

CHAPTER I

INTRODUCTION

1.1 Why MTO Processes?

Presently, the rapid growth up of the petrochemical industry becomes necessary to subsist human life because most of the products are produced from petrochemical substance, especially light olefins. A large increase in demand for ethylene and propylene is predicted for the future. Most of light olefins are obtained from thermal cracking of naphtha consisting of C_5 - C_{12} alkanes.¹ This is a very energy consuming and costly process. Accordingly, a number of investigations to produce light olefins from other sources have been studied. It was found that, the methanol conversion to olefins on a catalyst is an attractive process to produce light olefins.

Nowadays, a catalyst is an important factor in petrochemical industry, which diminishes the cost of a process and increases the yield of products. Zeolites were used as catalysts in petrochemical industry because of their properties, such as shape and size selectivity, high surface area, strong acidity and their nature as heterogeneous catalysts. However, there is a serious problem, coke deposition, which leads to rapid deactivation of catalysts. ZSM-5 zeolite having MFI structure becomes attractive, as its three-dimensional pore structure is considered to be responsible for its long life as catalyst and slow deactivation rate by coke.²

ZSM-5 zeolite is a microporous aluminosilicate material. The aluminum ingredient in the MFI structure is responsible for the formation of strong acid sites producing more gasoline and aromatics than olefins in methanol conversion to olefins (MTO)³ due to a strong

hydrogen shift function, resulting in valuable intermediate compounds, light olefins. The latter are easily hydrogenated into chemically stable and undesired light paraffinic hydrocarbons. Thus, the decrease of strong acidity of ZSM-5 can be achieved by replacing Al with other transition metals. This results in increasing the yield of light olefins. The methanol conversion to olefins on the resulting material, for example Fe-MFI, produces greater yield of light olefins and no aromatics and its rate of deactivation is slow. Therefore, Fe-MFI was preferred as a new MTO catalyst in order to solve the problem of coke deposited and to increase the yield of light olefins. However, there are quite a few reports on Fe-MFI catalyst for MTO process.

This project aims to study optimum condition for synthesis of Fe-MFI catalyst and their activities in the MTO reaction.

1.2 Objectives

1.2.1 To synthesize and characterize Fe-MFI with various Si/Fe ratios (the Si/Fe ratios in gel of 90, 30 and 10).

1.2.2 To study effects of Na ions, temperature, blank test, Si/Fe ratios and catalyst morphology on methanol conversion to olefins.

1.3 Related work

The Mobil Oil Company reported in 1976 that H-ZSM-5 was a highly efficient catalyst for the conversion of methanol to hydrocarbons. The reaction led to hydrocarbons in gasoline range and was commercialized as the Methanol to Gasoline (MTG) process. In relation to the MTG conversion, the importance of light olefins as intermediates in the conversion of methanol to gasoline, the so-called methanol to olefins (MTO) emerged.^{4,5}

A number of investigations have been made for methanol to olefins over several kinds of mixed feedstock together with several kinds of catalysts, for example using methanol only or mixed with hydrocarbons as reactants and using various molecular sieves as catalyst. Some of the prominent studies and the modified zeolites are reviewed below.

Coupled Methanol Hydrocarbon Cracking (CMHC) with liquid and gaseous hydrocarbons as the co-feed on H-ZSM-5 at high temperatures (400-700°C)^{7,8} was investigated. It was found that the yield of olefins depended on the type of hydrocarbons. An *i*-butene used as the co-feed produced higher conversion of methanol and higher yield of olefins than other hydrocarbons such as *n*-butane, *n*-hexane, cyclohexane, and naphtha because double bond of *i*-butene did not break. Nevertheless, the yield of olefins decreased when time on stream increased because of the deactivation by coke deposited in the pore of a catalyst. In addition, decreasing the reaction temperature and using pure methanol as reactant⁹ led not only to diminish the yield of volatile hydrocarbons, for example olefins, paraffins and aromatics but also to enhancement of the yield of non-volatile hydrocarbons and the amount of coke deposited. Also, %conversion of methanol was affected by temperature, such as it decreased from 99% to 25% when temperature decreased from 290 to 260°C at time on stream of 15 and 200 minutes, respectively.

Although the methanol conversion was carried out widely over various kinds of zeolites, such as the small pore zeolites: chabazite, erionite, zeolite T, ZSM-34, ZK-5,¹⁰ the large pore zeolites: zeolite Y,⁶ zeolite beta,^{11,12} mordenite.¹³ Furthermore, silicoaluminophosphate (SAPO-*n*) type molecular sieves, for example SAPO-17 (ERI), SAPO-18 (AEI), SAPO-34 (CHA), SAPO-35 (LEV),¹⁴ SAPO-11 (AEL),¹⁵ SAPO-5 (AFI), and SAPO-31(ATO)¹⁶ were used as the catalysts in this reaction. ZSM-5 zeolite was well known as a catalyst for converting methanol into hydrocarbons in the gasoline range. A durable activity for this reaction has not been obtained on any zeolite other than ZSM-5 and metallosilicates, which having MFI structure. However, the acid properties of zeolites may also affect the yield of light olefins and the catalyst lifetime in methanol conversion because the reaction proceeds on the acid sites of catalyst.

The methanol conversion on four SAPO-*n* molecular sieves (SAPO-17, SAPO-18, SAPO-34 and SAPO-35)¹⁴ at a weight hourly space velocity, WHSV of 0.5 h⁻¹, the reaction temperature of 400°C was studied. For the time on stream between 10 and 250 min, the selectivity towards C₂-C₄ olefins decreased in order SAPO-34 > SAPO18 > SAPO-17 >>

SAPO-35. Also, the lifetime of catalysts decreased in order: SAPO-18 > SAPO-17 > SAPO-34 >> SAPO-35, while their deactivation rate decreased in order: SAPO-35 >> SAPO-17 > SAPO-34 > SAPO-18. Moreover, selectivities to ethylene and propylene were found as a function of structure type, silica content, chromium location, and chromium concentration in methanol to olefins over SAPO-11, SAPO-34 and SAPO-35 with and without chromium incorporated at a WHSV of 1.25 h^{-1} , and the reaction temperature of 400°C .¹⁵ The deactivation rate decreased in order: SAPO-35 >> SAPO-34 > SAPO-11. The selectivity towards $\text{C}_2\text{-C}_4$ olefins decreased in order: SAPO-34 > SAPO-11 >> SAPO-35. Furthermore, incorporation of chromium into the framework of SAPO-n increased the lifetime and selectivity towards ethylene compared with chromium incorporation by ion exchange. Therefore, SAPO-34 is an attractive catalyst for producing light olefins. The effect of reaction temperatures ($375\text{-}450^\circ\text{C}$) on methanol conversion over SAPO-34 was investigated.¹⁷ It was reported that the selectivity to ethylene increased with increasing reaction temperature, whereas that of propylene and butene slightly decreased. Short-term catalyst deactivation through coke formation also occurred. In addition, the influence of metal incorporation other than silicon and aluminum into the framework of SAPO-34 on methanol conversion was investigated.¹⁸ Using SAPO-34, Fe-SAPO-34, Co-SAPO-34 and Ni-SAPO-34 for the methanol conversion at a gas-hourly space velocity, GHSV, of 1000 h^{-1} , and the temperature of 450°C . The selectivity to ethylene increased in order: Ni-SAPO-34 > Co-SAPO-34 > Fe-SAPO-34 > SAPO-34. Otherwise, the selectivity for all samples decreased with an increase in reaction time, however, the decreasing rate was very slow on Co-SAPO-34 compared with other catalysts. Consequently, the significant improvement of selectivity to ethylene was achieved by the incorporation of Ni into the framework of SAPO-34 (Ni-SAPO-34).^{19,20}

Tsoncheva and Dimitrova²¹ studied methanol conversion to hydrocarbons on aluminosilicates, (amorphous silica-alumina, MCM-41, H-beta and ZSM-5) and metallosilicates (H-B-beta and H-Ti-beta), at a WHSV of 1.5 h^{-1} , and temperatures from 400 to 490°C . For aluminosilicates, the yield of methane and the yield of $\text{C}_2\text{-C}_5$ olefins increased

with increasing the reaction temperature for MCM-41, H-beta and ZSM-5, while amorphous silica-alumina was inactive. Besides, ZSM-5 produced highest the yield of C₂-C₅ olefins. It was explained that the pore system of ZSM-5 improved light olefins formation. In case of metallosilicates, the yield of methane also increased when increasing the reaction temperature for B-beta and Ti-beta. Ti-beta produced high yield of C₂-C₅ olefins, but no C₂-C₅ olefins for B-beta due to the reduced Brønsted acid sites of sample. In addition, H-MCM-41 and Na-MCM-41 (Na⁺ exchanged H-MCM-41) were used as catalysts to study the role of Brønsted acid sites for methanol conversion. It was found that about two times decrease of hydrocarbon amount was observed when a part of Brønsted acid sites was blocked by Na⁺ ions.

Deactivation of H-beta zeolite turned out to be rather fast. Therefore, improvement of the catalyst lifetime in the process of methanol conversion to hydrocarbons was studied using H-beta with various contents of aluminum, obtained by dealumination of the parent sample with oxalic acid.¹² At the reaction temperature of 400°C, dealumination led to catalysts which were more resistant to deactivation than the parent H-beta. In addition, a feed rate was found to have a remarkable influence on conversion of methanol and deactivation rate. The conversion of methanol was high and deactivation rate was slow with increasing the feed rate. Moreover, in order to obtain a long-life zeolite catalyst for conversion of methanol to hydrocarbons, another work used dealuminated H-MOR prepared by leaching with hydrochloric acid at different conditions.¹³ The optimum acid concentration was 8 mol.dm⁻³, producing a significantly prolonged catalyst lifetime. The improvement of the catalyst life was related to the weakening of acid strength by dealumination. In addition, it was found that H-ZSM-5 used in methanol conversion was also subjected to dealumination by water produced during this reaction.²² The catalyst lifetime, however, increased after repeated use in methanol conversion to gasoline cycles. This was attributed to a decreased rate of coke formation in catalyst containing lower densities of acid sites as a result of a repeated use.

Barrer¹⁰ studied the effect of zeolite structure on the yield of olefins for methanol conversion at the reaction temperature of 370°C. The small pore zeolites, ERI, cannot easily

accommodate aromatics and therefore yield mainly lower olefins, while the medium-pore zeolites, ZSM-5 and ZSM-11, produced primary aromatics, light olefins and paraffins and some non-aromatic C_5^+ product, depending on the conversion level. Wide-pore zeolites, ZSM-4 and MOR, gave high yield of heavy aromatics and paraffins. Over the medium-pore zeolites the largest aromatic molecule produced was essentially durene (1,2,4,5-tetramethylbenzene) and although the wide-pore zeolites permitted further alkylation, they also exhibited a high selectivity to coke formation, which resulted in a short catalyst life.

Nowaz *et al.*²³ studied the deactivation of catalysts, such as ZSM-5, Chabazite, and SAPO-34 for methanol conversion to olefins at the temperature of 400°C. It was found that conversion of methanol depended upon time on stream. The very slow deactivation of ZSM-5 was in agreement with the generally known structure of this catalyst. Chabazite, which is isostructural to SAPO-34 (CHA structure), was deactivated much faster than ZSM-5 (10-ring) due to the size of channel 8-ring and 10-ring, respectively. Therefore, ZSM-5 was attractive catalyst to coke resistance.

Methanol conversion to olefins on H-ZSM-5 with Si/Al ratios of 50, 100, 200 and 400 was investigated.²⁴ It was found that a yield of light olefins depended on the Si/Al ratios of ZSM-5, the reaction temperature and partial pressure of methanol. H-ZSM-5 with the Si/Al ratio of 200 produced the highest yield of light olefins at the temperature of 480°C compared to H-ZSM-5 with other Si/Al ratios. The yield of olefins decreased when the reaction temperature decreased from 480 to 320°C. The yield of olefins also increased when the partial pressure of methanol decreased from 1.04 to 0.05 bar. In addition, the synthesis condition of ZSM-5 has an influence on catalytic activity.^{25,26} Rapid and slow crystallization methods for synthesis of ZSM-5 with the Si/Al ratio of 40 were performed and the resulting materials were used as catalysts for methanol conversion to olefins at a GHSV of 1100 h⁻¹, and the reaction temperature of 300°C. It was found that the ZSM-5 prepared by the rapid crystallization method produced more light olefins, and low paraffins and aromatics, than ZSM-5 prepared by the slow crystallization method. Rapid crystallization method increased the catalytic activity for methanol conversion to olefins because Al was more highly dispersed

in the crystals and acid sites were formed more effectively. Moreover, the crystal size of ZSM-5 affected the catalytic activity.²⁷ Increasing in crystal size showed a decreased of conversion of methanol. Besides using ZSM-5 only on methanol conversion, also composite catalysts comprising physical mixtures of the ZSM-5 with group 13 oxides (γ -Al₂O₃, β -Ga₂O₃, In₂O₃ and Ti₂O₃) were used as catalysts.²⁸ At the condition studied at a WHSV of 1.5 h⁻¹, the reaction temperature of 400°C, and the time on stream of 30 min, the composite catalyst comprising γ -Al₂O₃/H-ZSM-5 did not show any difference to the reaction with H-ZSM-5 alone. The addition of β -Ga₂O₃ to H-ZSM-5 significantly enhanced the formation of C₈ and C₉ aromatic hydrocarbons, which were formed by the dimerization and trimerization of the light olefins formed from methanol on the H-ZSM-5 catalysts. Both In₂O₃/H-ZSM-5 and Ti₂O₃/H-ZSM-5 were inactive. At the reaction temperature of 300°C, H-ZSM-5 alone was relatively inactive. Time on stream of 870 minutes was required to produce only trace of methane and C₂-C₃ olefins. Both In₂O₃/H-ZSM-5 and Ti₂O₃/H-ZSM-5 showed a remarkable enhancement in the yield of aromatic hydrocarbons at this temperature.

Inui *et al.*²⁹ studied the methanol conversion on a series of novel metallosilicates, having the MFI structure. The metallosilicates were synthesized by replacing the Al ingredient with various metals, for example Ga, Cr, V, Sc, Ge, Mn, La, Ni, Zr, Ti, Fe, Co, and Pt. The metallosilicates with Si/metal ratio of 3200 were used as catalysts for the methanol conversion at a GHSV 2000 h⁻¹, and the reaction temperature of 300°C. It was shown that Fe-silicate, Co-silicate, and Pt-silicate exhibited the highest selectivity to light olefins and low selectivity to gasoline. Fe-silicate produced aromatics less than other metallosilicates. According to the mechanism of methanol conversion, low activity for the formation of aromatics was very important for obtaining high selectivity to light olefins. Influence of the reaction temperatures (295-370°C) on the methanol conversion on Fe-silicate with the Si/Fe ratio of 3200 was studied as well. It was found that the selectivity to light olefins rapidly increased when the reaction temperature increased from 295 to 320°C, and insignificantly increased when the reaction temperature rose from 320 to 370°C. Moreover, NH₃-TPD profiles of Fe-silicate with Si/Fe of 12 and H-ZSM-5 showed that the acid strength for

Fe-silicate was weaker than H-ZSM-5. In accordance with this change in acid strength, the selectivity to light olefins on Fe-silicate was considerably higher than H-ZSM-5. Furthermore, Fe sources (Fe^{2+} and Fe^{3+}) for synthesis of Fe-silicates affected the crystallinity, acidity and catalytic activity.³⁰ Methanol conversion to hydrocarbons on Fe-silicate (II) and Fe-silicate (III) with the Si/Fe ratio of 12, and Fe-silicate (III) with the Si/Fe ratio of 25 at a GHSV 2000 h^{-1} , the reaction temperature of 300°C was investigated. It was found that %conversion of methanol and selectivity to light olefins increased in the following order: Fe-silicate (III) with the Si/Fe ratio of 25 > Fe-silicate (III) with the Si/Fe ratio of 12 > Fe-silicate (II) with the Si/Fe ratio of 12. The Fe-silicate (II) produced gasoline and aromatics more than the Fe-silicate (III). This is reasonable since the strength of acid sites on the Fe-silicate (II) is higher than that on the Fe-silicate (III).

Martin *et al.*^{2,3} studied methanol conversion to hydrocarbons at a WHSV of 0.8 h^{-1} , the reaction temperature of 400°C , the time on stream of 2 h using H-ZSM-5 with Si/Al ratio of 22, Fe-silicate with Si/Fe ratio of 25 and Fe-ZSM-5 with Si/Al of 50 and Si/Fe ratio of 50 as catalysts. Fe-silicate produced a higher yield of light olefins at high conversion of methanol than the Fe-ZSM-5 and H-ZSM-5 due to the increase in the order of acid strength as followed: Fe-silicate < Fe-ZSM-5 < H-ZSM-5. Thus, Fe-silicate was used as a catalyst for methanol conversion to olefins. The Si/Fe ratios in the catalysts played an important role as well. Fe-silicate with Si/Fe ratio of 30 produced higher yield of light olefins than Fe-silicate with Si/Fe ratios of 150 and 15. Furthermore, the yield of paraffins increased when the Si/Fe ratio decreased. In addition, methanol to hydrocarbons on H-ZSM-5, Fe-ZSM-5, Fe-silicate and Fe^{3+} exchanged H-ZSM-5 at different conditions (a WHSV of 2.9 h^{-1} , and the reaction temperature of 350°C) were also investigated.³¹ For H-ZSM-5 catalysts with the Si/Al ratios of 10, 57 and 104, there were no difference in the selectivity to light olefins though the selectivity to paraffins increased when the Si/Al ratio decreased. For all catalysts investigated, the order of selectivity to light olefins increased as follows: H-ZSM-5 < Fe^{3+} exchange H-ZSM-5 < Fe-silicate < Fe-ZSM-5. Since Fe-silicate produced less selectivity to paraffins, it was an attractive catalyst for methanol conversion to olefins. This was in agreement with

another study using catalysts as H-Fe-silicate with the Si/Fe ratio of 36 and H-Al-ZSM-5 with Si/Al the ratio of 43 at a WHSV of 2.9 h^{-1} , and the reaction temperature of 350°C .³² H-Fe-silicate produced higher yield of light olefins and less yield of paraffins than H-Al-ZSM-5. This was due to the fact that H-Fe-silicate had weaker acidity than H-Al-ZSM-5.



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