

CHAPTER II

LITERATURE REVIEWS

In 1972, Mobil Oil Corp. published zeolite "ZSM-5" that is the catalyst with synthesized gasoline shape-selectivity from methanol [14,15]. The investigation of shape-selective zeolite was undertaken in a lot of laboratory. Some of the more prominent studies and the modified zeolite for aromatization reaction were summarized below.

Bragin et al. [16] reported in 1974 the successful conversion of ethane into benzene on alumina-supported metal catalyst. The observed activities and better selectivity were reported for ethane aromatization on platinum- or palladium-containing pentasil-like zeolite, again by Bragin and co-worker [17,18]. Metal-containing ZSM-5 was claimed to be suitable catalyst for the ethane aromatization by Chen et al. [19] in 1981.

Buckles et al. [20] reported propane conversion over zeolite H-Y and Ga^{3+} exchanged zeolite Y. They observed that in the presence of Ga^{3+} the mechanism of propane activation is changed from a cracking pathway to a dehydrogenation pathway.

The transformation of ethane into aromatic hydrocarbons over Pt/H-Ga-silicate was reported by Inui and co-workers. A 41.5% selectivity for aromatics at the conversion of 14.0% was observed at 773 K [21,22]. Inui et al. also carried out methane conversion over Pt/H-Ga-silicate, A methane conversion of 4.2% was obtained at 973 K [22].

Steinberg et al. [23] studied the conversion of ethane into aromatics on Pt/H-ZSM-5 starting at about 670 K and reaching its best selectivity at normal pressure and at 600 h⁻¹. The reaction follows a bifunctional mechanism and process 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.

Minachev et al. reported that a Ga-containing pentasil zeolite gave a 46% conversion of ethane with a selectivity of 65% at 873 K [24]. Ono and co-worker [25] also studied ethane conversion over H-ZSM-5, Ga-ZSM-5 and Zn-ZSM-5. Over H-ZSM-5, conversion is only 2%, the only product is ethylene, and no aromatic hydrocarbons are found. Over Zn-ZSM-5, total conversion of ethane is 52%, and the yield of ethylene and aromatics are 10% and 31% respectively.

Chen and Tsoung described the “M2-Forming” process [26] of the conversion of a C₃ to C₆ hydrocarbon fraction into gasoline rich in aromatics on ZSM-5 type zeolite catalysts.

Inui et al. [27] reported 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. [28] studied 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 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 C₅⁺, gasoline product with higher

aromatics content than n-paraffins. It was concluded that zeolite with moderate acid strength was preferred for upgrading of C₃ to C₁₀ aliphatics to high octane gasoline.

Maggiore et al. [29] reported the conversion of propane to aromatics over Pt-Ir/ZSM-5, Pt-Re/ZSM-5, Pt-Pb/ZSM-5 and Pt-La/ZSM-5. At 550 °C the selectivity increased by:



Pt-Ir/ZSM-5 is the most selective catalyst, with an aromatic yield obtained at 61.2%.

Scire et al. [30] studied aromatization of propane on Pt-Tl/ZSM-5. A maximum yield of about 70% at 85% conversion has been obtained on the sample with a Tl/Pt ratio of 1. It is suggested that thallium diluted the platinum active sites thus reducing their cracking activity.

Wang et al. [31] reported 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.

The aromatization of propane over MFI-gallosilicates were studied by Bayense et al. [32]. It was found that the application of gallosilicates instead of aluminosilicate results in slightly lower conversions of propane but more higher aromatics 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.

Bayense and van Hooff [33] studied methods to introduce gallium into the zeolite in three different ways; isomorphous substitution of aluminium by gallium, impregnation of H-(Al)ZSM-5 with GaCl₃ or Ga(NO₃)₃ solution, and physically mixing Ga₂O₃ powder with a H-(Al)ZSM-5 zeolite. In all cases, addition of 0.6 Ga/unit cell or

more were enhanced the aromatics selectivity from about 35 C-% to 60 C-%, while the activity remained almost unaffected. A negative side effect was the enhanced rate of deactivation by coke formation, which was most severe for Ga/H-(Al)ZSM-5 catalyst prepared via impregnation or physical mixing, as the gallium is located on the outer surface of the zeolite particles in these samples.

Bucklets et al. [34] 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.

The effect of the hydride-forming intermetallic compound Zr_2Fe on the aromatization of propane over ZSM-5 modified by Zn, Ga or Pt cation has been investigated by Chetina et al. [35]. They showed that the use of an intermetallic compound as hydrogen acceptor I aromatization of propane over modified pentasils gave opportunity to obtain 2 to 5-fold higher aromatic yield coupled with a 1.8-fold higher selectivity of aromatization.

Carli et al. [36] prepared the cocatalyst by supporting gallium oxide on (Ludox colloidal) silica. They found that cocatalyst was capable of creating gallium sites which strongly absorbed hydrogen. Such a transfer which might occur upon drastic reduction and/or by solid-state ion-exchange during the catalyst preparation process, dramatically increased the number of stronger hydrogen chemisorption sites at the "zeolite-cocatalyst" interface. These sites were probably responsible for the high performance in the aromatization of light alkanes of hybrid catalysts.

Yao and Le Van Mao [37] showed that pure alpha-quartz used as co-catalyst can enhanced the aromatization activity of ZSM-5 zeolite. Higher conversion of n-butane and higher production of aromatics and molecular hydrogen are obtained when higher amounts of quartz are embedded within the hybrid catalyst and when the particle size of quartz smaller.

Giannetto et al. [38] reported effect of the calcination temperature on the catalytic properties of [Ga]-ZSM-5 zeolite at two different temperatures: 530 °C (C-530) and 750 °C (C-750). They suggested that C-750 is more active and selective than C-530 for propane aromatization, at 530 °C 1 atm. This is probably due to the fact that at high temperature the decomposition of organic compound used during the zeolite synthesis is accompanied by a partial degallation of the zeolitic support leading to the production of a bifunction catalyst.

Barre et al. [39] studied effect of the hydrogen pretreatment of a mechanical Ga₂O₃/HZSM5 mixture. The activity and selectivity were compare after pretreatment at 873 K under nitrogen and under hydrogen flow. It was thus demonstrated that hydrogen treatment provoked a significant increased in the dehydrogenating activity of the gallium species by only a small decrease in the protonic acidity. Moreover this hydrogen treatment created a significant hydrogenolysis activity.

The effects of co-feeding excess hydrogen on the propane aromatization over Ga₂O₃, H-ZSM-5 and Ga₂O₃/H-ZSM-5 described by Buckles and Hutchings [40]. They suggested for Ga₂O₃ alone co-feeding excess hydrogen gives a significant increase in the conversion and aromatic selectivity. For H-ZSM-5 alone co-feeding excess hydrogen gives a slight decrease in conversion and increase the selectivity to hydrogenated products. For Ga₂O₃/H-ZSM-5 physical mixtures co-feeding excess hydrogen leads to a significant decrease in the conversion and aromatic selectivity. They proposed that hydrogen can be used as a reactive probe molecule for this reaction. Experiments are also described for propane aromatization over physical

mixtures of powdered Ga_2O_3 and pelleted H-ZSM-5 that provide evidence for the reversible formation of the active site for this reaction.

Joly et al.[41] studied parameter affecting the dispersion of the gallium phase of gallium H-MFI aromatization catalyst. They found the dispersion of the gallium phase can be controlled either during the introduction of gallium in the catalyst or by hydrogen activation pretreatment. Incipient wetness impregnation of H-MFI with $\text{Ga}(\text{NO}_3)_3$ solution leads to the highest gallium dispersion compared with “wet” impregnation techniques at various pH. In every case, most of the gallium phase is found to be located closely to the outer surface of the zeolite grains as thin platelets from 5 to 400 nm in average size depending on the gallium introduction mode. Hydrogen activation treatment at 823 K induces gallium migration from gallium platelets to the zeolite micropores leading to a highly dispersed gallium phase located close to the acid sites.

Anunziata and Pierella [42] studied LPG transformation to aromatic hydrocarbons on Zn^{2+} modified pentasil zeolite. They found the zinc-zeolites (ZSM-5 and ZSM-11) increased activity and produced more aromatic hydrocarbons than H-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. [43] 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.

Kanai and Kawata [44] shown the proton forms of galloaluminosilicate and gallosilicate have much activity for the aromatization of n-hexane than Ga^{3+} exchanged H-ZSM-5 or Ga_2O_3 -supported H-ZSM-5. On the other hand, a proton form of gallosilicate exchanged with hydrochloric acid shows lower activity for the aromatization of n-hexane, but the activity of the proton form of gallosilicate is increased by a small addition of Ga^{3+} . It is suggested that the active gallium species over galloaluminosilicate and gallosilicate are not gallium species in the framework but those outside the framework.

Kanai and Kawata [45] also studied coke formation and ageing 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. It was found that the catalyst life depended on 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.

Convert methanol to aromatics on the H-Ga-Silicate were reported by Inui et al. [46]. H-Ga-Silicate exhibited a high performance in aromatization of methanol; i.e., a mixed gas of 20% methanol and 80% nitrogen was fed to the catalyst with a gaseous space velocity of 1000 h^{-1} at $400 \text{ }^\circ\text{C}$, and aromatic were obtained with a selectivity of 73% under 100% methanol conversion.

Waritswat et al. [47] reported methanol conversion to high octane-number gasoline over modified metallosilicate catalysts. It was found H-Fe.Zn-bimetallosilicate containing proper amount of Fe and Zn exhibited better catalytic performance than H-Fe- or H-Zn-monometallosilicate. Furthermore, modification of 0.5 wt% Pt to these H-Fe.Zn bimetallosilicates markedly enhanced aromatization, and still maintained its performance at least 9 h on stream without significant change in selectivity of products.

Fukase et al. [48] reported on 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 atom were less cationic and trended 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.

The effect of Pt loading to H-Ga-Silicate on propane conversion were studied by Inui et al. [49]. 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.

The Platinum promoting effects in Pt/Ga zeolite catalysts of n-butane aromatization were study by Shpiro et al. [50]. 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.