CHAPTER II

LITERATURE REVIEWS

Since Mobil's announcement of the MTG process [10] based on ZSM-5 zeolite [11], a lot of laboratory has been developed. Some of the more prominent studied and the modified zeolites are summarized below.

The conversion of methanol over ZSM-5 zeolites was investigated by Chang and Silvestri [1] who found the general reaction path. This reaction path has been confirmed in general by many workers [12-15].

Methanol conversion over a variety of small pore zeolites has been reported by Chang et al. [16]. At 339-538 $^{\circ}$C the products, restricted largely to the C_2-C_4 range, were mainly olefins. The presence of significant amounts of methane on some experiments is symptomatic of coke laydown.

The conversion of methanol to light olefins over various cation-exchanged chabazites has been investigated by Cobb et al.[17] and Singh et al. [18,19]. Both teams of investigators observed short-term catalyst deactivation due to coking, but found the catalyst to be regenerable. Cobb et al. observed long-term irreversible deactivation, which was attributed to structural degradation, based on drastic changes observed in the x-ray pattern. This was disputed by Singh et al., who saw no such deactivation in a three month study comprising 21 regenerative cycles. It was speculated that the discrepancy may have been due to differences in ion-exchange procedures.

Singh et al. contended that their method of preparation led to an "ultrastavle form of chabazite".

Wunder and Leupold [20] report that selectivity to ethene and propene is significantly enhanced over a mixture of chabazite and erionite when these zeolites are Mn-exchanged. A methanol/water mixture (30 vol.% H_2O) was reacted at 400 °C. The product was 66.3% C_2-C_4 olefins.

Whittam and Spencer [21] report that "zeolite MCH", which has an x-ray pattern similar to herschelite (isostructural with chabazite) but with line broadening due to small crystal size, is active for converting methanol to C_2-C_6 hydrocarbons at 300-550 °C. The product consists mainly of ethene(16.6 vol.%), propene (41.2%), and propane (22.4%).

Inui et al. [22,23] synthesized an erionite-offretite catalyst by rapid crystallization in the presence of tetramethylammonium hydroxide. Methanol (12% in N_2) was reacted over the calcined (540 °C) material at 400 °C,GHSV 1000 h^{-1} and gave ethane (25 mol%), propene (32.7 mol%), butene (19.2 mol%), methane (4.6 mol%),propane (6.4 mol%),and C^{5+}(7.5 mol%)at complete conversion.

The influence of acid strength of the protonic sites in zeolite Y on dimethylether conversion at 350 °C was investigated by Cormerais et. al. [24]. A series of zeolites containing varying concentrations of Na and K ions was prepared. The acid strengths were determined by pyridine adsorption-desorption at different temperatures. It was found that dimethylether reacted only when the total number of Na and K ions per unit cell was less than 16.4, and that the active sites must be of sufficient strength to retain pyridine at temperatures at least as high as 450 °C.

The catalytic dehydration of methanol by synthetic H-mordenite was studied by Swebb and Gates [25] at 99.5-240 °C . Olefins were detected at 240 °C; however, deactivation was rapid.

Natural mordenite, exchanged with various cations, was found by Zatorski and Krzyzanowski [26] to be highly active for methanol conversion

to C_1 -C_5 hydrocarbons at 350-500 °C, but to have a short life-time.

Mordenite and ZSM-4 were investigated by Chang et al. [27] for methanol conversion. Included for comparison are results from small pore erionite and intermediate pore ZSM-5 and ZSM-11.

Chang and Silvestri [1] report that olefins are intermediates in the conversion of methanol to aromatic hydrocarbons over zeolites. And also Chang et al.[28] found that olefin formation can be decoupled from aromatization via a combination of high temperature and low catalyst acidity.

Wu and Kaeding [29] report that ethylene was the major primary hydrocarbon produced from methanol at low conversion. The olefin mixtures isolated under various conditions of reaction were fitted to the chain-growth kinetics as described by the Flory equation. Good to excellent correlation coefficients were found at low and medium conversions of methanol. This is consistent with a stepwise growth in molecular weight of the olefins, starting with propylene, by alkylation of the olefins with methanol.

Inui et al. [30] studied the effects of seed materials on a zeolite and its performance of methanol conversion and found that olefin selectivity and the effective lifespan of zeolite catalysts prepared with seed crystals were increased in comparison to catalysts without seed crystals.

Kaeding and Butter [31] and Vedrine [32] studied catalytic and physical properties of phosphorus-modified ZSM-5 zeolite. Both teams report that phosphorus-modified zeolites gave a higher yield of light olefins ($C_2^=$-$C_4^=$) and subsequently a smaller yield of saturated aliphatics and aromatics than the parent zeolite in the methanol conversion reaction.

Derouane et al. [33] were the first to study the reaction in situ by using ^{13}C NMR of static samples.They observed three very broad signals and derived information on the relative numbers of CH_3-, CH_2-, CH_3-O, etc. groupings.

The effect of reaction conditions has been studied by Chang et al. Aromatization can be suppressed in favor of alkene formation via a combination of high temperature and low catalyst acidity.

Dehertog and Froment [34] report that H-ZSM-5 ion-exchange with Cs^+ did not result in an increased shape selectivity, while phosphorus modification increased the yield of $C_2^=$-$C_4^=$ significantly. At high temperature and low partial pressures of methanol lead to high selectivities towards light alkenes.

The effects of substrate composition, aging time, reaction temperature, and reaction time upon the crystallization of Fe-ZSM-5 were investigated by Kim and Alm [35]. Fe-ZSM-5 catalysts showed high selectivity towards low molecular weight alkenes in the methanol conversion reaction, and para- selectivity in the xylene isomerization reaction.

Effect of magnesium in the conversion of methanol on chryso-zeolite or zeolite ZSM-5 catalysts was studied by Levesque et al.[36]. Chryso-zeolite ZSM-5 catalysts, which were prepared from asbestos fibers, were found to be active and very selective in the conversion of methanol when compared to a "pure" zeolite ZSM-5. The amount of magnesium extracted from the fibers before the zeolite hydrothermal synthesis influenced the particle size, the selectivity and particularly the adsorption/desorption properties of the catalysts. The presence of a basic site generated by the magnesium led to catalysts with controlled selectivity and activity under normal reaction conditions.

Ikai et al. [37] studied H-ZSM-5 pelletized and modified with α -$Ca_3(PO_4)_2$ and HPO_4^{2-} as a catalyst for methanol conversion. The catalyst life was significantly longer than that of the parent HZSM-5 in the conversion of methanol to light olefins at high temperatures . The modification decreased catalyst deactivation due to both coking and dealumination. The

α-Ca$_3$(PO$_4$)$_2$ and non-stoichiometric hydroxyapatite transformed from α-Ca$_3$(PO$_4$)$_2$ were considered to reduce the acid sites on the external surface of HZSM-5 crystals and to supply HPO$_4^{2-}$ gradually, resulting in extension of the catalyst life.

Wang et al.[38] studied the effect of acidity of H-ZSM-5 type zeolite on conversion of alkenes and alkanes to gasoline and aromatics. Conversion and product distribution depend closely on the acid strength distribution and the reactant chain length. n-Paraffins are much less reactive than -olefins over the relatively weaker acid sites, but reactivity is enhanced by small amounts of olefins. α-Olefins always show much higher reactivity, and give more C$_5^+$, gasoline product with higher aromatics content than n-paraffins. It is concluded that zeolite with moderate acid strength is preferred for upgrading of C$_3$ to C$_{10}$ aliphatics to high-octane gasoline.

Kaliaguine et al. and Jean [39] studied chemical modification of H-ZSM-5 by adsorption of rhodium and phosphorus complexes. Phosphorus was shown to be responsible for very efficient poisoning of Bronsted acid sites irrespective of the presence or absence of rhodium. The metallic surface was found to be associated with the reactions of methanol decomposition and possibly methanation of carbon monoxide by hydrogen.

Martin et al. [40] studied coupled conversion of methanol and C$_4$ hydrocarbon to lower olefins over H-ZSM-5 zeolites catalyst at temperatures up to 953 K and a WHSV of 3-4 h^{-1}. High yields of approximately 0.6-1.1 kg lower olefins kg cat^{-1} h^{-1} were obtained.

Magnoux et al.[41] studied location of coke formed on hydrogen offretite during n-heptane cracking at 450 $^\circ$C. The deactivation of H-OFF occures through pore blockage of coke content. With a low content the small molecules located in the gmelinite cages occupy about 40% of the volume and block the access of n-heptane to their acid sites whereas with a high

content the highly polyaromatic molecules located on the outer surface block the access of n-heptane to all the inner acid sites.

Wilson et. al. [42-43] studied a new class of microporous inorganic solids. The novel aluminophosphate molecular sieves have been synthesized without silica. They were similar to zeolites in some properties. They might find many uses as adsorbents for seperations of molecular sieves and as catalyst supports.

Kaiser[44] disclosed the catalytic use of $AlPO_4$-17 for the interconversion of propylene to ethylene and butenes, of ethylene to propylene and butenes, and of 1-butene to ethylene and propylene.

Garska and Tellis [45] showed that the by-product streams from pyrolytic hydrocarbon cracking processes, containing monolefins and diolefins, can be treated to hydrogenate the olefins and aromatize the aliphatics with aluminophosphates as catalysts.

Lok et. al. [46-47] discovered the new family of silicoalumino-phosphate materials (SAPO-n) containing silicon, aluminum, and phosphorus. The catalytic properties of the SAPO materials on n-butane cracking could be classified as milding acidic, some with unique pore selectivity properties. Otherwise the SAPO materials are substantially more active than aluminophosphates but generally less active than zeolite analoques.

Liang et. al.[48] synthesized and characterized SAPO-34 materials. The catalytic conversion of methanol to lower alkenes was investigated. The resultant H-type catalyst HSAPO-34 was found to be of much higher selectivity and stability than erionite and erionite-offretite zeolites.

Inui et. al. [49] studied the preparation of silico-aluminophosphates within 4 hours of hydrothermal treatment by the rapid crystallization method. The SAPO materials were highly effective for the selective conversion of methanol to light olefins, such as ethene, propene, and butenes. It is shown

that these SAPO were more weakly acidic than typical H-ZSM-5 but more strongly acidic than H-Fe-silicates.

Synthesis of SAPO-41 and SAPO-44 and their performance as acidic catalysts in the conversion of methanol to hydrocarbons was investigated by Chen and Thomas [50]. Crystalline samples of medium pore SAPO-41 and small pore SAPO-44 have been prepared by respectively use of diethylamine and cyclohexylamine as templates. SAPO-44 has larger void volume and stronger framework acidity than SAPO-41. Whereas the product of methanol conversion on SAPO-41 are dominated by dimethylether, the main products on SAPO-44 are ethene and propene. Nevertheless, SAPO-44 is less active than SAPO-34 (which possesses a similar framework structure to SAPO-44) and suffers deactivation in about an hour at 450 $^{\circ}$C.