

CHAPTER II

LITERATURE REVIEWS

Since Mobil's announcement of the MTG process [3] based on ZSM-5 zeolite [4], a lot of laboratory has been developed regarding the influence of several parameters on the catalyst and on the process performance as follow:

The conversion of methanol over ZSM-5 zeolites was investigated by Chang and Silvestri [5] who found the general reaction path. This reaction path was confirmed in general by many workers [6-9].

Rollmann and Walsh [10-12] clearly demonstrated that intracrystalline coking of zeolites was a shape-selective process which was controlled directly by the zeolite pore structure and they investigated the mechanisms which led to coke formation.

Methanol conversion over a variety of small pore zeolites was reported by Chang et al. [13]. At 339-538 °C the products, restricted largely to the C₂-C₄ range, were mainly olefins. The presence of significant amounts of methane on some experiments was symptomatic of coke laydown.

The conversion of methanol to light olefins over various cation-exchanged chabazites was investigated by Cobb et al. [14] and Singh et al. [15,16]. 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 might be due to differences in ion-exchange procedures. Singh et al. contended that their method of preparation led to an "ultrastable form of chabazite".

Ceckiewicz [17,18] studied methanol over the hydrogen form of zeolite T. Coking was rapid and was attributed to the formation of nondesorbable cyclic hydrocarbons in the zeolite supercages.

Wunder and Leupold [19] reported that selectivity to ethene and propene was significantly enhanced over a mixture of chabazite and erionite when these zeolites were Mn-exchanged. A methanol/water mixture (30 vol.% H₂O) was reacted at 400°C. The product was 66.3% C₂-C₄ olefins.

Whittam and Spencer [20] reported that "zeolite MCH", which had an x-ray pattern similar to herschelite (isostructural with chabazite) but with line broadening due to small crystal size, was active for converting methanol to C₂-C₆ hydrocarbons at 300-550 °C. The product consisted mainly of ethene (16.6 vol.%), propene (41.2%), and propane (22.4%).

Inui et al. [21,22] synthesized an erionite-offretite catalyst by rapid crystallization in the presence of tetramethylammonium hydroxide. Methanol (12% in N₂) 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.

Schwartz and Ciric [23] were the first to achieve significant methanol conversion to hydrocarbons over zeolite catalysts. They reacted methanol over REX and ZnX at 330–390 °C. Coke formation was rapid, which might account for the high methane selectivity.

Topchieva et al. [24] studied methanol dehydration to dimethylether over various alkali metal-exchanged X and Y faujasites. Interestingly, the only hydrocarbon they reported (426°C) was 1-butene.

The influence of acid strength of the protonic sites in zeolite Y on dimethylether conversion at 350°C was investigated by Cormerais et al. [25]. 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 had to 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 [26] 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 [27] to be highly active for methanol conversion to C_1 – C_5 hydrocarbons at 350–500 °C, but to have a short life-time.

Catalyst deactivation due to coke deposition was fairly rapid

in small pore and large pore zeolites. The intermediate pore zeolites such as ZSM-5, on the other hand, had a high coke tolerance. Rollmann and Walsh [28] presented evidence that carbon formation in zeolites was a shape-selective reaction controlled by pore geometry. This was confirmed by Cormerais et al. [29] and Tsuruya et al. [30].

Mordenite and ZSM-4 were investigated by Chang et al. [31] for methanol conversion. Included for comparison were results from small pore erionite and intermediate pore ZSM-5 and ZSM-11.

Olson et al. [32] studied chemical and physical properties of a new silica-rich ZSM-5 zeolite that was synthesized with greatly differing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios. ZSM-5 thus constitutes a substitutional series whose physical, chemical, and catalytic properties were reported and discussed in terms of their structural and compositional dependence. Ion-exchange capacity, catalytic activity, and water sorption (at $P/P_0 = 0.006$) were shown to vary linearly with aluminum content and extrapolate smoothly to the end member of the series a pure silica ZSM-5.

Vedrine et al. [32] studied the deposition of carbonaceous residues, leading to aging and modifications in the acidic properties of three zeolite samples differing by the size and shape of their interconnecting channel networks (ZSM-5, offretite, and mordenite), was investigated during the conversion reaction of methanol to hydrocarbons. For zeolites ZSM-5, it was observed that carbonaceous residues were primarily formed on the outer surface of the crystallites, resulting only in a slight modification of its molecular shape-selective properties and producing a high resistance

to aging. For offretite and mordenite, by contrast, the channels were large enough to accommodate carbonaceous residues, which led to a drastic loss of catalytic activity and a very fast aging.

Chang and Silvestri [5] reported that olefins were intermediates in the conversion of methanol to aromatic hydrocarbons over zeolites. And also Chang et al. [34] found that olefin formation could be decoupled from aromatization via a combination of high temperature and low catalyst acidity.

Wu and Kaeding [35] reported 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 was consistent with a stepwise growth in molecular weight of the olefins, starting with propylene, by alkylation of the olefins with methanol.

Inui et al. [36] 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 [37] and Vadrine [38] studied catalytic and physical properties of phosphorus-modified ZSM-5 zeolite. Both teams reported 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. [39] 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^- , $\text{CH}_3\text{-O}$, etc. groupings.

Anderson and Klinowski [40] studied the shape-selective catalytic conversion of methanol into gasoline on zeolite ZSM-5 by using solid state NMR. They found that neither 1,2,3- or 1,3,5-trimethylbenzene was found in the products, but both were presented in the adsorbed phase, which was the first direct experimental demonstration of product selectivity. Tetramethylbenzenes were not found in the products of the reaction at 300°C , but all three were presented in the adsorbed phase in considerable concentrations. At 370°C the shape-selective action was still presented but it was different because of the increased effective channel diameters.

Dehertog and Froment [41] reported that H-ZSM-5 ion-exchange with Cs^+ did not result in an increased shape-selectivity, while phosphorus modification increased the yield of $\text{C}_2^=-\text{C}_4^=$ significantly. At high temperature and low partial pressures of methanol led to high selectivities towards light alkenes.

Comelli and Figoli [42] studied the effect of pressure on the transformation of methanol into hydrocarbons on an amorphous silica-alumina. The increase in pressure (above atmospheric) produced a sharp increase in the production of hydrocarbons with five or more C atoms (C_5^+), an increase in the total aromatics selectivity in the C_5^+ fraction, and a better catalyst stability. Small changes were observed in the selectivity for solid aromatics in the C_5^+ fraction when pressure increased.

Bragin et al. [43] reported in 1974 the successful conversion of ethane into benzene on alumina-supported metal catalysts. The observed activities and better selectivity were reported for ethane aromatization on platinum- or palladium-containing pentasil-like zeolites, again by Bragin and co-workers [44,45]. Metal-containing ZSM-5 zeolites were claimed to be suitable catalysts for the ethane aromatization by Chen et al. [46] in 1981.

Chen and Tsoung described the "M2-Forming" process [47] of the conversion of a C_3 to C_6 hydrocarbon fraction into gasoline rich in aromatics on ZSM-5 type zeolite catalysts.

The actual best results concerning lifetime, selectivity and activity were reported by Inui et al. [48] on propane conversion on a platinum-loaded H-Ga-silicate catalyst and have the model of the working mechanism of a platinum-loaded H-Ga-silicate on the propane to aromatics conversion and the action of hydrogen spillover in the conversion of hydrocarbons on bifunctional catalysts.

Steinberg et al. [49] studied the conversion of ethane into aromatics on Pt/H-ZSM-5 zeolites started at about 670 K and reached its best selectivity at normal pressure and at 600 h^{-1} . The reaction follows a bifunctional mechanism and proceeds via the primary formation of ethene, dehydrocyclization of ethene and consequent reactions of the aromatics formed. Hydrogen, although produced in the reaction, inhibited the complex processes but was necessary to prevent the coking.

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 [50]. 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.

Foger and Jaeger [51] studied redispersion of Pt-Zeolite catalysts with chlorine by using K-L, H-L, silanated H-L, H-ZSM-5 and silicalite as support to treat with chlorine in nitrogen or hydrogen chloride in air at 620 K. They reported that platinum redispersion was found to be linked to the formation of strongly bound platinum (IV) chloride species, which concentrations depended on the aluminium content of the zeolite.

Effect of magnesium in the conversion of methanol on chryso-zeolite or zeolite ZSM-5 catalysts was studied by Levesque et al. [52]. 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. [53] studied H-ZSM-5 pelletized and modified with $\alpha\text{-Ca}_3(\text{PO}_4)_2$ and HPO_4^{2-} as a catalyst for methanol conversion. The catalyst life was significantly longer than that of the parent H-ZSM-5 in the conversion of methanol to light olefins at high temperatures. The modification decreased catalyst deactivation due to both coking and dealumination. The $\alpha\text{-Ca}_3(\text{PO}_4)_2$ and non-

stoichiometric hydroxyapatite transformed from $\alpha\text{-Ca}_3(\text{PO}_4)_2$ were considered to reduce the acid sites on the external surface of H-ZSM-5 crystals and to supply HPO_4^{2-} gradually, resulting in extension of the catalyst life.

Wang et al. [54] 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 depended closely on the acid strength distribution and the reactant chain length. n-Paraffins were much less reactive than α -olefins over the relatively weaker acid sites, but reactivity was enhanced by small amounts of olefins. α -Olefins always showed much higher reactivity, and gave more C_5^+ , gasoline product with higher aromatics content than n-paraffins. It was concluded that zeolite with moderate acid strength was preferred for upgrading of C_3 to C_{10} aliphatics to high-octane gasoline.

Kaliaguine et al. and Jean [55] 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. [56] studied coupled conversion of methanol and C_4 hydrocarbons 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 $0.6\text{-}1.1 \text{ kg}_{\text{lower olefins}} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$ were obtained.

Magnoux et al. [57] studied location of coke formed on

hydrogen offretite during *n*-heptane cracking at 450°C. The deactivation of H-OFF occurred through pore blockage of coke content. With a low content the small molecules located in the gmelinite cages occupied about 40% of the volume and block the access of *n*-heptane to their acid sites whereas with a high content of the highly polyaromatic molecules located on the outer surface block the access of *n*-heptane to all the inner acid sites.



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