

## CHAPTER II

### LITERATURE REVIEWS

Since Mobil's announcement of MTG process [6] based on ZSM-5 zeolite [7], a lot of laboratory has been developed. Some of the more prominent studied on modified catalysts and the process performance are summarized below.

The conversion of methanol over ZSM-5 zeolites was investigated by Chang and Silverstri who found the general reaction path. This reaction path has been confirmed in general by many workers. And also Change. et al. found that olefin formation could be decoupled from aromatization via a combination of high temperature and low catalyst acidity [8].

Yingjie Jin et al [9] studied synthesis of liquefied petroleum gas (LPG) via methanol/dimethyl ether (DME) from natural gas. Acidic zeolite-based catalysts with small-, medium- or large-pore sizes were tested for selectively converting methanol/DME to LPG fraction, C<sub>3</sub> and C<sub>4</sub> hydrocarbons. Though small pore SAPO-34-base catalyst selectivity promotes the formation of C<sub>1</sub>-C<sub>3</sub> hydrocarbon with higher C<sub>2</sub> and C<sub>3</sub> hydrocarbons and the large C<sub>4</sub> and C<sub>5</sub> species are not observed and methanation occurs obviously. SAPO-34 with chabazite structure prohibits the formation of C<sub>4</sub> and C<sub>5</sub> hydrocarbons. SAPO-5 and Beta catalyst form much more C<sub>4</sub>-rich hydrocarbons. The medium-pore ZSM-5 catalyst offers the highest yield and selectivity for LPG fractions and the least selectivity for total by-product of C<sub>5</sub>+ nonaromatic and the aromatic among the catalysts tested. Medium-pore zeolite ZSM-5 with around 50 of silica to alumina was clarified to be one of the potential catalysts for that conversion.

C.D.Chang et al [6] studied the effect of increasing the temperature on the product distribution in the methanol-to-hydrocarbons reaction using H-ZSM-5. At higher temperatures, the olefin formation is favored with respect to the formation of aromatics. The effect of increasing the temperature over the same range of partial pressures of olefins is to shift the distribution towards the lower olefins.

Wang et al studied [10] the effect of acidity of H/ZSM-5 type zeolite on conversion of alkene and alkanes to gasoline and aromatic. Conversion and product distribution depended closely on the acid strength distribution and the reaction chain length. Normal-paraffin were much less reaction than olefin over the relatively weaker acid sites.

Taylor et al. [11] reported the dimethyl ether converted to propylene using a shape-selective H-ZSM-5 catalyst. Very high selectivity towards propylene can be achieved by using this catalyst at appropriate reaction and feed conditions. In general, higher temperatures, low partial pressures of dimethyl ether in the feed, and short contact times used over a H-ZSM-5 catalyst with low acidity increase the selectivity of dimethyl ether conversion to propylene by inhibiting competing as well as successive reactions which would otherwise form other olefins, paraffin and aromatics.

Tian-Sheng Zhao et al [12] studied the direct synthesis of propylene and light olefin from dimethyl ether catalyzed by modified H-ZSM-5. The H-ZSM-5 modified by  $ZrO_2$  and  $H_3PO_4$  possessed the adjusted acid properties, which were the enhanced acid site density but partly weaker acid intensity compared with H-ZSM-5, and displayed a high catalytic activity of converting DME to propylene while the selectivity of the lighter olefins was about 64%. Furthermore, the modified H-ZSM-5 maintained the shape-selective micropores even if the slight shrink occurred after the modification, which constrained larger hydrocarbons formation.

Yuchuan Fu et al [13] studied acidity and the dehydration of methanol to dimethyl ether. Among the solids used for methanol dehydration, H-ZSM-5 and  $\gamma-Al_2O_3$  are the two catalysts that have been studied. Although the DME selectivity is

high for methanol dehydration on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> exhibits much lower activity than that of H/ZSM-5. H/ZSM-5 was observed that the catalyst was seriously coked after the reaction at 553 K. The strong surface acidity of H/ZSM-5 catalyzed the conversion of methanol to hydrocarbons and caused serious coking.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> possessed strong Lewis acidity, but exhibited low activity for the dehydration of methanol, probably because water was preferentially adsorbed on the Lewis acid sites and poisoned the strong Lewis acidity under the reaction condition where the water was an inevitable product. The activities follow the order of H/ZSM-5 > SDY > Ti(SO<sub>4</sub>)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> >  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Micheal Stocker [14] reported the pentasil-type zeolite ZSM-5 has been the candidate among the medium-pore zeolites to be investigated as catalyst for the methanol to hydrocarbon reaction. Several major advantages of ZSM-5 when compared with other zeolite are its high resistance to deactivation by coke formation, high olefin yield, high olefin selectivity, low aromatics selectivity, high hydrothermal stability. The effect of space time on the methanol conversion and the hydrocarbon distribution clearly demonstrates that C<sub>2</sub>-C<sub>4</sub> olefins are intermediates in the MTG reaction. The yield of light olefin increases with space time. An important feature of methanol to hydrocarbons reaction on ZSM-5 is that a further increase of space time results in a continuing change of the hydrocarbon distribution, although the conversion is complete. The effect of increase temperature on the product distribution in the methanol to hydrocarbons reaction using H/ZSM-5 is similar to increasing the space time at a constant temperature. At high temperatures, the olefin formation is favored with respect to the formation of aromatic. H/ZSM-5 catalysts with varying Si/Al ratios showed that the maximum in the yield of intermediate light olefins shifted towards higher methanol conversion with increasing Si/Al. The effect of the Si/Al ratio on the coke formation on ZSM-5 zeolites in the methanol reaction was observed with decreasing Si/Al ratio. The amount of coke deposited on the zeolite after the reaction increased with decreasing crystal sizes. The rate of coke formation was independent in the crystal size. At complete conversion of methanol, the selectivity towards olefins on the various metal substituted ZSM-5 zeolites varied as followed: Ga = Cr < V < Ge < Mn < La = Al < Ni < Zr = Ti < Fe < Co = Pt. It was clear that ZSM-5 substituted with Fe, Co and Pt revealed the highest selectivity in the formation

of light olefins. One of the major advantages of ZSM-5 when compared with other zeolites is its high resistance to deactivation by coke formation. It was early recognized that intracrystalline coke formation on zeolites is a shape-selective reaction, directly related to the pore structure. By comparing coke formation on ZSM-5 and mordenite in the methanol conversion it was clearly demonstrated that the low selectivity towards coke formation on ZSM-5 must arise from structural constraints on the reaction of the same intermediates of coke.

T. Armaroli et al [15] studied the effect of crystal size and Si/Al ratio on the surface properties of H/ZSM-5 zeolites. Highly crystalline H-ZSM-5 zeolite samples with crystal size from 0.5-5  $\mu\text{m}$  and Si/Al ratios ranging from 20 to 70 have been prepared and characterized. The large particle size samples show the same external structures than low particle size samples and also the internal bridging OH groups, at the origin of the Brønsted acidity of the zeolites, appear to have a similar behavior. The samples characterized by a quite low Al content present external surface Lewis sites that means that at least part of Al ions are located at the external surface. The basic structures of the zeolite active site do not depend significantly on the crystal size. Brønsted acid sites of high acid strength are constituted by bridging OH groups located inside the zeolite channels, while Lewis acid sites and weakly acidic silanol groups are found on the external surface.

C. Chupin et al [16] studied identity and location active species for NO reduction by  $\text{CH}_4$  over Co-ZSM-5. Co-ZSM-5 of varying exchange degree was prepared by ion-exchange of H-ZSM-5 with cobalt acetate. Three different Co species were observed (i)  $\text{Co}^{2+}$  cations located at  $\alpha$  (along the wall of channels) and  $\beta$  (at the insertion of channels) sites in the zeolite channels. Cations are preferentially located at  $\alpha$  sites on the wall of channels is larger than the  $\beta$  sites. (ii) micro aggregates composed of cobalt and oxygen. The micro aggregates are mostly likely located inside the zeolite cage (diameter of about 8-9 Å). (iii) Cobalt oxide particle of type CoO and  $\text{Co}_3\text{O}_4$  including cobalt silicate for overexchange sample.

B. Lilliana et al [17] reported the preparation and characterization and characterization of a Co-microporous zeolite matrix with MFI structure by wet

impregnation. They have been able to identify some of cobalt species present in Co-ZSM-5 calcined and reduced materials. After calcinations, Co-zeolites contain  $\text{Co}_3\text{O}_4$  and  $\text{Co}^{2+}$  located at exchange positions.

D Chen et al [18] studied the effect of intracrystalline diffusion on the conversion of methanol to olefin over SAPO-34. Three types of shape selectivity could possibly be important for reaction catalysts. One type is due to the large differences in diffusivities of the various sized reaction products in the intracrystalline channel, and is termed "configurational diffusion-controlled selectivity". The second type is based on the principle of molecular exclusion. The third type is based on the difference in size and structures of reaction intermediates, resulting in different degrees of difficulty in accommodating them in the intracrystalline catalyst cavities, and is known as "transition-state shape selectivity". Transition-state selectivity depends only on the zeolite structure and the pore diameter. Configurationally diffusion-controlled selectivity is usually sensitive to the channel diameter and the crystal size.