

# CHAPTER I

## INTRODUCTION

### 1.1 Background

The porous structures of large-pore molecular sieves can easily host carbonaceous residues, which usually cause catalyst deactivation. The loss of activity by coke formation is rather rapid with mordenite than other zeolite catalysts for methanol conversion to olefins.<sup>1,2</sup> High acid-strength mordenite catalyst is important in methanol conversion to olefins (MTO) and methanol to gasoline (MTG). However, the acid properties of mordenite may also affect the catalyst lifetime in MTO, because the reaction proceeds on the acid sites. The dealumination of zeolites resulted in the increased amounts of the strong acid sites e.g. the improvement in the catalyst lifetime and the decrease in coke formation for MTO reaction. A large pore zeolite such as zeolite beta seems to produce olefins while a medium pore zeolites like H-ZSM-5 produce gasoline from methanol conversion. The olefin products can oligomerize to gasoline if the acid strength of catalyst is in excess, that is the case of ZSM-5. The main problem in the use of MTO catalysts is the rapid deactivation due to coke formation in those catalysts. Large pore zeolites such as mordenite was found to have durable activity due to coke deposited in a small amount. Therefore, this project aims to study how to prepare mordenite catalysts with controllable Si/Al ratios and their activities for the MTO reaction.

### 1.2 Objectives

- To create a precise method of acid leaching for dealumination of mordenite.

- To modify the mordenite catalyst (Si/Al ratio = 11) to various Si/Al ratios.
- To determine the catalytic property of the dealuminated mordenite catalysts for methanol conversion to olefins.

### 1.3 Related Work

Light olefins, *e.g.* ethylene, propylene and butylene are important components for the petrochemical industry, and the demand for high-quality gasoline is increasing as well because the light olefins are starting material for producing polymers, and plastics, as well as manufacturing of fine chemicals. Accordingly, the excessive supplies of olefins have become a serious problem, and the development of new routes for effective utilization of olefins become of great significance. This new route ( $C_1$ -chemistry) can make almost anything out of coal or natural gas that can be made out of crude oil. The new route is the catalyst involving chemistry, which uses synthesis gas (a mixture of carbon monoxide and hydrogen) as the starting material.  $C_1$ -chemistry is a general term for synthesis technology starting from compounds containing one carbon atom such as carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), methanol (CH<sub>3</sub>OH) and methane (CH<sub>4</sub>) from natural gas. Methanol is made from synthesis gas, which is formed, by steam reforming of natural gas or gasification of coal. The methanol is then converted to an equilibrium mixture of methanol, dimethyl ether and water, which can be proceeded catalytically to either gasoline or olefins, depending on the catalyst and/or the process operation conditions.

The catalytic conversion of methanol to lower olefins is a way of converting natural gas and coal to chemicals via methanol, the methanol is one of the major subjects in  $C_1$ -chemistry. The process originates from Mobil's process for converting MTG using the ZSM-5 zeolite as the catalyst, in which olefins were intermediates. Some of the prominent studies and the modified zeolites are reviewed below.

The methanol conversion on the H-ZSM-5 catalyst was studied at temperature 400-680°C.<sup>3-5</sup> At higher end of this temperature range, the methanol was converted completely. The amounts of carbon monoxide, hydrogen and methane increased. The light

olefin was decreased rapidly due to the increase of the coke amount. Recently, metal-ion-containing zeolites (e.g. containing gallium, vanadium, manganese, nickel and iron) with pentasil pore structure have been assumed to be potential catalysts for methanol transformation into olefins with both high selectivity and long lifetime but the catalytic activity was greatly decreased because of the reduction of acid strength. Hence, comparisons between H-ZSM-5, Fe-ZSM-5, and Al-Fe-ZSM-5 catalysts were compared in their activity for methanol conversion at 400°C. The conversion of methanol was nearly 100%. The olefin yields were the highest for MTO over Fe-ZSM-5.<sup>4</sup> The amount of paraffins increased with increasing aluminum content in the catalyst, while the amount of olefins decreased. H-ZSM-5 gave lower conversion of methanol and higher yield in liquid hydrocarbons. Increasing time on stream of reaction, coke formation on Fe-ZSM-5 was decreased because Fe-ZSM-5 has acidity lower than H-ZSM-5 does. In addition, it is reported that coupled methanol-hydrocarbon cracking (CMHC) could be carried out simultaneously on the same catalyst and under the same reaction condition. Pure hydrocarbons (*n*-butylene, isobutylene, *n*-decane, *n*-hexane, cyclohexane and isobutylene-*n*-butylene fraction from pyrolysis gases) and methanol were used as feed for this reaction, the optimum ratio was 1:3. The production of olefins depended on the type of hydrocarbon as co-feed, especially with the butylene or olefin mixture giving a better olefins yield and higher methanol conversion. One reason for the higher methanol conversion could be the existence of double bonds in the feed, which weakens the neighboring C-C and C-H bonds. There was a prolongation of the reaction time, resulting in decreasing of olefins because the formation of coke increased in pore zeolite. The problem of coke formation was given rise from using high temperature reaction. The MTG on H-ZSM-5 was studied also at low temperatures (260-290°C).<sup>6</sup> At 260°C, maximum conversion of methanol was 25% in 200 minutes, but at higher temperature (290°C) that was 99% in 15 minutes and the formation of coke was less. The volatile product hydrocarbons (e.g. paraffins, olefins, aromatics and methane) were less in amount at higher temperature because the polynuclear or coke-like materials in the pores of H-ZSM-5 were not decomposed at these ranges of temperatures.

The conversions of methanol to hydrocarbons catalyzed by the physical mixtures of the zeolite H-ZSM-5 with group-13 oxide ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, Tl<sub>2</sub>O) were reported.<sup>7-9</sup> Comparing to using H-ZSM-5 alone at  $\geq 400^\circ\text{C}$ , the addition of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has no effect whereas the addition of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> gave a fantastic enhancement in the yield of C<sub>8</sub> and C<sub>9</sub> aromatic compounds, at the expense of C<sub>2</sub>-C<sub>4</sub> olefins, without affecting the overall conversion. Both the In<sub>2</sub>O<sub>3</sub>/H-ZSM-5 and Tl<sub>2</sub>O/H-ZSM-5 were inactive. At 300°C, a remarkable enhancement in the yield of aromatic hydrocarbons was observed for the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> or In<sub>2</sub>O<sub>3</sub> addition. Less enhancement was observed for the Tl<sub>2</sub>O and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> presence. In particular, the In<sub>2</sub>O<sub>3</sub>/H-ZSM-5 mixture gave a significant enhancement in catalyst activity at 300°C. Ga<sub>2</sub>O<sub>3</sub> was also significantly enhanced the catalytic activity of a WO<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst when it was mixed with the WO<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. The results were explained in terms of a new active site that was formed at the point of contact of Ga<sub>2</sub>O<sub>3</sub> and H-ZSM-5 or WO<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles. In the case of H-ZSM-5/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, this new site catalyzes the formation of aromatic products from C<sub>2</sub>-C<sub>5</sub> olefins, whereas for WO<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>: $\beta$ -Ga<sub>2</sub>O<sub>3</sub> the new site catalyzes the formation of methane. In addition, the deposition of WO<sub>3</sub> on H-ZSM-5 (by metal oxide vapor synthesis methodology) and pure H-ZSM-5 were tested for their catalytic activity in the reaction at 500°C for 1 h.<sup>9</sup> When the activity was compared at equal conversion levels of methanol, the temperature for formation of hydrocarbons was higher over WO<sub>3</sub>/H-ZSM-5 catalyst than the pure support. Among the products formed over WO<sub>3</sub>/H-ZSM-5, selectivity of olefins was higher than that of paraffins. The H-ZSM-5 catalyst gave aromatic products because its surface contained strong acid sites while the WO<sub>3</sub>/H-ZSM-5 catalyst contained weak acid sites. Hybrid catalysts (CuZnZrO<sub>2</sub>/H-ZSM-5 and CuZnZrO<sub>2</sub>/SAPO-34) were studied for the methanol conversion through CO<sub>2</sub> hydrogenation at 400°C.<sup>10</sup> For the SAPO-34 hybrid system, C<sub>3</sub> hydrocarbons were major products. In the case of H-ZSM-5 hybrid system, however, the main hydrocarbon was ethane and neither higher hydrocarbons nor aromatics were formed.

Zeolite ZSM-5 was well known as a catalyst for converting methanol into hydrocarbons in the gasoline range. The methanol conversion was carried out widely over various kinds of zeolites such as the small pore zeolites: erionite, zeolite T, ZSM-45, ZSM-12, the large pore zeolites: zeolite Y,<sup>11,12</sup> zeolite beta,<sup>11-13</sup> mordenite.<sup>11,14-16</sup> However, the reaction was also carried out on the silico-alumino-phosphate (SAPO) molecular sieves, they are a new generation of crystalline materials; for example, SAPO-34,<sup>17-30</sup> SAPO-11,<sup>19,23,24,31</sup> SAPO-5,<sup>23,31</sup> SAPO-44.<sup>32</sup> A durable activity for this reaction has not been obtained on any zeolite other than ZSM-5 and pantasil metallosilicates. However, the acid properties of zeolites may also affect the catalyst lifetime in methanol conversion, because the reaction proceeds on the acid sites.

SAPO molecular sieves, with their mild acidity (weaker than H-ZSM-5), are very interesting alternatives to obtain high selectivity for light olefins. The performance of different small pore SAPO-type catalysts in the MTO process was influenced by their framework structure, such as chabazite-like SAPO-34, erionite-like SAPO-17, levyne-like SAPO-35 and SAPO-18. SAPO-34 showed the highest selectivity toward formation of C<sub>2</sub>-C<sub>4</sub> olefins,<sup>17-19,23-25</sup> because of its highest acidity among the SAPO series (SAPO-34 > SAPO-18 > SAPO-17 > SAPO-5) as well as the shape selectivity of its eight-member ring pore aperture. SAPO-5 having larger pore than SAPO-34 facilitated the production of C<sub>4</sub>-C<sub>7</sub> olefins with the presence of branched hydrocarbons and a very small amount of aromatics.<sup>23</sup> SAPO-11 (medium pore and acidity is lower than SAPO-34 and SAPO-5) favored the formation of aromatics, C<sub>5</sub> and C<sub>6</sub> hydrocarbons<sup>23,24</sup> but SAPO-11 showed the highest lifetime for catalytic activity compared with SAPO-34 and SAPO-5.<sup>19,23</sup> Furthermore, the incorporation of transition-metal ions into framework sites of SAPO molecular sieves is also interesting for the design of novel catalysts. Transition-metal-substituted SAPO catalysts, such as M-SAPO-34 (M = Ni, Co, Cr, Fe),<sup>17-22</sup> M-SAPO-18 (M = Ni, Mg, Zn),<sup>17,33</sup> M-SAPO-35 (M = Ni, Cr),<sup>17,19</sup> Ni-SAPO-11,<sup>17</sup> and Ni-SAPO-17,<sup>17</sup> had been investigated for MTO reaction. The methanol conversion on these catalysts, the selectivity to C<sub>2</sub>-C<sub>4</sub> olefins (as to ethylene) and the lifetime were enhanced compared with the non-metal loading

material because of M-SAPO catalysts exhibited lower acidity and acid sites compared with the non-metal loading catalyst. The highest selectivity to ethylene was obtained using Ni-SAPO-34 as the catalyst.<sup>17,18</sup>

MFI type and SAPO type catalysts were used for methanol conversion reaction to compare the hydrocarbon distribution of the products.<sup>10</sup> For MFI type catalysts such as H-ZSM-5 or H-Ga-silicate, the main products were higher hydrocarbons such as aromatics and C<sub>5</sub>+ hydrocarbon. For SAPO-34 and SAPO-5, the main product was C<sub>2</sub>+C<sub>3</sub> and C<sub>4</sub> hydrocarbon, respectively. The selectivity toward C<sub>2</sub>-C<sub>4</sub> olefins decreased in the order: SAPO-34 > SAPO-5 > H-Ga-silicate > H-ZSM-5. Above 300°C, dimethyl ether was formed as the main product<sup>30</sup> and no significant yields of methane were obtained from the methanol conversion catalyzed by amorphous silica-alumina and H-MCM-41. Methane and olefins were mainly obtained on the H-beta catalyst. On contrary, predominantly olefins and negligible amount of methane were formed using H-ZSM-5 as the catalyst. A considerable increase of methane in the order: H-ZSM-5 < H-beta < H-MCM-41 was obtained, despite of the intimate acidity of the aluminosilicate structures.

The methanol conversion to hydrocarbons over zeolite H-beta (Si/Al = 13)<sup>11</sup> was studied at two different feed rates: weight-hourly space velocity (WHSV) of 0.8 and 7.2 h<sup>-1</sup>. In the case of the low feed rate, the conversion at 400°C was complete after a very long period. The initial conversion was lower and the catalyst was deactivated in a much shorter time than those at the high feed rate. In addition, mordenite (Si/Al = 52) and H-ZSM-5 (Si/Al = 45) were also studied similarly. The mordenite catalyst exhibited a lower initial activity than the other two catalysts, however the deactivation rate is slow compared to H-beta. The H-ZSM-5 catalyst exhibited a remarkable resistance to deactivation and no change in effluent composition. The C<sub>2</sub>/C<sub>3</sub> product ratio on the H-beta was not far from 1 but on the mordenite it was above 10 after moderate deactivation. The behavior of H-ZSM-5 is moderate, with the C<sub>2</sub>/C<sub>3</sub> ratio of about 2.5. The methanol conversion to multi-branched-chain alipatics was studied at 350°C on HY (Si/Al = 2.4), H-ZSM-5 (Si/Al = 12.5), and H-MOR (Si/Al = 7.5).<sup>1</sup> The comparison of the acid strength was H-MOR > HY > H-ZSM-5.

The methanol conversion was H-MOR (62.3%) > HY (54.6%) > H-ZSM-5 (40.3%) but the deposition of coke was significant on H-MOR. H-MOR was modified by dealumination (D-MOR), or dealumination and subsequently 33% Na ion-exchanged (NaD-MOR).<sup>1</sup> The methanol conversion was decreased on modified mordenite catalysts but the amounts of coke deposited on D-MOR (12%) and NaD-MOR (2.5%) were much less than that on H-MOR (26.4%). However, Na-MOR (fully Na-ion exchanged mordenite) which is generally inactive for methanol conversion, exhibited some catalytic activity in this reaction. The product distributions were related to the catalyst lifetime in methanol conversion. Light (C<sub>1</sub>-C<sub>4</sub>) hydrocarbons, olefins and alkanes, were abundant on the short-lifetime mordenite (lower Si/Al ratio), whereas light olefins were increased on the long-lifetime mordenite (higher Si/Al ratio). The rate of coke formation for the MTO reactions was decreased and the catalyst lifetime was increased with reduction in aluminum content.



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