

CHAPTER II LITERATURE REVIEW

2.1 Petrochemicals

Petrochemicals are defined as chemicals, which can be isolated or derived from petroleum or natural gas as the origin. Almost everything used in today's activities have a certain degree of dependence on petrochemicals. The industry depends on two key raw materials categorized as aromatics and olefins.

2.1.1 Aromatics

Aromatics are unsaturated hydrocarbons containing benzene ring in the structure and three key types of aromatics are involved as feedstock for petrochemical industry. Benzene, toluene, and xylene are among aromatic feeds and xylene has three types as para-xylene (p-xylene), meta xylene (m-xylene), and orthoxylene (o-xylene). Other than those aromatics ethyl benzene also another type used as a raw material in the industry. Their structures are presented in Table 2.1.

Table 2.1	Key aromatics	used as petroche	mical feedstock
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Benzene	Toluene	p-xylene	m-xylene	o-xylene	Ethyl benzene
	CH ₃	CH ₃ CH,	CH3 CH3	CH3 CH3	CH ₂ CH ₃

Main products originated from aromatic feedstock are styrene, nylon, resins, pharmaceuticals, polyurethanes, surfactants, etc.

2.1.2 Olefins

Olefins are unsaturated hydrocarbons containing double or triple bond in the carbon backbone and main olefins involve in petrochemical industry are ethylene, propylene, and butylenes. Structures of the key olefins are illustrated in Table 2.2.

Table 2.2 Key olefins used in petrochemical industry

Ethylene	Propylene	α-butylene	β-butylene	Butadiene	Isobutylene
	$ \begin{array}{c} H \\ C = C \\ H \\ H \end{array} $	H ĊH,—ĊH, C=Ċ H H	H ₃ Ċ Ċ=Ċ H	н н 	H C=C H CH ₃

Some products derived from olefin feedstock are polyethylene (PE), Polyvinyl chloride (PVC), polypropylene (PP), alcohols, rubbers, co-polymers, etc.

2.2 Synthesis Gas (Syngas)

Synthesis gas is defined as a mixture having varying compositions of carbon monoxide (CO) and hydrogen (H₂) and the compositions can be varied depending on the origin of syngas. The origins can be coal, natural gas, and other carbon containing materials such as biomass. From natural gas or other liquid hydrocarbons, syngas can be produced by steam reforming while from coal or biomass syngas is produced mainly by gasification.

2.2.1 Steam Reforming

This is reaction between high temperature steam and methane or light hydrocarbon to form hydrogen and carbon monoxide over a metal based catalyst such as nickel (Ni). The reactions are as in following scheme.

$$CH_4 + H_2O \rightarrow CO + 3 H_2$$
 $\Delta H_{298} = -35.65 \text{ kJ/mole}$

Additional hydrogen is produced by water gas shift (WGS) reaction

$$CO + H_2O \rightarrow CO_2 + H_2$$
. $\Delta H_{298} = -283.0 \text{ kJ/mole}$

2.2.2 Gasification

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Gasification is used to produce hydrogen and carbon monoxide mixture from coal, petroleum, organic wastes, or biomass by allowing them to react at high temperature with controlled oxygen or steam. The reactions in the process are as follows,

$C + H_2O$	\rightarrow CO + H ₂	$\Delta H_{298} = -110.5 \text{ kJ/mole}$
$C + O_2$	\rightarrow CO ₂	$\Delta H_{298} = -393.5 \text{ kJ/mole}$
$CO_2 + C$	→ 2CO	$\Delta H_{298} = 172.5 \text{ kJ/mole.}$

Synthesis gas is used as a fuel and especially as an intermediate raw material for different industry. Synthesis gas can be also converted to liquid hydrocarbons or chemicals using technology called Fischer-Tropsch synthesis which was invented in 1920's.

2.3 Fischer – Tropsch Synthesis

Fischer – Tropsch (FT) synthesis is an alternative to natural formation of hydrocarbons in petroleum. Normal way to produce liquid fuels or chemicals with higher molecular weight is refining the naturally occurred petroleum. FT synthesis combines single carbon containing carbon monoxide to form long chain hydrocarbons in hydrogen environment to form hydrocarbons.

2.3.1 Fischer – Tropsch Products

The products from FT synthesis by typical commercial catalysts are typically matched with non-selective Anderson – Schulz – Flory (ASF) distribution limiting the selectivity to required products. However, FeCuK-ZSM5 as a catalyst comparative to mordenite and beta-zeolite supported catalysts gives higher olefin selectivity according to activity and selectivity tests carried out with H₂/CO = 2, T = 300 °C, P = 1.0 MPa and SV = 2,000 ml/g.catalyst.h (Kang *et al.*, 2008). The ASF distribution represents the relation with selectivity and chain growth probability as shown in Figure 2.1 and normally FT synthesis leads to alkane production. The product selectivity is defined for ASF as $W_n = n(1-\alpha)^2 \alpha^{n-1}$ where W_n is weight fraction of hydrocarbon molecules containing n number of carbon atoms and α is the chain growth probability or the probability that a molecule will continue reacting to form a longer chain. Determination of α is largely conducted by the catalyst and the specific process conditions.





The chain growth probability depends on several factors like temperature, H_2/CO ratio, as well as carbon number leading to lower probability when temperature and H_2/CO ratio increase producing lower chain length molecules and hence high methane selectivity. In addition, the change of chain growth probability with carbon number, proposes a deviation from ASF distribution for FT synthesis over Fe-Cu-K catalysts (Ma *et al.*, 1999).

Two main types of products possible are alkanes and alkenes according to the following reactions,

$$n \operatorname{CO} + (2n+1) \operatorname{H}_{2} \xrightarrow{} \operatorname{C}_{n} \operatorname{H}_{2n+2} + n \operatorname{H}_{2} \operatorname{O} \xrightarrow{} (1)$$

$$n \operatorname{CO} + 2n \operatorname{H}_{2} \xrightarrow{} \operatorname{C}_{n} \operatorname{H}_{2n} + n \operatorname{H}_{2} \operatorname{O} \xrightarrow{} (2).$$

First equation represents the production of alkanes and the second represents the alkenes production. Alcoholic products can also be formed either as by-products or as main products depending on the catalytically active metal and the reaction pressure.

A comprehensive kinetic model was proposed by considering all reaction pathways which are possible in FT synthesis and the proposed mechanism is as shown in Figure 2.2. The scheme is matched with what observed over Fe-Mn catalysts (Botao *et al.*, 2007).



Figure 2.2 Reaction mechanism FT synthesis via the CH₂ insertion mechanism (R: $C_{n-1}H_{2n-1}$).

2.3.2 Fischer – Tropsch Catalysis

Several metal-based catalysts have been studied for FT synthesis but only two types were commercially successful. Those two catalysts which are successfully commercialized are iron (Fe) based or cobalt (Co) based. Two types of catalysts have their own advantages and drawbacks.

Co based catalysts promote the yield of mainly straight chain hydrocarbons while Fe based catalysts are more useful when H_2/CO ratio is low due the high water-gas-shift (WGS) activity of Fe or for production of alkenes, oxygenates and branched-hydrocarbons depending on promoters and process conditions (Kang *et al.*, 2010).

Depending on promoting metals in above catalysts, conversion and selectivity can be modified and several attempts have generated successful results to obtain good catalysts. Cu as a promoter has proven in lowering reduction temperature of Fe-oxide in catalysts to Fe metal which is then convert to the active from in FT catalysis and hence lowers sintering which is more prominent at high temperature catalyst reduction. Other metals tested as promoters for bulk Fe catalysts can be identified as Mn, Cr, K, and Pd but all are inferior to Cu due to tendency of forming alloys with Fe and this suggests that there is less chance of desired Fe catalysts are altered by promoters (Kang *et al.*, 2010).

However, a series of research on metal promotion for Fe based FT catalysts has generated significant results. The addition of Cr, Mo, Mn, Ta, V or Zr to Fe-Cu FT catalysts as third metal can be used to improve the catalytic activity for both CO hydrogenation and WGS reactions in varying degrees due to the increased dispersion (Lohitharn *et al.*, 2008). Also addition of Cr, Mn or Zr as third metals to typical precipitated Cu and SiO₂ modified Fe catalysts can be used for improved activity but have less influence on change in selectivity and that increase of activity is due to the increased dispersion (Lohitharn *et al.*, 2008). Further K promotion for Fe and Fe-Mn catalysts also increased the activity at low K concentrations for both CO hydrogenation and WGS reactions but when K content increases the activity declined due to high carbon deposition (Lohitharn *et al.*, 2008).

Further, Fe based FT catalyst with Pt promotion has shown increased activity for FT synthesis due to increase of Fe dispersion. Some change in selectivity

has also been observed leading to suppression of light hydrocarbon and olefin selectivity while increasing the C_{12+} hydrocarbon selectivity (Yu *et al.*, 2008).

In another study, Fe and Co co-catalyst preparation technique has been studied with comprehensive pretreatment for catalyst activation by researches in Exxon Research and Engineering Company. This study shows that powder form of FeCoK catalyst can be synthesized by co-precipitation of Fe and Co salts formed with an alpha hydroxyl carboxylic acid and then introduction of K by impregnation on calcined FeCo catalyst. The work has also given a higher emphasis on proper pretreatment to form Fe and Co carbides which are isostructural to Fe_5C_2 which is the active from of oxide for FT synthesis. The suitable carbiding conditions best for above carbide has been identified as elevated temperatures below 400 °C and preferably between 300 to 400 °C with a mixture of CO and H₂ with 1:1 ratio. In addition, carbiding can also be conducted by reduction with H₂ followed by carbiding with mixture of above carbiding gas mixture or by a single step reduction and carbiding with a mixture of CO and H₂ (Soled *et al.*, 1985).

Ru is also a highly active metal for FT synthesis and commercialization is not possible due to its high cost. Another group of researches has studied the addition of Ru to Fe based FT catalyst to form co-catalyst and Mn promotion on Fe FT catalysts for olefins selectivity enhancement with catalysts prepared by metals supported on γ -alumina. The results show that, addition of Ru to Fe catalyst has shown a significant increase in carbon monoxide conversion from around 2 % to 15 % and decreased the carbon dioxide selectivity from around 65 % to 10% leading to a significant influence (Reaction conditions: H₂/CO = 1, SV 4700 h⁻¹, P = 20 kg/cm² and T = 290 °C). In addition, Fe-Mn-Ru catalyst has shown a stable product distribution for range of temperatures from 230 °C to 320 °C but only Ru shows a drastic increase of methane selectivity with increase of temperature from 230 °C to 320 °C from 10 % to 80 %. Further, addition of Mn to Fe catalyst has shown a significant increase of olefins while having no influence on olefin content in Fe-Ru catalyst with Mn addition (Inui *et al.*, 1990).

Other than activity enhancement, selectivity alterations have also been investigated by different groups to produce chemicals by FT synthesis instead of normally occurring alkanes. Together with product selectivity, the structural stability of catalysts also a co-objective of developments because it is an important parameter when operate in fluidized and slurry reactors. Al_2O_3 , SiO_2 , TiO_2 and ZrO_2 have been used as supports to enhance the stability but those have disadvantage of forming Fe complexes with supports easily (Kang *et al.*, 2010). Two requirements like selectivity enhancement and structural stability of catalysts have promoted the studies of zeolite as supports for FT catalysis.

2.3.3 Modified FT Catalysts for Aromatics and Olefins Production

Selectivity enhancement of FT catalysts has been studied for a long period targeting olefins and aromatics, which are essential raw materials for petrochemical industry. In most cases, the support properties have been tried and a special concentration has been given to zeolite as a support for conventional Fe or Co based FT catalysts.

With SiO₂ support, for Fe based FT catalysts the product selectivity toward aromatization has been observed with small addition of Pd as secondary metal. Formation of different forms of Fe leads to promote this selectivity shift by producing paraffin and olefins in Fe (Fe_xC) carbide sites and aromatization of them by Pd-Fe alloy due to aromatization properties of Pd. The result has been obtained by CO hydrogenation experiments with 0.5 g of catalyst in a continuous flow reactor with H₂/CO = 2, flow rate = 0.75 dm³/h and T = 347 °C have resulted a 30.5 % aromatics in products with only 1.0 % conversion. (Nimz *et al.*, 1988).

Acidic zeolites have been studied to change the FT selectivity to obtain products that are more valuable. Acidic function in zeolites can be used as aromatization catalyst and combining both Co-Mn FT catalysts with ZSM5 acidic catalysts has increased the aromatic selectivity in dual bed experiments carried out with Co-Mn FT catalyst in the first and HZSM5 or Ga modified ZSM5 in the second reactor. The highest aromatic selectivity has been observed with HZSM5 as 18 % with Si/Al = 19, T (FT reactor) = 240 °C, T (aromatization reactor) = 470 °C, P = 1 bar, SV = 5600 h⁻¹ and H₂/CO = 1. (Bäurle *et al.*, 1992)

Further, another study on Fe based catalysts for FT synthesis shows that Ga modified ZSM5 zeolite mixed together with Fe-MnO₂ FT catalyst and pelletized produces aromatics in CO hydrogenation. A promising shift of selectivity towards aromatics has been observed and the highest aromatics selectivity has been observed as 50 % at 543 K after 5 h on stream with GaZSM5, which is much higher than 11 % aromatic selectivity with HZSM5. This proposes a positive effect by Ga modification but rapid deactivation of Ga promoted catalysts has been observed (Guan *et al.*, 1996).

An interesting application of zeolites is in the so-called modified FT, where primary FT products (mostly α -olefins and long-chain n-paraffin) are upgraded in-situ to high-octane gasoline components (aromatics, iso-paraffin) by the action of an acidic (or bi-functional metal/acid) zeolite. The zeolite can be physically mixed with a typical FT catalyst (hybrid systems) or arranged in a dual layer configuration. In the former case, the degree of intimacy between the two components largely determines the extent of the acid-catalyzed reactions (isomerization, cracking, oligomerization, cyclization, etc.) and thus product distribution. In this sense, more effective hybrid catalysts have been reported by using a core (FT catalyst)-shell (zeolite) approach. A rapid zeolite deactivation of zeolite compare to FT catalysts by coking is a serious obstacle for a possible commercialization of this process (Martinez *et al.*, 2009).

In another study, physically mixed FeCuK/ZSM5 catalysts has shown high olefin selectivity and catalyst stability than modernite and beta-zeolite and also impregnated FeCuK/ZSM5 catalyst has shown higher olefin selectivity while showing slightly lower activity comparative to physically mixed FeCuK with ZSM5 (Kang *et al.*, 2008). Further ZSM5 support with Si/Al ratio of 25 has lead to higher conversion and olefin selectivity than ZSM5 with Si/Al ratio higher than 25 due to low reducibility of Fe species and the density of weak acid sites (Kang *et al.*, 2010).

A comprehensive study has been conducted by a group of Spanish researchers on the influence of ZSM5 zeolite composition and the crystal size on in situ conversion of syngas to produce high octane gasoline for Si/Al ratios of 15,25,40 and 140 to observe the influence of Si/Al ratio and hence the acidity. They have also studied the influence of crystal size and Ga and Pd promotion on ZSM5 zeolite.

Addition of ZSM5 zeolite with 1:1 ratio in weight to the Fischer Tropsch catalysts which is FeCoK with atomic composition of 45Fe:3Co:1K has influenced to increase the CO conversion significantly from around 80 % to over 98 % except in the case of Si/Al ratio of 140. Further, selectivity has also been influenced by ZSM5. Even though the selectivity for hydrocarbons, alcohols and CO_2 was not affected much by ZSM5 addition, the selectivity inside the hydrocarbon fraction shows a significant change to the direction of aromatics. Decline in aromatics in total hydrocarbons was observed with time on stream for all Si/Al ratios studied. Even though the initial selectivity to aromatics was higher with lower Si/Al ratio. The distribution of types of aromatics with selected catalysts and TOS were observed as shown in Table 2.3.

Catalyst	TOS (h)	Benzene	Toluene	Ethyl Benzene	Xylenes	A ₉₊
FeZ25	0.5	6.0	34.7	8.0	33.9	17.4
	7.3	1.9	15.3	6.8	35.0	41.0
	14.6	1.0	11.0	6.6	31.5	49.9
FeZ140	0.2	0.9	9.6	6.8	24.4	58.3
	5.4	1.9	9.1	6.7	35.0	66.3
	14.3	1.0	7.0	9.4	31.5	69.4
FeZN50	0.2	1.7	14.1	6.9	35.3	42.0
	6.8	1.0	10.4	4.9	28.2	55.5
	14.0	0.5	7.5	4.9	25.3	61.8

Table 2.3 Composition of the aromatics fraction (wt.%) at different TOS forselected hybrid catalysts (Martinez et al., 2005)

In addition, nanocrystaline zeolite shows a higher stability for aromatics selectivity than other ZSM5 zeolite. Also, addition of Ga to ZSM5 influenced to give higher aromatic selectivity but rapid deactivation. In contrast, addition of Pd to ZSM5 leads to a slightly lower aromatic selectivity but improved stability. Further, among aromatics produced with metal promotion, increase in xylene fraction was observed while decreasing the C_{9+} selectivity with Pd addition to HZSM5 zeolite.

FeCoK catalyst preparation and pretreatment has been considered as a highly important factor that influential the activity of the catalyst. The catalyst preparation and pretreatment steps has been done in extremely controlled conditions to form the most active form iron carbide for FT reaction. The technique followed in this work is based on the United States patent with the patent number of 4,518,707 which was granted to Exxon Research and Engineering Company in 1985 (Martinez *et al.*, 2005).

2.3.4 Forms of Active Species in Fe-based FT Catalysts

Fe-based FT catalysts hold this activity due to formation of various species of iron oxides and carbides inside the reactor with pretreatment for activation or in the reaction stage. Several studies have been conducted on determining the active species in the catalyst in different stages of of reaction.

Normally, Fe-based catalysts starts with hematite (Fe₂O₃) phase with which converts to different species of iron oxide and iron carbide phases during reaction and pretreatment. The active species for FT synthesis is recognized as iron carbide phases formed. In a study conducted on active species by Linda D. and coworkers, it was observed that existence of different iron carbide phases are insufficient to sustain the FT activity leading to rapid deactivation. In addition, they concluded that the most active phases in slurry reactor is co-existence of ϵ '-carbide (Fe₇C₃) and alpha-iron (α -Fe) together with χ -carbide (Fe₅C₂) which is less active.

In the work on high octane gasoline production, the use of intense pretreatment with CO and H_2 after reduction with H_2 was conducted with the objective of forming iron carbide species (Martinez *et al.*, 2005).

It has been emphasized that the sample preserving is quite important before characterization to avoid oxidation of α -Fe exists. If the sample is not preserved sufficiently, formation of magnetite (Fe₃O₄) could be observed in the catalyst.

2.4 Alternative Method for Syngas Aromatization

Production of aromatics from syngas has been studied in different route than FT synthesis. The other interesting pathway is to go through methanol as an intermediate product. The process is normally two-step as production of methanol and conversion of methanol to aromatics.

A study on alcohol production from syngas over mixed metal oxide catalyst has been conducted to study the effect of metal mixture as well as the process variables. The metals used for the study are Zr, Cr and K and it has been observed that different alcohols can be produced from the above catalysts. By a series of tests conducted, it has been observed that 420 °C and 10 Mpa are optimum conditions for methanol and iso-butanol production over Zr-K catalyst. In addition, it has been observed that 400 °C is the optimum temperature for Zr-Mn-K catalyst and higher pressure is favorable (Yaning *et al.*, 1996).

Further, a study on methanol aromatization over Mo_2C based catalysts has been observed that, only Mo_2C or Mo_2C supported on silica is effective on methanol decomposition at high temperatures above 573 K but not for aromatic production. In addition, ZSM5 itself is active for methanol decomposition and depending on the composition it produces aromatics at high temperature. Mo_2C deposited on ZSM5 has shown high aromatic selectivity producing benzene, toluene, xylenes and C_{9+} aromatics (Barthos *et al.*, 2007).

A comprehensive study on syngas aromatization through methanol has observed that $ZnO-Cr_2O_3$ catalyst and acidic crystalline Aluminosilicates produces aromatics as products. The catalyst with Zn:Cr less than 4:1 when combined with acidic zeolite gives good selectivity to aromatics including toluene and xylenes (Chang *et al.*, 1979).

Other than acidic zeolite like ZSM5 which is significantly studied, the other potential type of non-acidic zeolite which is KL- zeolite, has been seldom studied for aromatic production from syngas.

2.5 Aromatization Catalyst for Paraffins and Olefins

Aromatization is a proven technology when we consider on paraffin and olefins in the C range from 3 to 10. In different range of C numbers different catalysts are showing better performance. In our study two different catalysts are interesting.

2.5.1 Aromatization with KL-Zeolite Supported Catalysts

Aromatization is the conversion of paraffinic or naphthenic hydrocarbons to aromatics and commercially proven technology used in petroleum refineries or petrochemical complexes to form high-octane gasoline or BTEX. Commercial naphtha reforming catalysts are bi-functional and both metallic and acidic functions have their specific reactions to produce aromatics in final products. Pt is the most commonly used metal with promotions by Re and Al₂O₃ support. Mono-functional (only metal) has definite advantage over bi-functional due to eliminations of isomerization and cracking path leading to high aromatic selectivity and catalyst stability.

KL-zeolite has taken high attention as a non-acidic support on aromatization as a mono-functional catalyst and Pt has been studied as metal, which is supported on KL zeolite in many cases. Further LTL (KL zeolite) has been identified as commercial support for catalytic aromatization. In addition, the presence of highly dispersed Pt clusters inside the zeolite channels and the shapeselective effects imposed by the mono-directional framework structure of the KLzeolite is responsible for the very good aromatization performance of this zeolite, which has pore diameter of 0.71 nm. One of the main drawbacks of this zeolite is the high sensitivity towards sulfur poisoning, responsible for the fast catalyst deactivation (Stocker., 2005).

A study conducted for methyl cyclopentane (MCP) and n-hexane aromatization over Pt/KL-zeolite and Thulium promoted Pt/KL-zeolite (Pt-Tm/KLzeolite) has showed that addition of proper amount of Tm leads to increase the dispersion of Pt on KL-zeolite giving high sulfur tolerance as well as high aromatic selectivity for both reactants. By tests with varying amounts of Tm addition, it has been observed that high Tm concentration leads to reduction in aromatic selectivity due to blockage of channels in KL-zeolite support (Fang *et al.*, 1996). Further, a study on addition of heavy rare earth metals as promoters has shown that Pt-Rh/KL-zeolite also has better performance for aromatization than Pt/KL-zeolite but Tm is the best promoter over Rh for aromatic selectivity (Fang *et al.*, 1997).

Other than n-hexane aromatization, n-octane has also been studied by different research groups targeting C_8 aromatics directly, which are more interesting in petrochemical industry. It has been observed that Pt/KL-zeolite catalysts are not effective for whole range of carbon numbers for aromatization. Pt/KL-zeolite catalyst, which exhibits excellent performance for n-hexane is not effective for n-octane aromatization showing rapid deactivation with n-octane and low C_8 aromatic selectivity. This low C_8 aromatic selectivity is due to secondary hydrogenalysis of C_8 aromatics to form benzene and toluene which are defused through zeolite channels more rapidly than xylenes particularly o-xylene (Jongpatiwut *et al.*, 2003).

In addition to that, the morphology of the catalysts has also been observed as a key factor affecting the C_8 aromatic selectivity. Results have shown that zeolite with longer channels and irregular channel mouth promotes production of more benzene and toluene by secondary hydrogenalysis of C_8 aromatics due to prolong residence time of C_8 aromatics inside channels. Hence, the small Pt crystal size and located close to channel mouths leads to high C8 aromatic selectivity. Further the same study gives results as catalyst deactivation is low when Pt clusters located in channels compare to outside of channels and hence the larger or smaller zeolite crystal leading to low stability and intermediate size of crystals are prefer (Trakarnroek *et al.*, 2006).

The key step in n-hexane aromatization over Pt supported on KLzeolite is ring closure in metals sites to form cyclohexane in single step that rapidly dehydrogenate to benzene. The superior property of L-zeolite is that tight confinement of channel for n-hexane to bend inside the channels. L-zeolite is one dimensional with pores of about 0.71 nm apertures leading to cavities about 0.48x1.24x0.74 nm in size (Ko *et al.*, 1999). The structure of the L zeolite with dimensional parameters and channel orientation and channel shape with cross section can be illustrated as in Figure 2.6 (Ruiz *et al.*, (2005).



Figure 2.3 A) Zeolite L framework projected along the c-axis; B) side view of the main channel; C) its dimensions.

Even though the aromatization of alkanes has been widely studied with KL-zeolite supported catalysts, direct applications of KL-zeolite supported catalysts for aromatic production from syngas have been inadequately studied.

A study done with Fe supported on LTL zeolite and Cs modified LTL zeolite for FT synthesis proposed that Cs modification has improved the conversion by five times while increasing the olefins/paraffin ratio and reducing the methane selectivity (Gallegos *et al.*, 2005). Also, Fe was observed as secondary metal for Pt/C catalysts in fuel cell anode catalysts to improve the CO tolerance (Pereira *et al.*, 2009).

2.5.2 Aromatization with ZSM5 and ZSM5-Zeolite Supported Catalysts

ZSM5 is also a well-known aromatization catalyst for paraffinic feedstock with especially low C numbers such as C_3 and C_4 . In addition, several studies have been conducted in syngas applications as discussed in previous sections.

Ga modified HZSM5 is commonly used bi-functional aromatization catalyst in most of the cases.

With all those information, the proven aromatization activities of Pt/KL-zeolite catalysts for range of paraffin is promoting the idea of studying the possibility of direct aromatization of CO by incorporating the conventionally used Fe for FT synthesis together with Pt on KL-zeolite which itself promotes aromatization. Also, Fe-based Fe catalysts with different proportions of HZSM5 zeolite are interested to study the influence in converting syngas to aromatics.