differences between sample 2, 3, 4 and 5. Sample 1 has fewer peaks in region 700 cm<sup>-1</sup> and 1000 cm<sup>-1</sup> compare to sample 5, which has more peaks. The different in the amount of peaks in the region is because of presence of different metal composition in both samples. In sample 1, the fewer peak shows the presence of Nickel loaded in zeolite. Meanwhile in sample 5, there is more peak vibration shown due to the presence of Copper metal in zeolite sample. In other samples, sample 2, 3 and 4 contain both peak pattern as discussed. This showed that sample 2, 3 and 4 contain both metal, Nickel and Copper metal in the modified zeolite.

Thus it can be concluded those IR spectra of sample 1 and other modified zeolite sample match quite closely, indicating the presence of similar structural units and formation of identical chemical moieties of the modified zeolite samples.

## 4.2 X-ray Diffraction (XRD)

X-ray Diffraction (XRD) is used to check the structure of catalyst and presence of the crystalline phases as shown in Table 4.2 based on the XRD diffractograms (Figure 4.2). The diffractogram reveals that there are no obvious changes in the crystalline structure of the modified zeolites. The XRD pattern also illustrated peak characteristic of CuO and NiO crystalline on the respective sample indicated that metal species were distributed on the zeolite surfaces. The characteristic peak of CuO happened at  $2\theta = 35.5^\circ$ ,  $38.7^\circ$  and  $48.7^\circ$  (Irmawati et al, 2007), while characteristic peak of NiO happened  $2\theta = 43.5^\circ$ ,  $51.2^\circ$  and  $76.6^\circ$  (Kan-Sen Chou et al, 2007).

The crystallinity was calculated from the XRD diffractograms (Rayalu et al, 2005). The detailed calculation is shown in the Appendix.

The sum total of relative intensity of zeolite standard is obtained from Rayalu et al (2003) assuming the standard zeolite sample has the same structure and be used in the comparison of the findings. The crystallinity of each modified zeolite samples are summarized into Table 4.2.

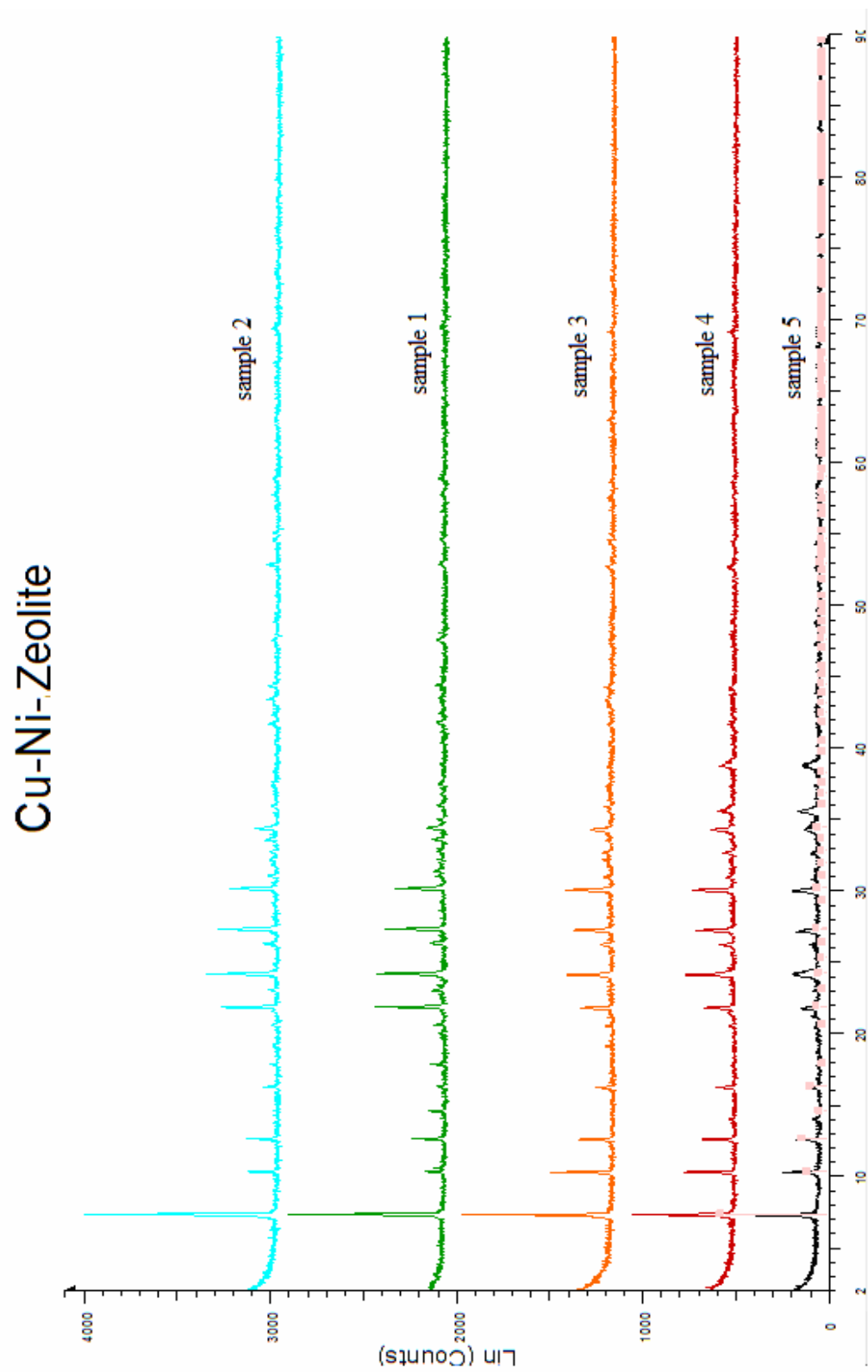


Figure 4.2 XRD pattern for modified zeolite

**Table 4.2** Crystallinity of zeolites from XRD analysis

Sample	Crystallinity %
1	108.57
2	82.02
3	85.14
4	102.46
5	113.96

Table 4.2 showed the percentage of crystallinity based from the XRD analysis. It is shown that the crystallinity of each modified zeolite sample varies from 82% to more than 100%. Sample 1, 4 and 5 have percentage of crystallinity more than 100% means that the structure of the modified zeolite is more crystallite than its parent zeolite. Meanwhile, sample 2 and 3 which is combination of copper and nickel loaded on the zeolite has lower crystallinity which is around 82% to 85%. High crystallinity means that the sample has high thermal stability and mechanical strength (Yushan Yan et al, 2004). The results from Table 4.2 indicate that sample 5 which contain 10% wt Cu loaded zeolite is more favorable to crystalline phase. The diameters of each modified zeolite sample are also summarized in Table 4.3 for the comparison of size for each sample.

**Table 4.3** Diameter of modified zeolite sample from XRD analysis

Sample	Diameter, d (Å)
1	3.685
2	3.689
3	3.699
4	3.697
5	3.704

The data of the diameter for each modified zeolite sample is obtained from XRD analysis in Table 4.3 indicates that all sample has almost the same diameter which is around 3.6 – 3.7 Å. This is supported because the samples are mainly composed of the zeolite and loaded with copper and nickel metal. Sample 5 has the highest diameter 3.704 Å which is zeolite loaded with copper 10% weight. Meanwhile, sample 1 has the smallest diameter, 3.685 Å, composed of 10% weight nickel loaded in zeolite. From the XRD analysis, it is found that the synthesized modified zeolite possesses a high crystalline structure and has small particle size, around 3.7 Å.

### 4.3 Thermogravimetric Analyzer (TGA)

The thermal stability of the catalysts was determined using a thermogravimetric analyzer (TA Instruments Model Q 500 TGA with TA 5000 Controller). Figure 4.3 shows the result obtained from TGA for all modified zeolite samples. The first stage of weight loss for sample 1 at temperature 50°C to 200°C is due to the removal of impurities and water absorbed in the sample. Sample 1 starts to lose weight again starting from temperature 700°C, until temperature 1000°C (maximum temperature of TGA). However, sample 1 still does not lose all its weight. At 1000°C, sample 1 retains 85% of its initial weight. From this analysis, it is seen that sample 1 only loses about 15% of its weight during the TGA analysis, and is able to maintain its weight at 90% in the temperature range 200°C to 700°C.

Meanwhile, sample 2 and sample 3 have the most weight loss during the analysis. Sample 2 and sample 3 both had maintained their final weight at 78% and 83% respectively. Both samples rapidly lose weight during the first stage (50°C to 200°C). Thus showing that there are many impurities contained in the sample. Both samples lost about 15% of their weight in the first stage.