

**A SINGLE-STEP CATALYTIC PROCESS FOR THE  
CONVERSION OF METHANE TO GASOLINE OVER  
TUNGSTEN ZEOLITE CATALYSTS**

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In the name of Allah the Most Beneficent, the Most Merciful  
All praises and thanks be to Allah the lord of mankind  
and all that exist.

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## ABSTRACT

The catalytic conversion of methane to higher hydrocarbons in the gasoline range has been performed. The dehydroaromatization of methane (DHAM) over a series of 3 wt% W-based catalysts prepared with different supports, under different preparation conditions and several Si/Al ratios of HZSM-5 was carried out. The DHAM was also investigated over a series of W-supported on ZSM-5 modified with varying degrees of Li<sup>+</sup> content. The reaction was conducted with and without the presence of oxygen. It was found that modified Li<sup>+</sup> in the 3 % W loaded-HZSM-5 catalyst having 74% of the original HZSM-5 strong acid sites exhibited maximum activity and stability under both conditions: with and without oxygen addition in the feed gas. The improved performance in the catalyst activity and stability is attributed to the suitable amount of Brønsted acid sites in the catalysts and addition of oxygen in the feed. The methane conversion up to 20% was obtained over the most active catalyst. The main products are benzene, naphthalene (80–90% selectivity), and coke (10% and even higher). Furthermore, direct one-step methane co-transformation with other light alkanes as co-feed into heavier hydrocarbons in the gasoline range product was studied on W/HZSM-5 catalysts. Catalysts were characterized by BET surface area and pore size distribution measurements, X-ray diffraction (XRD), Fourier transform infrared (FT-IR), ammonia temperature-programmed desorption and oxidation (TPD-NH<sub>3</sub> and TPO), UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS), thermogravimetric analysis (TGA). The catalytic conversion of a mixture of methane, ethylene and methanol to gasoline has been studied over W/HZSM-5 catalyst. The effect of process variables such as temperature, % vol. of ethylene in the methane stream, and catalyst loading on the distribution of hydrocarbons was studied. The reaction was conducted in a fixed-bed quartz micro reactor in the temperature range of 300 to 500 °C using % vol. of ethylene in methane stream between 25 – 75 % and catalyst loading of 0.2 – 0.4 gram. The reaction of methane-ethylene feed over W/HZSM-5 catalyst produces gasoline rich hydrocarbons in the C<sub>5</sub>-C<sub>10</sub> non-aromatics and also aromatics range. Kinetic study of the methane conversion in the presence of co-feeding ethylene and methanol to produce higher hydrocarbons in gasoline range has been performed over W/HZSM-5 catalyst. The kinetic model was proposed based on a Langmuir-Hinshelwood-Hougen-Watson reaction mechanism. The correlation between experimental and calculated reaction rate indicates that the model fits the data very well.

## ABSTRAK

Penukaran bermangkin metana kepada hidrokarbon yang lebih panjang di dalam julat gasolin telah dijalankan. Dehidropengaromatikan metana (DHAM) dilakukan menggunakan mangkin berasaskan 3% berat W yang disediakan menggunakan pelbagai sokongan, di bawah penyediaan dan nisbah Si/Al bagi HZSM-5 yang berbeza. Kajian DHAM juga dilakukan menggunakan mangkin W yang disokong oleh HZSM-5 yang diubahsuai menggunakan kandungan ion  $\text{Li}^+$  yang berbeza. Tindakbalas dilakukan dengan kehadiran oksigen dan juga tanpa kehadiran oksigen. Hasil menunjukkan bahawa mangkin 3WLi-HZSM-5 yang mempunyai 74% asid kuat mempamerkan aktiviti dan kestabilan maksimum di bawah kedua-dua keadaan: dengan dan tanpa penambahan oksigen. Peningkatan aktiviti dan kestabilan mangkin disebabkan oleh kuantiti asid Brönsted yang sesuai dan juga oleh kehadiran oksigen di dalam suapan. Penukaran metana sehingga 20% boleh diperolehi bagi pemangkin yang terbaik. Hasil utama yang diperolehi adalah benzene, naphtalina (kepemilihan 80-90%) dan kok (10% atau lebih). Transformasi metana secara terus bersama dengan mana-mana alkana ringan yang lain kepada hidrokarbon yang lebih panjang di dalam julat gasolin juga dikaji pada pemangkin W/HZSM-5. Pencirian mangkin telah dilakukan menggunakan pengukuran luas permukaan BET dan agihan saiz liang, XRD, FT-IR piridina, TPD-NH<sub>3</sub>, TPO, UV-Vis DRS, dan TGA. Penukaran bermangkin campuran metana, etilena dan metanol kepada gasolin juga dilakukan menggunakan mangkin W/HZSM-5. Kajian kesan pembolehubah proses seperti suhu, % isipadu etilena di dalam aliran metana dan kuantiti mangkin keatas agihan hasil hidrokarbon telah dijalankan. Tindakbalas telah dijalankan didalam reaktor kuarsa padatan tetap antara 300-500°C menggunakan % isi padu etilena didalam aliran metana di antara 25-75% dan juga kuantiti mangkin 0.2-0.4 gram. Tindakbalas methane-etilena menggunakan mangkin W/HZSM-5 menghasilkan gasolin yang kaya dengan C<sub>5</sub>-C<sub>10</sub> hidrokarbon tak-aromatik dan juga aromatik. Kajian kinetik terhadap penukaran metana dengan kehadiran suapan etilena bersama metanol untuk menghasilkan hidrokarbon yang lebih panjang didalam julat gasolin juga dibuat menggunakan mangkin W/HZSM-5. Model kinetik telah dicadangkan berdasarkan kepada mekanisma tindakbalas Langmuir-Hinshelwood-Hougen-Watson. Korelasi antara kadar tindakbalas ujikaji dan pengiraan menunjukkan bahawa model tersebut adalah bersesuaian dengan data.

## CHAPTER 1

### INTRODUCTION

#### 1.1 General Background

Fossil oil plays an important role as a source of feedstocks for chemical industry and supply of energy. Until now, the supply of energy is heavily dependent on those energy resources. Among the fossil oils, such as natural gas and coal, liquid oil has been primarily used particularly for generating energy as presented in Figure 1.1. Based on this figure, the world consumption of energy forecast shows great increase. It shows that liquid oil continues to be the world's dominant source of energy compared to renewable source and other fuels i.e. natural gas and coal.

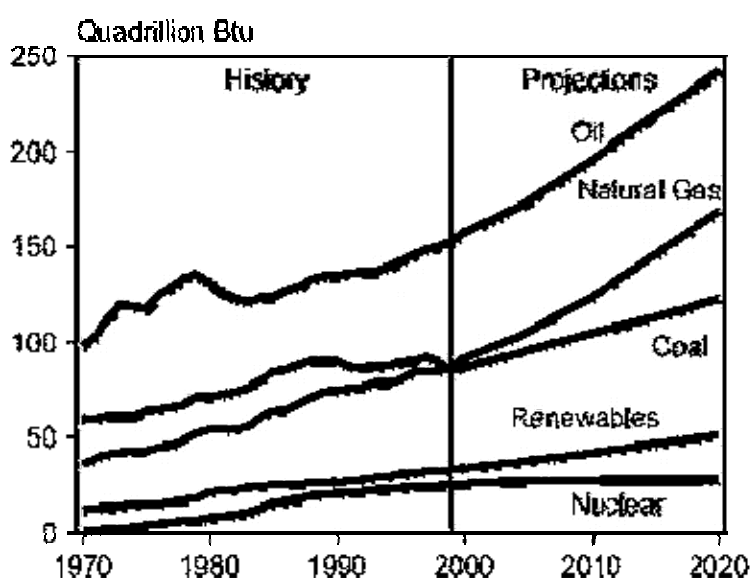


Figure 1.1: World energy demand, 1970-2020 ([www.eia.doe.gov/iea/](http://www.eia.doe.gov/iea/))

According to the data *Energy International Annual* ([www.eia.doe.gov/iea/](http://www.eia.doe.gov/iea/)), in 2002 the consumption of petroleum stood at 78.21 million barrels per day which made up 40 percent of total energy consumption in the world. Based on the current consumption rates, petroleum reserves are expected to last for another 36 years only.

By far, the most important product from oil is for transportation fuel. Table 1.1 presents some characteristics of the three main fuels in the transport sector; gasoline, kerosene, and diesel (De Jong, 1996). One important characteristic of these fuels is that their state is liquid at ambient condition. Liquid oil has easiness for storage in tanks, distribution in bulk by road, rail, or pipelines and supplying by pumping, therefore making it more preferable as a fuel. The fuel consumption grows due to the increasing number of vehicle ownership in the world as presently there are no economically competitive alternatives to the liquid fuel oil. Accordingly, the world requires more production of oil for energy consumption.

Table 1.1: Characteristics of fuel oils (De Jong, 1996).

<b>Fuel</b>	<b>Boiling range ( ° C)</b>	<b>Key properties</b>	<b>Main Processes</b>
Gasoline	< 200	Octane number	Catalytic reforming, FCC, Alkylation
Kerosene	200-250	Smoke point	SR(HDS),HC
Diesel	250-350	Cetane number	SR(HDS),HC

FCC=fluid catalytic cracking, SR=straight run,  
HDS=hydrodesulfurisation, HC=hydrocracking

However, excessive exploitation of oil causes faster oil depletion which leads to the scarcity of oil since it is not a renewable source. Considerable efforts have been devoted to the development and exploitation of alternative feedstock to reduce heavy dependence on petroleum. Natural gas has been considered as the most promising alternative energy resource due to its availability in large quantities (Hamid *et al.*; 2000; Xu and Lin, 1999; Zaman, 1999), comprising many similar properties with petroleum that makes easy use of existing infrastructure. In addition, natural gas is considered as a clean energy resource and cheap raw material (Halabi *et al.*, 1997). Accordingly, with the decline of crude reserves, the energy supply is



changing from being primarily oil based to become more gas based (Shu and Ichikawa, 2001).

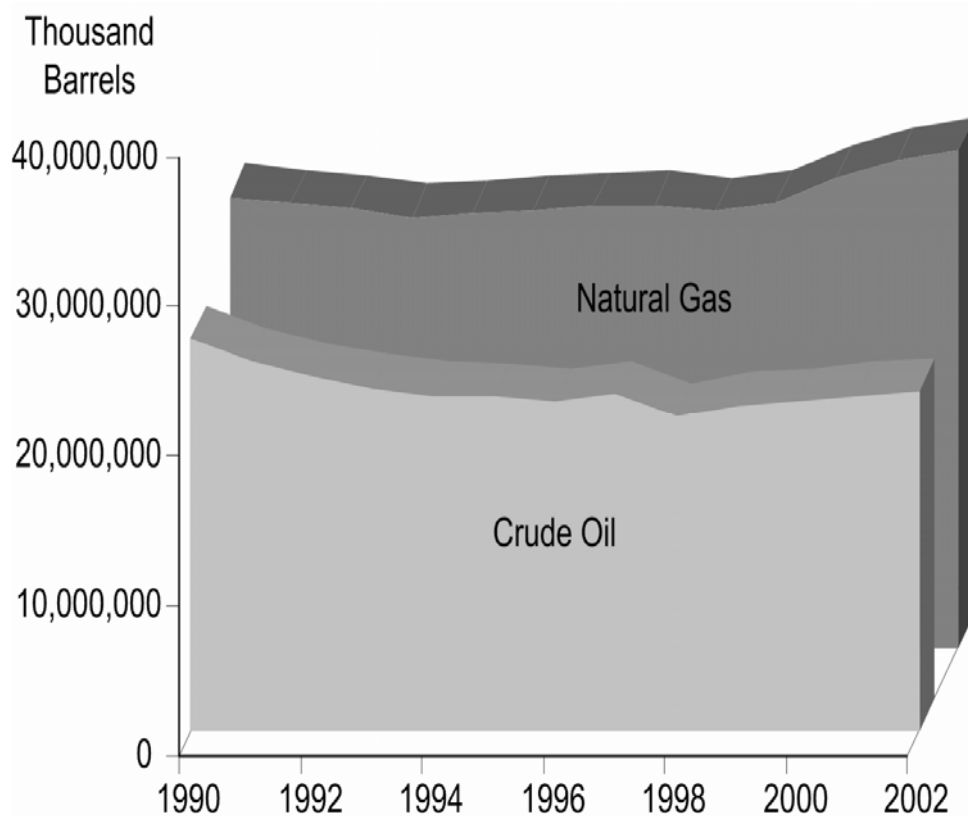


Figure 1.2: Proven world oil and natural gas reserves

(<http://www.eia.doe.gov/emeu/aer/resource.html>)

Natural gas exploitation has increased significantly over the years with higher than oil supply as shown in Figure 1.2. The main use of natural gas is in combustion process for heating purposes (Ogura and Kataoka, 1987; Zhantoff, 1988; Ernst and Weitkamp, 1989; Ross *et al.*, 1996; Zaman, 1999; Lunsford, 2000). Currently, it is being used to generate power from gas turbines. On the other hand, natural gas is an underutilized resource for chemicals and liquid fuels with only 7% going to the production of chemicals such as methanol and ammonia (Poirier *et al.*, 1991). The widespread natural gas usage is limited due to the low energy content per unit volume of natural gas makes its transport from wellheads to the consumers difficult. Indeed, it is found in remote areas which require considerable costs to transport gas

by pipeline to the desired places (Gesser *et al.*, 1985; Arutyunov *et al.*, 1994). Moreover, natural gas which mostly consists of methane is a stable substance to convert to a wide range of chemicals (Vasina *et al.*, 1993; Shu and Ichikawa, 2001).

The use of natural gas as fuel is not always the most economical solutions for natural gas utilization, especially when the reserve is small and in remote areas. It is sometimes more attractive and viable to convert the natural gas to liquid fuels or higher hydrocarbons (Suhartanto, 2001). The existing routes for natural gas conversion to higher value products require the formation of synthesis gas ( $\text{CO} + \text{H}_2$ ) as an intermediate product which is formed by steam reforming process. Figure 1.3 shows a brief of existing commercial routes for natural gas utilization (Peterson *et al.*, 2001).

Although natural gas has been used in a variety of scopes and areas, the contribution of natural gas for liquid fuel supply in transportation sector has not yet reached significant amount compared to its reserves. Commercial technology has already been accomplished for producing liquid oil from natural gas on a large scale. The process includes Metanol to Gasoline (MTG) process and Fischer Tropsch (FT) processes. Currently, gasoline is produced in Sasol, South Africa and Malaysia using FT process, while the New Zealand government selected the MTG process over FT for converting natural gas to gasoline (Fox *et al.*, 1990; Stocker, 1999). The production of syngas from natural gas suffers due to the high cost for conventional method of steam reforming (Edwards and Tyler, 1988; Fox *et al.*, 1990). Gradassi and Green (1995) evaluated the economic aspects of FT and MTG processes confirmed that the gasoline manufacture from both processes are suffering from a relatively low cash margin, requiring high capital investment, as well as having a long payout time.

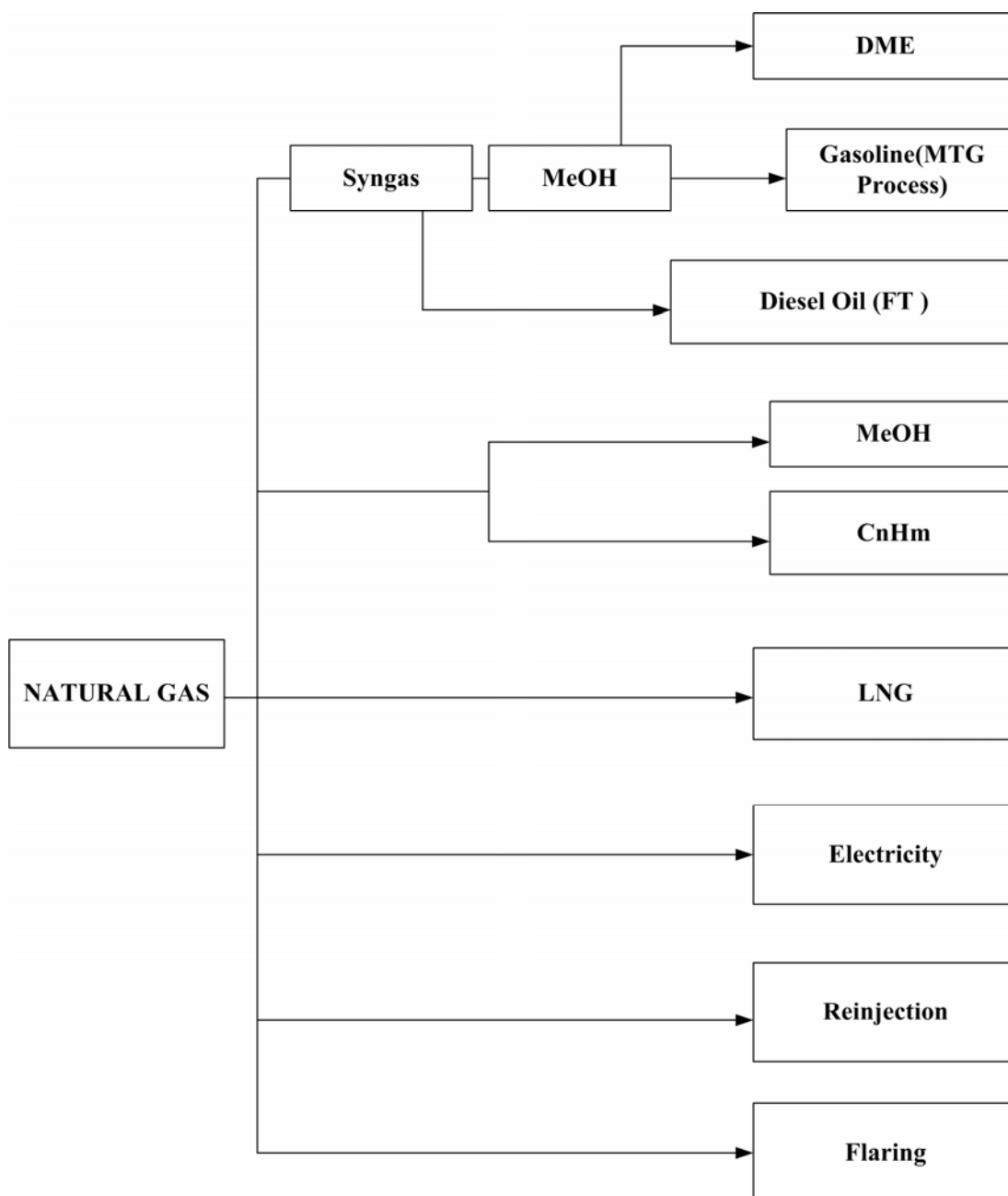


Figure 1.3: A brief utilization of natural gas (Peterson *et al.*, 2001)

Much attention has been focused to convert methane into useful chemical and easily transportable liquid fuels directly to avoid high cost step of syngas formation. The direct conversion of methane to a liquid hydrocarbon fuel without reforming methane to synthesis gas conceptually appears attractive and it is a challenge to industrial catalysis (Pierella, 1996; Fox *et al.*, 1990; Petersen, 2001). Presently, there

is an increasing interest towards methane conversion since the utilization of methane as a raw material would be markedly increased if it could be directly converted to higher value hydrocarbons. The direct catalytic conversion of methane, the main component of natural gas, to liquid fuels and chemicals of commercial importance is still an intensively sought goal. There is a large volume of literature on the investigation for the methane conversion to higher chemical products. The activation of methane has been attempted from different view points which cover catalytic and non catalytic processes, including oxidation or non oxidation processes. So far, there are some potential routes for methane conversion such as partial oxidation to methanol (POM), oxidative coupling of methane (OCM), direct methane aromatization (DHAM) and single step direct methane to gasoline hydrocarbons range product.

## 1.2 Direct Catalytic Conversion of Methane to Higher Hydrocarbons

Direct conversion of methane to more valuable chemicals without involving synthesis gas has long been considered good in catalysis studies. Methane can be converted to higher hydrocarbons *via* the oxidative coupling of methane (OCM) (Anderson *et al.*, 1985; Bi *et al.*, 1988; Burch and Maitra, 1993; Burch *et al.*, 1991; Chalker *et al.*, 1991; Conway *et al.*, 1991; Conway *et al.*, 1991; Ernst and Weitkamp, 1989; Korf, *et al.*, 1992; Krylov, 1993; Maitra, 1993; Mleczko and Baerns, 1995). It can also be partially oxidized to methanol (Rytz and Baiker, 1991; Casey *et al.*, 1994; Arutyunov *et al.*, 1996; Lu, 1996; Liu, 1996; Lee and Foster, 1996; Raja and Ratnasamy, 1997; Lange, 2001; Otsuka and Wang, 2001). In addition, it has been demonstrated that formaldehyde could be obtained by partial oxidation of methane using molecular oxygen as oxidant (De Lucas *et al.*, 1998). Furthermore, the direct catalytic conversion of methane into higher aromatic hydrocarbons has been extensively studied by many researchers (Wechuysen *et al.*, 1998; Szöke and Solymosi, 1996; Shu and Ichikawa, 2001; Xiong *et al.*, 2001a and 2001b, Choudary *et al.*, 1997; Meriaudeau *et al.*, 2000; Pierella *et al.*, 1997; Liu *et al.*, 1999, Liu *et al.*, 2000; Xu and Lin, 1999). In particular, the single step conversion of methane into higher hydrocarbon in the range of gasoline ( $C_5^+$ ) has been reported by some researchers (Han *et al.*, 1994; Didi, 1998).

The oxidative coupling of methane to  $C_2^+$  hydrocarbons (OCM) has been intensively studied since 1980s (Maitra, 1993; Mleczko and Baerns, 1995). The heterogeneous catalytic OCM has been the major subject of a large body of research activities. A large number of catalysts have been tested in the OCM process, but these reactions have some problems namely low conversion, low selectivity to ethylene, and high-energy cost. Until recently no catalysts could reach a  $C_2$  yield beyond 25% and the selectivity to  $C_2$  higher than 80 % is the principal criteria for industrial application of the OCM (Xu and Lin, 1999).

Methane, the most inert of the hydrocarbons has been extremely difficult to activate for direct conversion to higher hydrocarbons. The conversion of methane to ethane and ethylene has been achieved in the presence of oxygen by oxidative coupling of methane (OCM) over a number of basic catalysts. However, the OCM process involves formation of undesirable products such as  $CO_2$  because of the highly exothermic hydrocarbon combustion reaction, which can also be hazardous (Liu *et al.*, 1991). In an attempt to avoid the use of oxygen in the gas phase, many approaches have been tested and investigated in order to avoid the total oxidation of methane. Recently, it has been reported that methane can be activated to aromatic products under non-oxidizing. Transformation of methane to aromatics is thermodynamically more favorable than the transformation of methane to ethylene (Xu and Lin, 1999).

Dehydroaromatization of methane (DHAM) in the absence of oxygen have attracted considerable attention from many researchers. However, the methane conversion as low as 6-8 % with the selectivity to aromatic of about 70-80 % was obtained on the conversion of methane to aromatic with non oxidative condition at 700 °C (Shu *et al.*, 1997). Most of the existing DHAM catalysts, mainly Mo/HZSM-5-based catalysts, operated at about 973 K, which results in rather low methane conversion ( $X_{CH_4}$ ) due to the thermodynamic limitation. Thermodynamic calculations showed that the equilibrium conversions of 11.3, 15.8, 21, 27 and 33% for methane to benzene (i.e.,  $6CH_4 \rightleftharpoons C_6H_6 + 9H_2$ ) are predicted at 973, 1023, 1073, 1123 and 1173 K, respectively. This indicates that an operation temperature as high as ~1073 K is required for methane conversion to reach ~20%. However, under

such high temperature, Mo-based catalysts suffer inevitably from the disadvantage of serious loss of Mo component by sublimation (Xiong *et al.*, 2001).

The commonly accepted processes of the methane transformation into higher hydrocarbons or motor fuels are usually multistage and involve an intermediate energy consuming conversion of methane into syngas. In spite of the direct aromatization of methane, it is highly desirable to convert methane into liquid hydrocarbons like gasoline, diesel fuel, etc. Han *et al.* (1994), reported the direct partial oxidation of methane to  $C_5^+$  hydrocarbons over HZSM-5 catalyst when a  $C_3$  additive (propane or propene) is present in the feed or sorbed heavy hydrocarbons are present on the partially coked HZSM-5 catalyst.

### 1.3 Problem Statements

Previous, studies on a single step conversion of methane to higher hydrocarbon such as aromatic and gasoline range products showed promising results. However, lower conversion of methane and selectivity of higher hydrocarbons range product was obtained over metal loaded ZSM-5. Han *et al.* (1994 a , b) obtained a  $CH_4$  conversion of 4.7- 6.3 % with product selectivity to  $C_5^+$  of 7.7 % with the presence of oxygen in the reactant. Direct conversion of methane to aromatic product in the absence of oxygen over molybdenum loaded on HZSM-5 has obtained a conversion of about 6-8 % and selectivity of about 70-80 %. Unfortunately, the reaction is conducted at very high temperatures, over 950 K, which leads to the major problem in the non oxidative aromatization of methane, yielding carbon being deposited in the catalyst. Thus, the improvement of the activity and stability of the catalysts is significantly important to enhance the conversion of methane and selectivity to higher hydrocarbons range products as well as the stability of the catalyst.

Introduction of second reactant into  $CH_4$  feed is an alternative way to activate methane and eliminate the coke deposition. The catalytic conversion of methane to higher hydrocarbons in the presence of oxidative reactants such as  $O_2$ , CO and  $CO_2$  has been studied; however, the catalytic performance needs further improvements, since the process now results in the formation of  $CO_2$  as an undesirable product.

The transformation of methane in the presence of co-feeding is an interesting approach for the effective utilization of methane to produce liquid fuel. Previous studies have reported that CH<sub>4</sub>, in the presence of small amounts of light hydrocarbons as co feeding under non-oxidizing conditions could be converted to form aromatic products over at low pressures (1–2 atm) (Pierella *et al.*, 1997). Purely acidic ZSM-5 zeolites are active for this reaction but the activity and selectivity to higher hydrocarbon are much lower.

#### **1.4 Research Objectives**

The purpose of this research is to improve the methane conversion and selectivity of gasoline products by using a –single step process over tungsten zeolite based catalyst to achieve the commercializable rates of methane conversion of 35% and selectivity of gasoline of 85% (Zaman, 1999). In order to achieve the objectives, the following works will be conducted:

Improving the activity and stability of tungsten zeolite catalyst for the conversion of methane to gasoline under oxidative and non oxidative conditions.

1. Developing a single-step process by the addition of co-feeding to increase the conversion of methane and the selectivity to gasoline.
2. Optimizing reaction process variables to obtain the maximum gasoline selectivity.
3. Developing a new kinetic model for the conversion of methane in the present of co-feeding to gasoline.

#### **1.5 Research Scope**

In Chapter 4, the activities of the catalysts with different zeolite support for dehydroaromatization of methane in the absence of oxygen to aromatics was investigated. The effect of different supports will be studied on 3 wt. % metal W loaded on different zeolites such as ZSM-5, H- $\beta$ , USY and Al<sub>2</sub>O<sub>3</sub>. The catalysts

were prepared under different preparation conditions and several Si/Al ratios of HZSM-5. The relationship between the nature of tungsten species and the acidic sites of the catalysts with the catalytic activity is affected by various zeolite characteristics on the stability, methane conversion activity, and selectivity to aromatic product was reported. W/HZSM-5 was reported to be active and heat-resisting catalyst for methane aromatization as reported by Zeng *et al.* (1998). Xu *et al.* (1999) found that W/HZSM-5 could increase methane conversion and aromatics selectivity. However, W supported on various zeolites has not been studied for the direct methane conversion to  $C_5^+$  hydrocarbons. Liu *et al.* (1999) studied the conversion of methane into aromatic product on molybdenum supported catalysts by varying the supporting materials such as HZSM-5, Mordenite, USY,  $Al_2O_3$ ,  $SiO_2$ , FSM-16. In addition, Shu and Ichikawa (2001) investigated various types of zeolites such as H-ZSM-11, H-Beta, H-Y, and H-mordenite for the dehydroaromatization of methane in the absence of oxygen. The activity over these catalysts showed different performance. The result implies that the channel structure as well as the acidity of zeolite plays an important role in the catalytic performance of the methane conversion to higher hydrocarbons product such as aromatic as well as gasoline selectivity.

In Chapter 5, the relationship between acidity and activity of dehydroaromatization of methane in the absence and the presence of oxygen was studied over Li modified W/HZSM-5 catalysts. In order to prolong the catalyst lifetime and reduce undesired coke formation, alkali metal is used to modification of the catalyst acidity. The catalysts were prepared by subsequence ion exchange of Li ion with different concentrations followed by impregnation of W on HZSM-5 support. The catalyst acidity was studied in detail by *in situ* FT-IR. Pyridine was used as the probe molecule to study the acid sites of Li modified W/HZSM-5 samples. The results are correlated with corresponding catalytic evaluation. To improve the activity and stability of catalyst the dehydroaromatization of methane over a series of Li modified W/HZSM-5 was conducted in the presence of oxygen in the methane feed. Modified Li on W supported HZSM-5 catalysts have not been used in the dehydroaromatization of methane (DHAM) reaction. Xun and Lin, (1999) studied DHAM reaction over molybdenum supported HZSM-5 catalyst and found that the optimum metal loading was around 4 wt %. For the metal loading



below of the optimum value, the catalyst activity increased with the increase of metal loading. In contrast, the activity of the catalyst decreased drastically when the metal loading over the optimum content due to the considerable elimination of acidity which is responsible in the process reaction (Shu *et al.*, 1997; Weckhuysen *et al.*; 1998; Liu and Xu, 1999). In addition, some efforts have been made to add selected oxidative reagents such as oxygen and carbon dioxide (10% or higher) to the methane gas feed in order to reduce coke formation on molybdenum supported on HZSM-5 catalyst as reported previously (Ohnishi *et al.*, 1999; Wang *et al.*, 2000; Shu *et al.*, 2002)

Chapter 6 undertaken for investigating the chemical transformation of methane in the presence of co-feeding such as ethylene and methanol into more transportable substances or liquid motor fuels ( $C_5^+$  hydrocarbons). The effect of process variables such as temperature, % vol. of ethylene in the methane stream, and catalyst loading, on the distribution of hydrocarbons was studied according to statistical method with the application of experiment design utilizing the Statistica software (version 6.0 of Statsoft Inc). Furthermore, in Chapter 7, the effect of co-feeding i.e. ethylene and methanol for the conversion of methane to gasoline was studied. The optimization studies of methane conversion in the presence of co feeding have not been performed. Previously, Pierella *et al.* (1997) observed that natural gas could be converted to higher hydrocarbons under lower temperatures (773–873 K) over Mo/HZSM-5 catalyst. Choudhary *et al.* (1997) found that methane could be highly activated, yielding a high rate of conversion to higher hydrocarbons at low temperatures (673 –873 K) by its reaction over H-galloaluminosilicate ZSM-5 type (MFI) zeolite in the presence of alkenes or higher alkanes. Han *et al.* (1994a) reported the single step methane conversion to  $C_5^+$  hydrocarbons over HZSM-5 catalyst when a  $C_3$  additive (propane or propene) is present in the feed.

There is very little information available on the kinetic study of methane in the presence of co-feeding to  $C_5^+$  hydrocarbons. Finally, in Chapter 8, kinetic study of methane conversion in the presence of co-feedings methanol and ethylene to produce higher hydrocarbons in the gasoline range were conducted over W/HZSM-5 catalyst. The reaction was conducted in a fixed-bed reactor at the temperature range of 973 to 1073 K. The kinetic model was proposed based on the mechanism of the

reaction. And, the reaction parameters such as the rate constant, the activation energy, and the adsorption constants were determined.

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