

**SYNTHESIS AND CHARACTERIZATION OF CU/ZN-ZEOLITE A FOR THE
CONVERSION OF METHANE TO LIQUID HYDROCARBON**

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requirements for the award of the degree of
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I declared that this thesis entitled “*synthesis and characterization of CuZn-Zeolite A for the 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.

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Special dedicated to my beloved mother and father

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ABSTRACTS

The direct conversion of methane to liquid hydrocarbon has not yet been successfully economized in an inexpensive process. Acidic zeolite was shown to have reasonable activities for the formation of higher hydrocarbon from methane. The presence of acid site leads to the oxidation of the higher hydrocarbon formed. The modification of Zeolite A with copper and palladium for methane conversion is expected to get higher hydrocarbon. The purpose of this project is to investigate the performance of the modified Zeolite A catalysts based on their physicochemical properties. The catalysts were characterized using Thermogravimetric Analysis (TGA), Fourier transform infrared (FTIR) and X-Ray Diffraction (XRD). The effects of amount of copper and zinc loading on the activity of the catalyst were studied. From this research, Zeolite A catalyst with higher crystallinity and surface area are expectable more tolerant to promote the formation of C₅₊ products. Zeolite A catalyst would rearrange the structure and the activity of the Zeolite A could be increased by the addition of metal ions into the framework. So, the catalytic reactions of Cu/Zn- Zeolite A mainly depend on the quantity and their crystallinity.

ABSTRAK

Proses penukaran terus metana ke cecair hidrokarbon masih belum mencapai tahap ekonomi yang sesuai untuk dikomersialkan. Keasidan zeolite dilihat mempunyai aktiviti yang munasabah untuk pembentukan hidrokarbon yang lebih panjang daripada metana. Kehadiran tapak berasid menyebabkan pengoksidaan hidrokarbon panjang terbentuk. Modifikasi Zeolite A dengan menggunakan kuprum dan palladium dalam penukaran metana dijangka hidrokarbon yang lebih panjang dapat diperolehi. Tujuan penyelidikan ini dibuat adalah untuk menyiasat prestasi zeolite yang telah dimodifikasi berdasarkan sifat kimia-fiziknya. Mungkin ini akan dicirikan menggunakan Thermogravimetric Analysis (TGA), Fourier transform infrared (FTIR) dan X-Ray Diffraction (XRD). Kesan daripada jumlah bilangan kuprum dan zink dan aktivitiya akan dikaji. Daripada penyelidikan ini, Zeolite A yang mempunyai luas permukaan dan kekristalan yang tinggi akan lebih berpotensi untuk pembentukan produk C_{5+} kerana ia mempunyai kekuatan asid yang tinggi. Zeolite yang dimodifikasi akan menimbulkan mengubah struktur dan aktiviti Zeolite A boleh ditingkatkan dengan penambahan ion logam ke dalam strukturnya. Jadi, aktiviti pemangkin Cu/Zn- Zeolite A bergantung kepada kuantiti dan kekuatan asidnya.

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LIST OF ABBREVIATIONS

C₅₊	Higher hydrocarbon with carbon number equal to five and above such as pentane, hexane and pentane.
FTIR	Fourier Transform infrared Spectra
TGA	Thermogravimetric Analysis
XRD	X-Ray Diffraction
ZSM-5	Zeolite Socony Mobil number

CHAPTER 1

INTRODUCTION

1.1 Research Background

1.1.1 Natural gas

Natural gas is a combustible mixture of hydrocarbon gases. It is colorless, shapeless, and odorless in its pure form. As a safety measure, natural gas companies add an odorant, mercaptan, to the gas so that leaking gas can be detected. While natural gas is formed primarily of methane, it can also include ethane, propane, butane and pentane. The composition of natural gas can vary widely. Natural gas is considered 'dry' when it is almost pure methane, having had most of the other commonly associated hydrocarbons removed. When other hydrocarbons are present, the natural gas is 'wet' (Thomas and Dawe, 2003). Natural gas is a fossil fuel like oil and coal, this means that it is, essentially, the remains of plants and animals and microorganisms that lived millions and millions of years ago. There are many different theories as to the origins of fossil fuels.

The most widely accepted theory says that fossil fuels are formed when organic matter (such as the remains of a plant or animal) is compressed under the earth, at very high pressure for a very long time. This is referred to as thermogenic methane

(Lunsford, 2000). Similar to the formation of oil, thermogenic methane is formed from organic particles that are covered in mud and other sediment. Methane represents over 90% of the natural gas content and hence is considered as promising source for higher hydrocarbon in the new millennium. Not all the available and produced methane is utilized. At present, most of the methane is used as fuel and only in a few instances it is applied as a chemical feedstock. Modern industry supports a change of feedstock towards better and cheaper raw material. Therefore, the direct conversion of methane to desirable commodity chemicals such as liquid hydrocarbon is a challenging approach to the utilization of methane resources. Numerous recent research projects have been demonstrated the feasibility of direct transformation of methane into products of higher added values such as olefins, aromatics and oxygenous derivatives. (Weckhuysen et al., 1998).

The abundance of natural gas, together with steadily depleting oil reserves, highlights methane conversion to higher hydrocarbons as an extremely attractive goal. Activation of methane is very challenging due to its refractory nature and has made this one of the most extensively investigated processes in catalysis. The processes of conversion of natural gas into liquid higher hydrocarbons products can be divided into two types: direct conversion and indirect conversion.

However, the high stability of the methane molecule creates a series of technical problems to make the chemical reactions involved viable. Thus, the research and development efforts of the direct conversion processes are focused on the improvement of the catalysts in the elucidation of the mechanisms of reaction and the development of new equipment.

1.1.2 Gas to Liquid Technology (GTL)

Gas to liquid fuels is produced from natural gas, coal and biomass using the Fischer-Tropsch synthesis (FTS) process. The potential route to obtain clean liquid fuels based on FTS is shown in Figure 1.1.

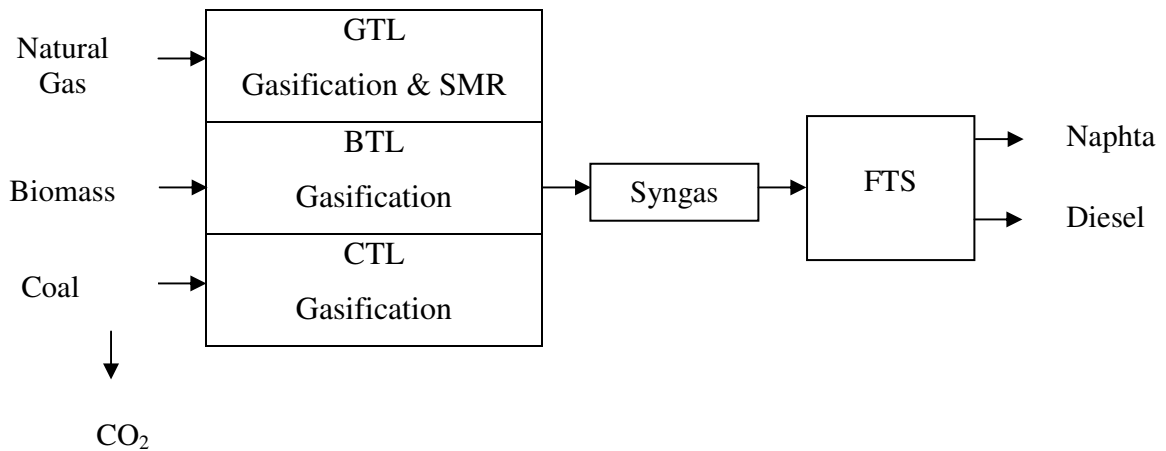


Figure 1.1: Potential routes to clean liquid fuels based on the Fisher Tropsch synthesis (FTS) process.

Different routes to convert methane to useful liquid hydrocarbons include indirect methane conversion and direct methane conversion (Keshav., 2006). GTL technology is based on the conversion of natural gas to liquid fuels in three stages: synthesis gas generation, production of heavy-chain hydrocarbons by Fischer-Tropsch synthesis and heavy fraction hydrocracking for production of useful compounds such as naphtha, diesel and lubricants (Figure 1.2) (Aguiar et al., 2005 and Yagi et al., 2005). Although the three stages of the GTL process by indirect means have been individually well studied and are available for commercialisation, an optimal combination that

permits the reductions of costs of the commercial production plants still does not exist. Additionally, the synthesis gas generation stage corresponds to the greatest costs in investments and operation, being responsible for around 50–75% of the capital costs (Vosloo, 2001).

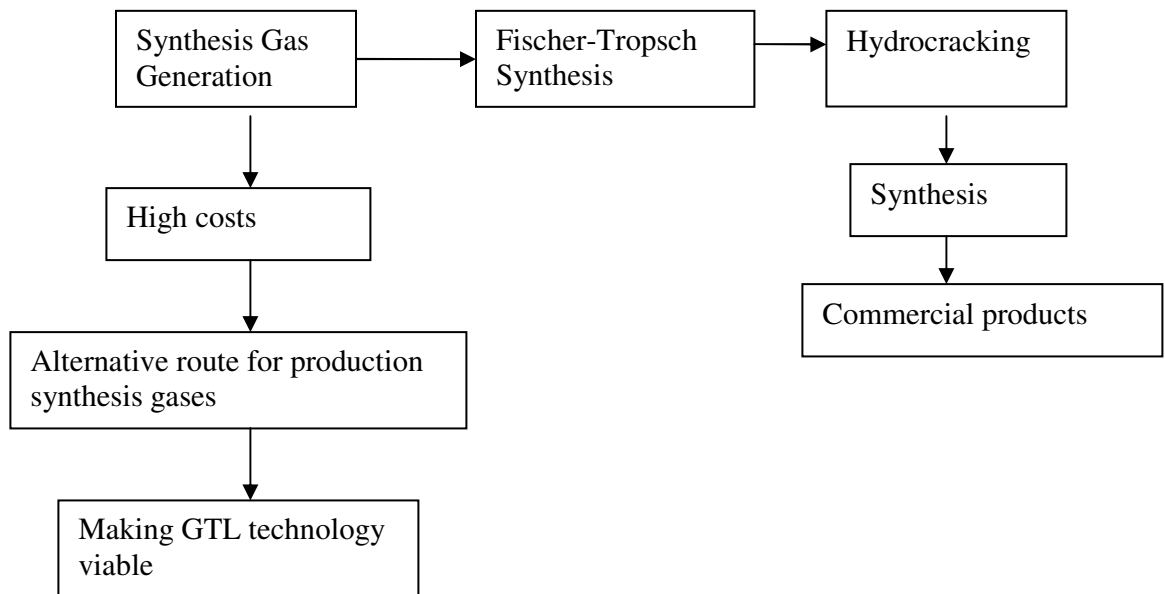


Figure 1.2: Typical stages in GTL technology (Yagi et al., 2005)

Fuels production directly from syngas (in former times obtained from coal) has been reported by Fischer and Tropsch in 1923 for the first time (Wilhelm et al., 2001), using an alkali-promoted iron catalyst. Fuels manufactured via the Fischer–Tropsch route reveal an excellent quality since they consist mainly of linear paraffin and olefins and do not contain sulfur and aromatics. Figure 1.3 is a block flow diagram of the GTL process.

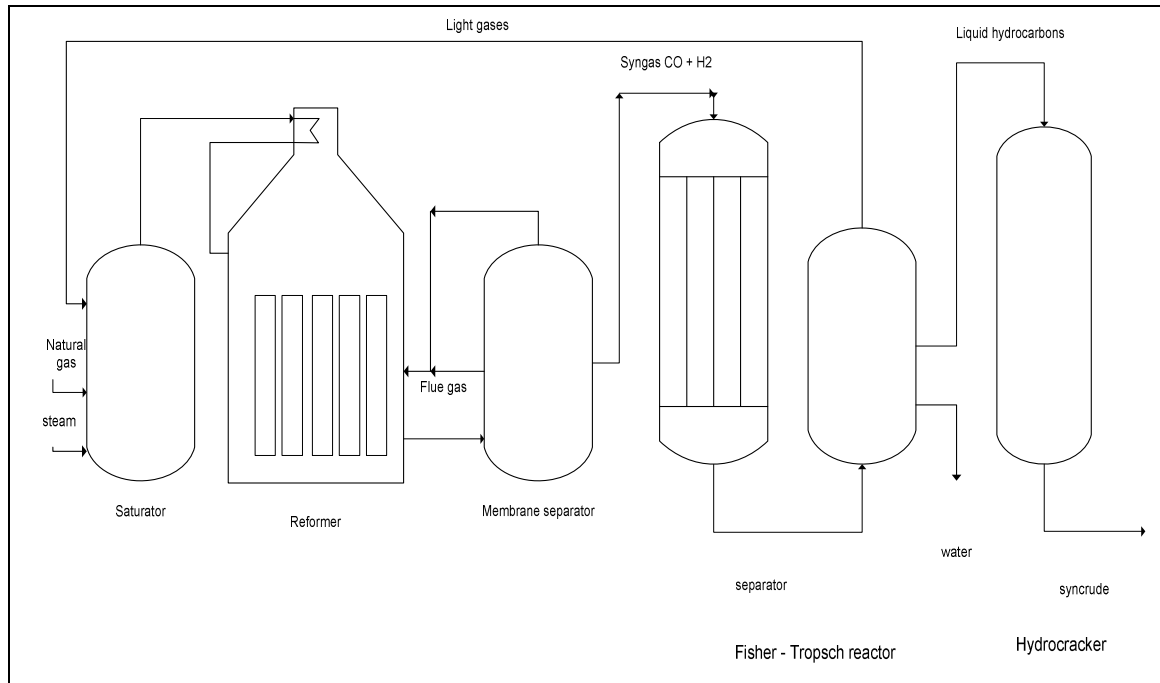


Figure 1.3: Flow diagram of the GTL process (Aguiar et al., 2005)

1.1.3 Direct conversion

The direct conversion processes utilize catalysts and specific synthesis routes to chemically transform the molecules of methane, the main component of natural gas, into more complex chained substances with heavier molecules. The desired products that can be obtained include the alcohols (mainly methanol), the olefins (ethylene and acetylene) and the aromatics (benzene, toluene and naphthalene) (Tirupati et al., 2006).

The direct routes are one step processes in which the natural gas is reacted with oxygen (or another oxidizing species) to give the desired product directly. Apart from complete combustion for heating purposes (giving CO₂ and water), all other possible processes are still at the research stage; this is mostly because the conversions and

selectivities are insufficiently high for the reaction to be of interest for commercial application (Ross et al., 1996)

1.1.4 Indirect Conversion

The primary step of the indirect route involves two step process whereby natural gas is first converted into synthesis gas which is a mixture of hydrogen, H₂ and carbon monoxide, CO via steam reforming, partial oxidation, CO₂ reforming or a combination of two of these reactions; the synthesis gas is then converted into the desired product. (Ross et al, 1996)

The indirect route is technically easier than that of the direct conversion processes. The processes of indirect conversion are characterized by a preliminary stage of transformation of natural gas into syngas. Syngas 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) (Tylor et al., 1991). Figure 1.4 shows the various direct and indirect routes for the productions of useful chemicals from natural gas. (Ross et al., 1996)

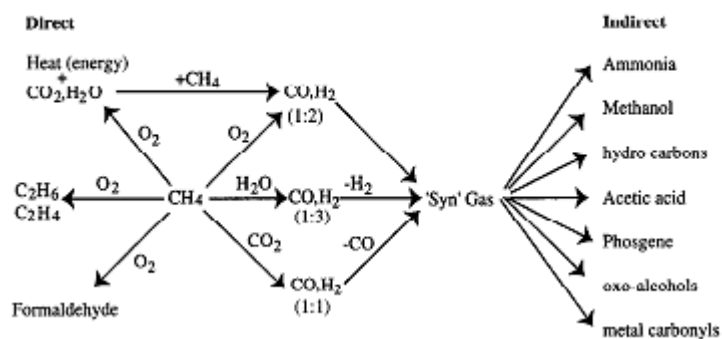


Figure 1.4: Various direct and indirect route for the productions of useful chemicals from natural gas. (J.R.H Ross et al, 1996)

1.2 Problem Statement

In oxidative coupling of methane process the C_{2+} selectivity and yield are too low and technological novelty results in uncertainty for scale-up. Higher C_{2+} selectivities and yields have to be achieved mainly by development of more selective catalysts, but optimization of reaction conditions, reactor design and operation also offers possibilities to improve catalytic performance.

During the early days, ZSM-5 zeolite, which is one of the synthetic zeolite, was found to be a suitable catalyst for the conversion of methane to higher hydrocarbons. Later, ZSM-5 was modified to increase the conversion of methane and the selectivity of targeted hydrocarbons products. But, this catalytic process has not reached the commercializing stage and it needs development to obtain a more promising result. However, some earlier studies have demonstrated that acidic ZSM-5 catalyst has shown a reasonably good oligomerization performance for olefin products to higher

hydrocarbons. The problem is that the yield of higher hydrocarbons is still rather low at present; more catalysts that are effective are needed.

There are new processes for direct methane conversion to hydrocarbon processes. One of the processes is called Partial Oxidation Process where methanol is produced. In this process methane reacts with oxygen in the presence of catalyst to produce methanol. Depending on the catalyst, the process temperature ranges from 700 up to 900°C, and the pressure being close to atmospheric. In most cases, mixed oxide catalyst is used as a catalyst. Unfortunately, the yield of methanol is too low (below 10%) and beyond industrial interest.

The successful of methane conversion to hydrocarbons over metal- containing Zeolite A catalyst is due to two effects which is the ability of the metal to show limited activity to generate olefins from methane and sufficient low olefin oxidation activity to allow the olefin produced to the remain in the system. The metal loading of copper and zinc will be investigate due to the physicochemical properties in order to increased the conversion of methane to liquid hydrocarbon.

1.3 Objectives

- i) To synthesis Cu/Zn-Zeolite A.
- ii) To investigate the performance of the modified Cu/Zn-Zeolite A catalysts based on the physicochemical properties.

1.4 Scopes of Research

The few economic evaluations available in the literature indicate that the feasibility of methane conversion to higher hydrocarbons mainly depends on the catalyst performance; Only by furthering a knowledge of the reaction mechanism and the role of the catalyst will it be possible to achieve this difficult but hopefully not impossible goal. The development of the heterogeneous catalyst may be regarded as an interactive optimization process, basically consisting of three steps, namely preparation, characterization and testing of the catalyst. Therefore, the scopes of work in this study were divided into three stages:

- i) Preparation and modification of the catalysts
- ii) Characterization of the catalysts for its physicochemical properties
- iii) Relating the physicochemical properties of the catalyst with the performance in methane conversion to liquid hydrocarbon.

CHAPTER 2

LITERATURE REVIEW

2.1 ZSM-5

Zeolites are industrially used in numerous numbers of acid catalyzed reactions due to their strong acidity and shape selective properties. It is evident that the acid strength and concentration of active sites play a very important role in the catalytic performance of zeolite and thus the possibility to prepare zeolites with a given type and number of acid sites is highly required. In the case of zeolites, the concentration of Lewis sites usually increases with calcinations or activation temperature and number of examples can be found in the literature describing the negative role of these sites in deactivation of zeolites. For the characterization of the amount and different types of acid sites temperature programmed desorption is usually used, however this technique does not allow to distinguish between Broensted and Lewis sites. For this reason, infrared spectroscopy is advantageously used in combination with the adsorption of proper probe molecules like acetonitrile or pyridine (Aiello et al., 2002).

Modification means that a given material is manipulated by appropriate treatment in order to change its properties. Cation exchange method is performed in order to obtain various cation forms of zeolites. According to Kurama et al., (2002) the fine tuning of zeolite properties can be achieved by variation of the cation type which is located at preferred sites within the framework of the zeolites. At the same time cation

exchange may also produce some remarkable change in zeolite properties, such as thermal stability, pore size and catalytic activity.

The ordered, crystalline structures imply that the micropores in zeolites have very well-defined dimensions and connectivities. In addition, the framework composition can be tuned to enhance chemical selectivity. These features combine to ensure that zeolites form a very important category of cheap, highly reproducible size and shape selective molecular sieves and adsorbents which find widespread use in industry (Weitkamp., 2000).

Zeolite based catalysts are successfully employed in a variety of commercial processes in the petroleum and petrochemical industries (Szostak, 1989). Despite this fact, there are only a few investigations on the potentials and usefulness of modified zeolites as catalysts for the formation of higher hydrocarbons from methane. Stimulated through the observation of polycondensation of methane in liquid super acids by Olah et al. (1968), strong acidic zeolites have been tested for their ability to catalyze the formation of higher hydrocarbons (Anderson, 1985; Kowalak et al., 1988; Weckhusyen et al., 1998; Xu and Lin, 1999; Yuan et al., 1999; Liu et al., 2004 and Burns et al., 2006).

2.2 HZSM- 5

The conversion of methanol has been investigated over HZSM-5 zeolite for the purpose of methylation of benzene and toluene. The aim of this work is to obtain details about the mechanism of methanol to hydrocarbon reaction. The conversion of methanol on HZSM-5 had been studied by several investigators. The strong Bronsted acid site of HZSM-5 zeolite can be methylated by methanol to form dimethyl ether intermediate

with further conversion to light olefins and then paraffins. Compared to ^{14}C tracer technique, the application of no carrier added radiochemical method precludes the disturbing effect of natural carbon impurities starting from labeled methanol and at the same time it was sensitive enough to detect very low amounts of methanol or hydrocarbon products. The catalyst was characterized using X-ray powder diffraction, scanning electron microscope, X-ray fluorescence and nitrogen adsorption. The HZSM-5 zeolite catalyst is suitable for the conversion of methanol to ^{11}C labeled olefins through dimethyl ether intermediate. The catalysis is simple and applicable not only for the production of C_2H_4 , C_3H_6 and C_4H_8 olefins but for methylation of aromatic compounds, too. H-ZSM-5 zeolites can be synthesized with a broad range of Si-Al ratio from 6 to infinity. In principle, the acid strength and acid types are the key properties of zeolites, which play a crucial role in the activity and selectivity of the zeolites. The range of zeolite-catalyzed reactions can be extended by the incorporation of metal atoms both inside and outside the zeolite framework (Goursot, et al. 2003).

2.3 Cu-ZSM-5

Amin and Anggoro, (2003) found that Cu loaded on ZSM-5 catalysts via acidic ion exchange method is a potential catalyst for the conversion of methane to liquid hydrocarbons. However, infrared study of metal loaded ZSM-5 catalysts indicated that the catalysts are not resistant to high temperature.

Le Van Mao and Dufresne, (1989) used a physical mixture of H-ZSM-5 with a ZnO/AlO, co-catalyst and proposed a hydrogen back-spillover from internal acid sites of the H-ZSM-5 to the ZnO co-catalyst located on the surface of the zeolite crystals. A physical mixture of H-ZSM-5 and ZnO calcined subsequently was studied by Osako et al (1993). They concluded from IR results on the

generation of Lewis sites by a solid state ion exchange of zinc. A reaction mechanism with zinc ions as active sites was proposed. Also, ion exchange was used by Yakerson et al.(1989) for preparation of zinc modified H-ZSM-5 catalysts that were used for conversion of ethane and propane. Only Roessner et al. 1993 applied all three preparation methods and compared the catalytic activity of the resulting samples. Nearly no influence of the mode of zinc addition on the catalytic activity was obtained in the conversion of ethane.

Berndt et al.(1996) tried to vary the location of the zinc species by applying different zinc loading techniques in order to obtain relations between the structural properties and the catalytic activity of the modified H-ZSM-5 catalysts in the conversion of propane.

2.5 Cu /W-ZSM-5

The optimization of methane conversion to liquid fuels over copper loaded W/ZSM-5 catalyst was studied by utilizing experimental design from 'Statsoft Statistica' version 6.0 software. Response surface methodology was employed to determine the optimum methane conversion and C₅₊ selectivity. Numerical results indicated the optimum methane conversion of 29.4% with the corresponding C₅₊ selectivity of 57.2% were achieved at 12.3 vol% of O₂, 203.9 ml/min of total feed flow rate, and %W doped of 3.2 wt%. The optimum C₅₊ selectivity of 70.2% was attained at 7.6 vol% of O₂, 208.9 ml/min of total feed flow rate, and 3.2 wt% of W content with the corresponding methane conversion of 26.7%. By means of variance analysis and additional experiments, the adequacy of this model was confirmed (Amin et al, 2004).

Amin and Anggoro, (2006) found that loading HZSM-5 with tungsten and copper enhanced the methane conversion, CO₂ and C₅₊ products. However, it reduced the CO, C₂₋₃, and H₂O selectivities. The process of converting methane to liquid hydrocarbons (C₅₊) is dependent on the metal surface area and the acidity of the zeolite. The W/3.0Cu/HZSM-5 is the potential catalyst, because over this catalyst high methane conversion and C₅₊ selectivity, and low H₂O selectivity are obtained.

2.6 Zeolite A

The plasma methane conversion to higher hydrocarbons in the presence of CO₂ was experimentally investigated in a Dielectric Barrier Discharge (DBD) reactor over zeolite A at low temperature and atmospheric pressure. Syngas, light hydrocarbons and liquid fuels can be produced this way. High conversion of CH₄ and CO₂ can be achieved. Flow rate of the feed, molar ratio of CH₄/CO₂ and the input power have significant effect on the plasma conversion of CH₄ and CO₂. The application of zeolite A inhibits the formation of carbon black and plasma polymers and leads to a higher selectivity of light hydrocarbons (C₂–C₄). (Jiang et al, 2002)

IR method is successfully used for identifying zeolite structure as a complementary technique to XRD. The crystallinity estimated using IR and XRD methods is quite comparable and hence can be used as a method for monitoring the synthesis of zeolite-A from a complex matrix like flyash. Further studies are in progress for determining the sensitivity and accuracy of the method. The phase purity of the sample is important from the point of view of its usage as a catalyst. In case of

environmental remediation, wherein it is to be used as an adsorbent/exchanger, purity of the sample is not a significant issue and can be compromised as a trade-off between cost and efficiency. Ultimately, the adsorbent medium is being used as a phase transfer for the pollutant and may either be disposed-off safely or converted into some value-added ceramic precursor, which may differ substantially in phase. (Rayalu et al., 2005)

Chitra et al. (1995) found that the methane molecule exhibits a strong orientation preference during its passage through the bottleneck which is an eight-membered ring. As the passage through this rather narrow window is the rate determining step for diffusion within the zeolite, such orientation preference could be of considerable importance. This finding is likely to be of considerable importance in understanding diffusion of not only methane but also other higher hydrocarbons within zeolitic voids. The importance of hydrocarbon zeolite system in petrochemical industries cannot be overemphasized.

CHAPTER 3

METHODOLOGY

3.1 Introduction

In this chapter, the experimental techniques employed for the preparation and characterization through this research are summarized and descriptions of rig setup are also presented. The flow chart of the experimental work is shown in Figure 3.1. The first stage of this experimental work was preparation of catalysts. The catalyst which is CuZn/Zeolite A was prepared. Then, the catalyst was characterized using X-Ray Diffraction (XRD) in order to determine the crystallinity of the catalyst. Besides, Thermogravimetry Analysis (TGA) was used to determine the thermal stability and the weight loss. Fourier Transform Infrared (FTIR) was used to determine the functional group of the sample. Finally, conclusions were drawn based on the findings obtained from this study.

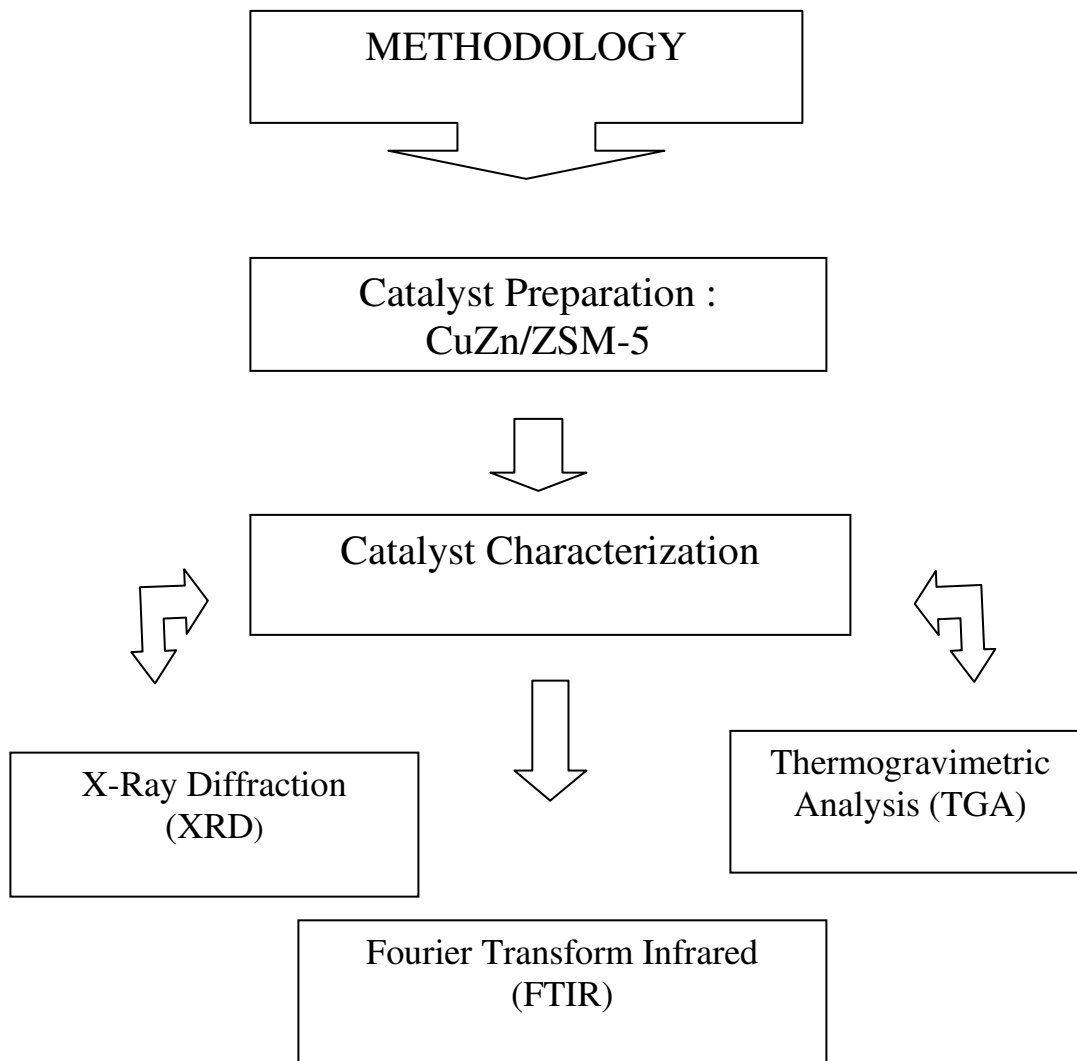


Figure 3.1: Flow chart of overall experimental work.

3.2 Preparation of Cu/Zn-ZSM-5

Zeolite A (supplied by Fluka) in granular form was blended to change it's form into powder. The incorporation of copper and zinc into the ZSM-5 catalyst was carried out through ion exchange method described by Öhman et al, (2002). The metal salts which used to modify the Zeolite A in this study are shows in Table 3.1.

Table 3.1: Metal salts and their manufacture assay data

Name of Salt	Molecular Formula	Molecular Weight (gram/mol)	Purity (%)	Supplier
Copper Nitrate	$\text{Cu}(\text{NO}_3)_2$	241.60	99.9	Merck
Zinc Sulphate	ZnSO_4	287.54	99.5	Genee Chemical
Zeolite A				Fluka

The Zeolite A catalyst with copper and zinc loading 0%, 2%, 5%, 8% and 10% of were prepared, the calculations are summarized in Table 3.2. The details calculations are shown in Appendice A. After the sample was weighed, it was mixed with the 10 ml deionized water in a beaker. Figure 3.2 shows the experimental setup for the preparation of Cu/Zn-ZSM-5. Then, the samples were placed in crucible and dried overnight at 110°C in the oven followed by calcinations process for 4 hours at 550°C to remove organic material. (Yin et al., 2005). The calcinations process was set up at 5°C min⁻¹ for the ramping temperature. The solid catalyst was labeled as CuZn/Zeolite A.

Table 3.2: Summarization of metal loading to zeolite

Sample	1	2	3	4	5
Ratio of Cu:Zn	0:10	2:8	5:5	8:2	10:0
Mass of Cu (g)	0	0.040	0.100	0.160	0.200
Mass of Zn (g)	0.20	0.160	0.100	0.040	0
Source of Cu (g)	0	0.152	0.380	0.608	0.760

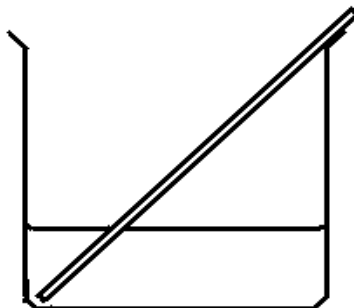


Figure 3.2 : Experimental setup for Cu/Zn-ZSM-5 preparation

3.4 Catalyst Characterization

The synthesized catalyst was characterized using FTIR to identify the functional group, X-Ray Diffraction to identify the structure and Thermogravimetric Analysis to determine its thermal stability and its fraction of volatile components.

3.4.1 Fourier transform infrared (FTIR)

FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitative some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. FTIR is perhaps the most powerful tool to use in this research for identifying types of chemical bonds (functional groups) and the spectrum analysis. The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. The FTIR was performed in Membrane Research Unit at Universiti Teknologi Malaysia.

3.4.2 X-Ray Diffraction (XRD)

The structures of the Cu/Zn-ZSM-5 catalyst were determined by X-Ray Diffraction techniques. The XRD analysis was performed in Ibnu Sina Research Centre at Universiti Teknologi Malaysia This method was based on the fact that every crystalline material has its own characteristics diffractogram. XRD patterns were acquired on a Siemens D5000 goniometer using $\text{CuK}\alpha$ radiation in the range of 2θ from 2° to 60° at a scanning speed 3° per minute. All the samples were fully dried before diffractograms were measured.

3.4.3 Thermogravimetric Analysis

Thermogravimetric analysis (TA Instrument Model Q 500 TGA with TA 5000 Controller) is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. The measurement is normally carried out in air or in an inert

atmosphere, such as Helium or Argon, and the weight is recorded as a function of increasing temperature. The samples were heated under the flow air which is 25 ml min^{-1} from ambient temperature (25°C) to 1000°C at the heating rate of $10^{\circ}\text{C min}^{-1}$. The TGA was conducted at Clean Room, FKKSA laboratory.

CHAPTER 4

RESULTS & DISCUSSION

4.1 X-Ray Diffraction

The prepared samples with different metal loading were characterized using XRD to determine zeolite crystallinity and the morphology of the modified catalyst. The XRD diffractograms of modified catalysts with different metal loadings at 550°C for 12 hours are shown in Figure 4.1. The analysis reveals that there are no obvious changes in the crystalline structure of the modified zeolites. The crystallinity has been estimated for the synthesized samples by taking the sum total of relative intensities of ten individual characteristic peaks that shown in Table 4.1. Figure 4.1 shows that only sample e has the percentage of crystallinity that more than 100%. It means that the structure of the modified Zeolite A is more crystalline than its parent zeolite. Meanwhile, the percentage of crystallinity for other sample which are sample a, b, c and d are 30.9, 38.0, 46.8 and 52.0 respectively. This result was confirmed by the smallest pore diameter value which indicating largest surface area was the biggest compare to others. Table 4.2 shows pore distribution and crystallinity of the catalysts. Considering the possible error in this method, there was hardly any increase in the zeolite crystallinity with the increasing of copper loaded to the Zeolite A.

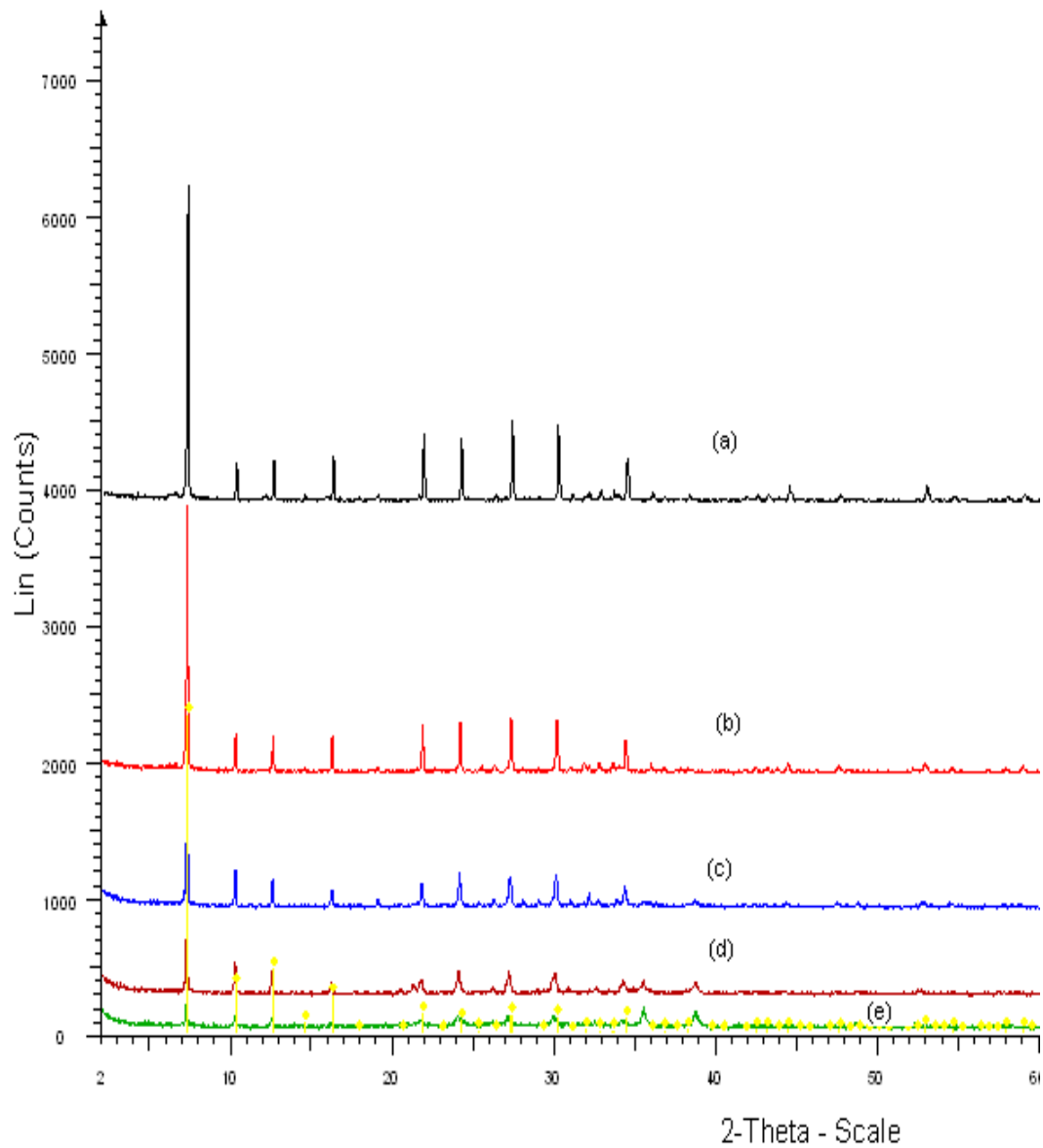


Figure 4.1 : XRD pattern of Zn-Zeolite A (a), 0.2Cu/0.8Zn- Zeolite A (b), 0.5Cu/0.5Zn- Zeolite A (c), 0.8Cu/0.2Zn- Zeolite A (d) and Cu- Zeolite A (e).

Table 4.1: Ten characteristic peaks and their relative intensities

Characteristic peak 2 θ	Relative intensity for Sample a	Relative intensity for Sample b	Relative intensity for Sample c	Relative intensity for Sample d	Relative intensity for Sample e
29.95	1.8	20.8	27.2	20	73.2
24.01	20.5	19.3	27.3	32.2	70.5
7.21	100	100	100	100	100
27.13	25.9	21.7	25.8	32.4	69.3
10.205	12.3	15.7	31.3	43.6	61.4
34.165	14.2	13.2	17.6	15.8	54.5
21.68	2.6	18.7	20.9	23.1	56.5
12.49	2.1	14.6	24.2	31.3	54.1
16.13	14.6	14.6	15.5	18.5	42.2
26.095	2.6	3.4	8.1	14.1	69.3
Total	196.6	242	297.9	331	651

Table 4.2: Pore distribution and crystallinity of the catalysts.

Catalyst	Average pore diameter, d (Å)	Crystallinity %
Zn-Zeolite A	2.34283	30.9
0.2Cu/0.8Zn-Zeolite A	2.33026	38
0.5Cu/0.5Zn-Zeolite A	2.3262	46.8
0.8Cu/0.2Zn-Zeolite A	2.32357	52
Cu-Zeolite A	2.32281	102.2

The changes are due to the size, charge and locations of the cations that lead to the arrangement of other ions in the Zeolite structure. These values are lower compared to the Cu-Zeolite A sample. Besides, the decrease is a sign that copper atoms probably occupied the aluminum position in the aluminium positions in the framework compared to the zinc atoms.

The surface area is bigger if the particle size is smaller. So, all these samples have surface area and crystallinity smaller than Cu-Zeolite A. The reduction in surface area of the metal loaded Zeolite A indicates a strong interaction between the surface of the zeolite and the zinc species, which enables a good dispersion of the metals on the surface.