



CHAPTER II

LITERATURE REVIEW

Since Mobil's announcement of the MTG process [5] based on ZSM-5 Zeolite [6], 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 [7] who found the general reaction path. This reaction path has been confirmed in general by many workers [8 - 11]. And also Chang. et al. [12] found that olefin formation could be decoupled from aromatization via a combination of high temperature and low catalyst acidity.

Natural mordenite, exchanged with various cations, was found by Zatorski and Krzyzanowski [13] to be highly active for methanol conversion to C₁-C₅ hydrocarbons at 350-500 °C, but to have a short life-time.

Olson et al. [14] studied chemical and physical properties of a new silica-rich ZSM-5 zeolite that was synthesized with greatly differing SiO₂/Al₂O₃ 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/P₀ = 0.006) were shown to vary linearly with aluminum content and extrapolate smoothly to the end member of their series a pure silica ZSM-5.

Kaeding and Butter [15] and Vedrine [16] 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.

Anderson and Klinowshi [17] studied the shape-selective catalytic conversion of methanol into gasoline of zeolite ZSM-5 by using solid state NMR. They found that neither 1,2,3- nor 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.

Comelli and Figoli [18] 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 their selectivity for solid aromatics in the C_5^+ fraction when pressure increased.

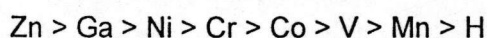
The actual best results concerning lifetime, selectivity and activity were reported by Inui et al. [19] on propane conversion on a platinum-loaded H-Ga-silicate catalyst and have the model of the working mechanism of a platinum-loaded H-Ga-

silicate on the propane to aromatics conversion and the action of hydrogen spillover in the conversion of hydrocarbons on bifunctional catalysts.

Wang et. al[20] 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, 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.

Steinberg et al. [21] 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 effect of ion-exchanged with transition metal for the protons of H-ZSM-5 reported by Inui et. al. [3] The protons of H-ZSM-5 having Si/Al atomic ratio 40 were ion-exchanged with an aqueous solution of various kinds of transition-metal salts. The concentration of the metal exchanged was set at 0.5 wt%, the results of aromatics selectivity increased by :



Matsuda [4] carried out the research methanol conversion and found that the H-Ga-silicates and H Zn-silicates much more aromatics compared with ZSM-5, and the selectivity to aromatics increased with increase of the Ga content. However, the maximum content showed a tendency decrease the selectivity to aromatics with consisted with the decreasing tendency of the strong acid sites.

Anunziata and Pierella [22] studied LPG transformation to aromatic hydrocarbons on Zn_2^+ modified pentasil zeolite. They found the zinc-zeolites (ZSM-5 H-and ZSM-11) increased activity and produced more aromatic hydrocarbons than ZSM with the best BTX selectivity. The primary role of the Zn_2^+ species is in C-H activation and the transformation of the intermediates into aromatic hydrocarbons.

Inui et. al. [23] studied propene-to-aromatic on typical zeolite catalysts; H-ZSM-5, H-Zn-Silicate, platinum ion-exchanged H-Zn-Silicate and H-Pt.Zn-bimetallosilicate. It was found that platinum modified Zn-Silicates, platinum ion-exchanged H-Zn-Silicate and H-Pt.Zn-bimetallosilicate, were the most effective for aromatization of propene and aromatics were obtained with a selectivity of 57 wt.-%. The effect of platinum on the deactivation was found on Pt-modified H-Zn-Silicate, on H-Pt.Zn-bimetallosilicate almost no coke formation was observed. This result was reflected in a duration test for 20 h, in which no significant change in aromatic formation was observed, although a considerable amount of aromatics as precursors of coke was produced.

The effect of Pt loading to H-Ga-Silicate on propane conversion were studied by Inui et al.[24]. They observed that the Pt loading not only enhanced the catalytic activity but also dramatically moderated the catalyst deactivation caused by coke

deposit. The Pt loading also markedly accelerated the combustion rate of coke in the regeneration process. Therefore, the reduction of coke formation and the increase of coke combustion rate were attributed to the effect of spillover in which Pt played the role of porthole for the spillover.

Nagata and Inui [25] reported synthesis and catalytic performance of Fe-Cr bimetallosilicate on propene conversion. On H-type Fe-Cr silicate catalyst, the selectivity to alkenes was high, and the formation of C1-C4 alkanes and aromatic decreased, as compound with the case of H-type Fe-Silicate catalyst. This result is attributed to the weaker acid strength of the strong acid sites in H-type Fe-Cr-silicate catalyst than in H-type Fe-silicate catalyst.



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