

CHAPTER II

LITERATURE REVIEWS

In 1972, Mobil Oil Corp. published zeolite "ZSM-5" that is the catalyst which synthesized gasoline shape-selectively from methanol [20,21]. The investigation of shape-selective zeolite was undertaken in a lot of laboratory. Some of the more prominent studies and the modified zeolite for dehydrogenation and aromatization reactions are summarized below.

Ono et al. [13] studies the reactions of ethane, propane, pentane, and hexane over H-ZSM-5, Ga-ZSM-5, and Zn-ZSM-5 zeolite. In the ethane conversion, zinc cations act as dehydrogenation center for ethane. For other hydrocarbons, the cracking of the starting hydrocarbons on acid center is the first step of the conversion, and metal cations act as catalyst for the dehydrogenation of the olefinic intermediates.

Steinberg et al. [22] studied the conversion of ethane into aromatics on Pt/H-ZSM-5 zeolites starts at 670 K. and reaches its best selectivity at normal pressure and at 600 h⁻¹. They reported the reaction mechanism involves the primary dehydrogenation of ethane to ethene followed by oligomerization and aromatization. Hydrogen, although produced in the reaction, inhibits the complex processes but is necessary to prevent the coking.

Wang et al. [23] studies the effect of acidity of H-ZSM-5 type zeolite on conversion of alkene 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 -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.

Kanai and Kawata [24] also studied coke formation and aging in the conversion of light naphtha into aromatics over galloaluminosilicate (ZSM-5 type zeolite), the acid density of which was controlled by changing the pretreatment temperature of the zeolite and had its maximum at 1053 K. Furthermore, it was found that the acid density of the zeolite decreased, and non-framework gallium species increased, with increasing pretreatment temperature. Thus, it is suggested that the trends in the catalyst life result from: (1) the appropriate combination of the dehydrogenation activity and the acidic activity, (2) the rapid decrease of coke formation with increasing pretreatment temperature, and (3) pore blockage by coke formation inside the crystals.

The kinetics of propane conversion on acidic zeolites were investigated by Bandiera and Taarit [4]. The kinetic measurement were conducted under conditions that ensure the true kinetic rates for dehydrogenation and cracking to be determined.

The ratio of dehydrogenation to cracking rates was shown to be independent of temperature. It was not affected by the acid strength or topology.

Buckles et al. [25] reported propane conversion over zeolite H-Y and Ga³⁺ exchanged zeolite Y. They observed that in the presence of Ga³⁺ the mechanism of propane activation is changed from a cracking pathway to a dehydrogenation pathway.

Bandiera and Taarit [26] studied the hydrogenation and cracking properties of an authentic H(Ga)-MFI. The cracking of propane over the H(Ga)-MFI decreased dramatically in comparison to results obtained over a comparable H(Al)-MFI. Conversely, the dehydrogenation of propane over the H(Ga)-MFI was very much increased. The Bronsted acid sites associated with the framework gallium seem to operate in a similar manner to those associated with framework aluminium in H(Al)-MFI. However, since their strength is attenuated, their greater dehydrogenation activity is ascribed.

Bayense et al. [15] studied the results of propane aromatization over gallium containing HZSM-5 zeolites. It was found that the application of gallosilicates instead of aluminosilicate results in slightly lower conversions of propane but more higher aromatic selectivities. The active sites for dehydrogenation are coordinatively unsaturated gallium species in combination with strong Bronsted acid sites. The deactivation by coke formation is much faster over gallosilicates when compared to the aluminosilicates.

Buckles et al. [14] studied the aromatization of propane on Ga_2O_3 , H-ZSM-5 and $\text{Ga}_2\text{O}_3/\text{H-ZSM-5}$ catalysts. They found that on addition of a gallium phase to H-ZSM-5, the yield of methane is significantly decreased. These results are discussed with respect to the mechanism of formation of the initial reaction product from propane. It is proposed that the synergy observed between the gallium compound and the zeolite can be explained in terms of a mechanism in which the role of the gallium phase is to induce C-H bond polarization in the propane, which leads to attack via the Bronsted acid sites of the zeolite, which leads to initial C-H bond cleavage occurring.

Anunziata and Pierella [17] studied LPG transformation to aromatic hydrocarbons on Zn^{2+} modified pentasil zeolite. They found the activity of zinc-zeolites (ZSM-5 and ZSM-11) increased activity and produced more aromatic hydrocarbons than H-ZSM-5 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.

Fukase et al. (27) reported the electronic and geometric effect of platinum on the catalyst activity and decay in the aromatization of n-pentane over platinum ion-exchanged zinc-aluminosilicate. They found the deactivation of catalyst decreased with increasing density of strong acid sites of the zeolite. Because platinum atoms became more cationic and were located inside the zeolite pores when platinum was loaded onto zeolites with a higher strong acid site density. Platinum atoms were less cationic and tended to migrate to external surface where aggregated when platinum was loaded onto zeolites that had a lower strong acid site density and they assumed to the deactivation of catalyst cause the migration and aggregation of platinum.

Guisnet et al. [16] studied the conversion of ethane, propane, n-butane, isobutane and of the corresponding alkenes at 530 °C on a H-ZSM-5 zeolite (Si/Al = 40). From propane and butanes the primary products result from dehydrogenation and cracking, cracking being more rapid than dehydrogenation. Ethane undergoes mainly dehydrogenation and leads slowly to methane. It is suggested that these reactions occur through scission of carbonium ions formed by alkane protonation. The more stable the carbonium ion the higher the reaction rate. The olefinic primary products undergo very rapid reactions through carbonium ion intermediates : oligomerization, cyclization of the oligomers followed by aromatic formation through hydrogen transfer from naphthenes to light alkenes. Whatever the reactant, the limiting step of aromatization is the initial formation of alkenes.

Wang et al. [9] reported the dehydrogenation and aromatization of methane over modified ZSM-5 by incorporating a metal cation (Mo or Zn). A 100 % selectivity of benzene, conversion being 7.2 %, was obtained at 970 K and pressure 200 kPa.

Inui et al. [28] 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 hr, in which no significant change in aromatic formation was observed, although a considerable amount of aromatics as precursors of coke was produced.

Burch and Crabb [7] studied the pyrolysis and the oxidative dehydrogenation of propane on V/MgO catalysts. It has been found that by optimizing the propane/air ratio. It has been possible to obtain very high yields of propene and ethene. They founded that the maximum to propene at a specific conversion of propane is never higher than can be obtained in the absence of a catalyst. The results also show no obvious correlation between catalytic properties and the presence of specific crystalline phases. It is suggested that lower than optimum selectivities to propene may arise because of the presence in the catalysts of small, but undetected, amounts of pure V_2O_5 .

Wang et al. [12] investigated the conversion of C_3 - C_9 paraffins to small olefins over ZSM-5 zeolite. The small olefins are primary products and are usually converted into other more stable secondary products such as aromatics on the ZSM-5 zeolites. Thermally treated HZSM-5, K/HZSM-5 and Ba/HZSM-5 catalysts were developed and favourable oxidative conditions were introduced for the conversion process to maximize selective conversion of light paraffins to small olefins at the relatively low temperature of 873 K.

The platinum promoting effects in Pt/Ga zeolite catalysts of n-butane aromatization were study by Shpiro et al. [29]. They suggested that the Pt and Ga synergy was also found to increase significantly selectivity to aromatics at the account of rapid dehydrogenation and suppressing such side reactions as hydrogenolysis and hydrogenation (Pt), cracking and isomerization (Ga). Both far distance effects (hydrogen spillover) and intimate contact between Pt particles and reduced Ga(I) ion seem to be responsible for the enhancement of aromatization activity and stability of Pt-Ga zeolite catalysts.

Buckles and Hutchings [11] studied the conversion of propene and aromatic hydrocarbons has been studied using cofed NO, O₂, and H₂ to probe the reaction mechanism with H-ZSM-5 and Ga₂O₃/H-ZSM-5 physical mixtures as catalysts. No co-feeding with H-ZSM-5 causes a decrease in the conversion of propane and in the yields of methane and aromatic products. Although propane conversion decreases, NO does not affect the yield of propene. O₂ co-feeding with H-ZSM-5 leads to an increase in propane conversion, propene yield, and deactivation rate, whereas, as observed with NO, the yields of methane and aromatic products are decreased. Co-feeding of excess H₂, which is a major product from the aromatization of propane, has very little effect on the conversion of propane over H-ZSM-5 although the selectivities to alkanes are increased.

Cheung et al. [30] tested solid acid catalysts, namely sulfated zirconia, iron- and manganese-promoted sulfated zirconia, and USY zeolite for conversion of propane at 1 atm, 200-450 °C, and propane partial pressures in the range 0.01-0.05 atm. Both promoted and unpromoted sulfated zirconia were found to be active for conversion of propane into butanes, pentanes, methane, ethane, ethylene, and propylene in the temperature range 200-350 °C, but catalyst deactivation was rapid. At the higher temperatures, only cracking and dehydrogenation products were observed. In contrast to the zirconia-supported catalysts, USY zeolite was observed to convert propane (into propylene, methane, and ethylene) only at temperature > 400 °C.

A. Sriphusitto [19] studied the conversion of liquefied petroleum gas (LPG) such as propane, butane to aromatic hydrocarbons over MFI-type catalysts containing various metals. It has been shown that zinc and gallium improved both the

activity and selectivity of propane aromatization. He has found that NH_4 -Zn-silicate catalyst exhibited high propylene selectivity from propane but the propane conversion was low.

From the reviews, it was found that Zn cation play the role in C-H activation and act as dehydrogenation center for paraffin. NH_4 -Zn-silicate catalyst exhibited high propylene selectivity but the propane conversion was low. Inui et al. reported that Al in the structure of Zn-silicate will increase the strong acid site that responsible for the higher activity of propane conversion. Thus to investigate this property of Zn,Al-silicate, which has both Zn and Al in structure of MFI type catalysts, these catalysts was prepared by adding zinc sulfate solution in stage of gel formation and synthesizing MFI type catalyst (Al-silicate).



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