CHAPTER I

INTRODUCTION

Since 1925 when Franz Fischer and Hans Tropsch discovered that carbon monoxide and hydrogen reacted in the presence of active iron and cobalt catalysts at atmospheric pressure producing higher gaseous, liquid, and solid hydrocarbons, intensive research has been done on the feasibilities of upgrading the products to acceptable motor fuels and chemical feedstocks. However this technology has not been generally considered economical for the U.S. due in part to the low octane number of the product gasoline cut and the complex refining needed to process the liquid streams from the conversion units.

But now with the ever present possibility of future energy shortages, the Fischer-Tropsch technology is again being studied. One area of this technology presently being studied with some success is the catalytic upgrading of the Fischer-Tropsch products to high quality gasoline and chemicals.

The objective of this research was to gather kinetic and catalytic data for the upgrading of a Fischer-Tropsch liquid over a modified ZSM-5 catalyst. This catalyst, developed by Mobil in the early 70's has consistently shown

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This thesis is presented in the style and format of the AIChE Journal the ability of being able to be used for this purpose with great success. One reason is the selective production of gasoline due to the inherent geometry of the crystal. The crystal was composed of a combination of zig-zag and nearly straight channels which allow only compounds of C_{11} or smaller to pass through. This cutoff corresponds very closely to the cutoff of gasoline type compounds.

Numerous studies have been conducted using ZSM-5 on seperate components which form Fischer-Tropsch products, along with possible reaction mechanisms. Chang and Silvestri, (1977) studied the conversion of compounds containing oxygen over ZSM-5 to high octane gasoline. The conversion of C_5 through C_7 paraffins were conducted by Chen et al. (1978). The upgrading of water soluble constituents from a Fischer-Tropsch process were studied by Stowe and Murchison, (1982). But there has been limited attention given to the specific process variables in the upgrading of the Fischer-Tropsch liquids.

The major objective of this thesis work was to use model compounds, n-heptane, n-decanol, n-decanal, and mixtures of these, to study the upgrading of Fischer-Tropsch liquids. The catalyst used was ZSM-5 ion exchanged with nickel or zinc. Hydrogen was co-fed with most runs to reduce coking. The products obtained were analyzed by GC, GC/MS, and the catalyst was examined by x-ray diffraction. Product distributions, limited kinetic data, and process variable effects were obtained for each feed and those results compared with results obtained from the conversion of an actual Fischer-Tropsch oil.

CHAPTER II

LITERATURE SURVEY

The catalyst ZSM-5 was described and patented by Aurgauer and Landolt, (1972). This patent described the formulation and diffraction patterns of the zeolite. Also described was the unit cell which had the form

$$Na_nAl_nSi_{96-n}O_{192} \times 16H_2O$$

The structure of the ZSM-5 catalyst was described by Kokotailo et al. (1978). As shown in Figure 1, the framework consists of eight five-membered rings. These units join through the edges to form chains as shown in Figure 2. These chains can be connected to form sheets and the linking of the sheets lead to a three dimensional framework structure, Figure 3. The framework can be seen to contain two intersecting channel systems, one sinusiodal and the other straight. The elliptical 10-membered ring openings controlling the channels have an effective diameter between those of zeolites Linde type A and faujasite. The framework density of Si + Al per 1000 A^3 is 17.9 which compares with 17.2 for mordenite, 17.3 for dachiardite, and 17.7 for ferrierite.

As with all catalysts the coking behavior is of great importance in the activity of ZSM-5. The coking behavior of ZSM-5 was studied by using radiotracer analysis, Walsh and Rollmann, (1979). The reaction conditions were 633K, 200 psig, H2/HC = 1.4, WHSV of 6, and 3 hours on stream. The

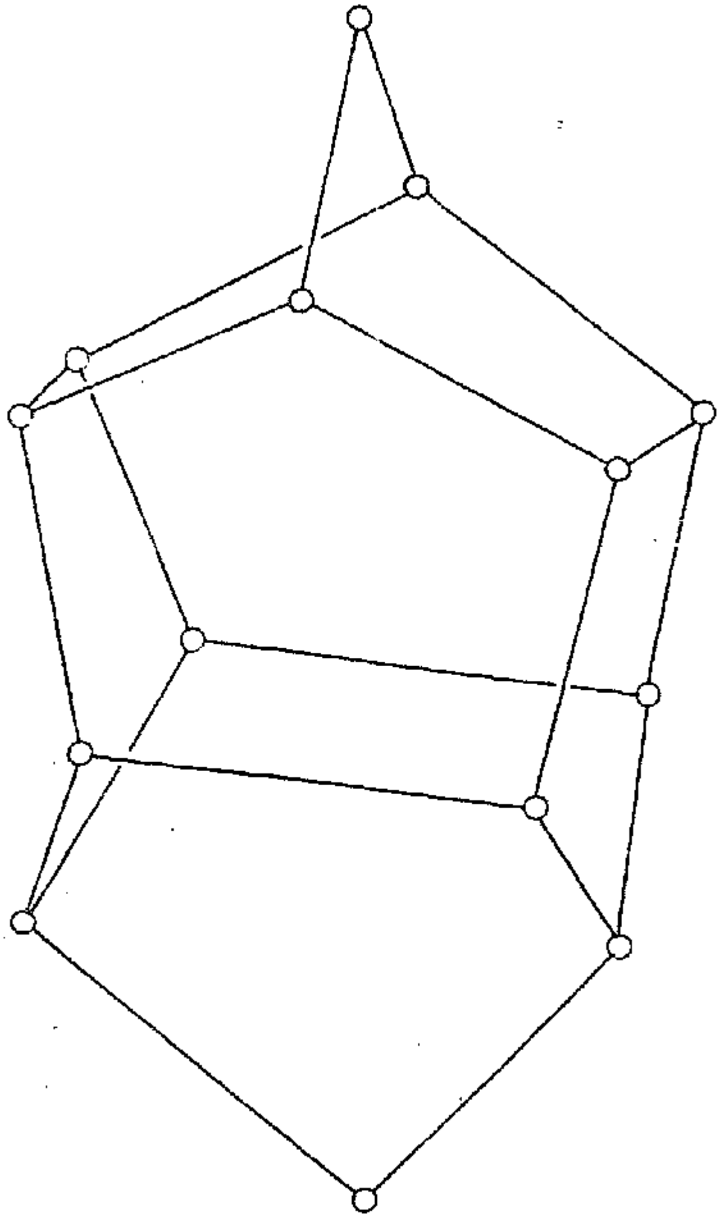


Figure 1. Characteristic Configuration of ZSM-5

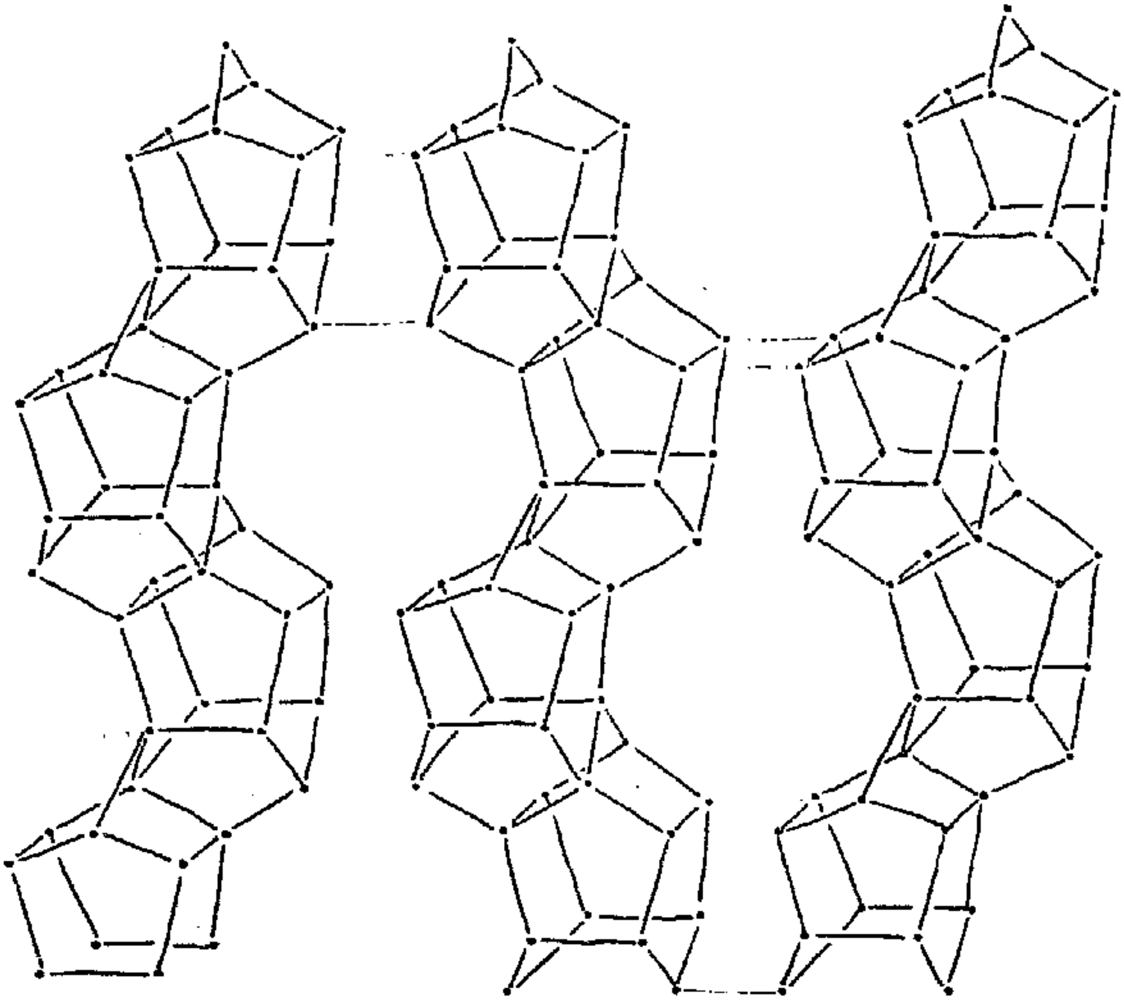


Figure 2. Connection of Cells to Form Chains and Sheets

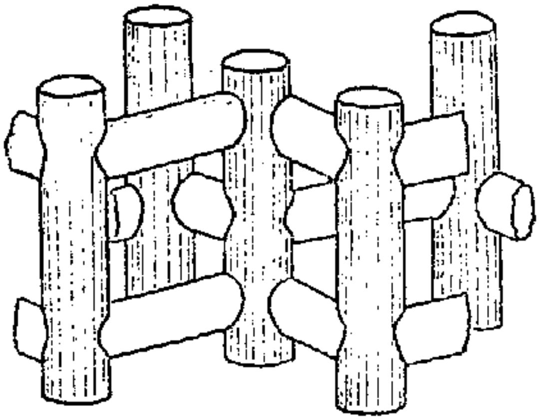


Figure 3. Framework of ZSM-5

conversion of n-hexane was held between 75 and 90 mole percent. The n-hexane was co-fed with either benzene or 1,2,4-trimethylbenzene. Two samples of the ZSM-5 were used, one with a 78 SiO_2/Al_2O_3 mole ratio and the other with a 25 mole ratio.

The results showed with a high SiO_2/Al_2O_3 ratio benzene and hexane participated equally in coke formation, a result which could not be attributed to residual, sorbed hydrocarbons. Also shown was the proportional contribution of aromatics and paraffins to carbon deposition was unaffected by H_2 partial pressure, temperature, or by aromatic reactivity. The mole ratio of SiO_2/Al_2O_3 was shown to be a factor in aromatic contribution to coke. This is a distinct contrast from the observation with 12-ring zeolites. Finally in no case did aromatics contribute significantly to light gas formation.

These results were compared to similiar results for a 12-ring zeolite, mordinite, Walsh and Rollmann, (1977). The results show an order of two magnitudes of difference in coke yields between the ZSM-5 and mordenite. The difference was postulated to be in the difference in the pore size. The coke yields between the two structures were readily understood in terms of pore constraints. The alkyl aromatics, once formed, were prevented from reacting further to produce coke in the smaller ZSM-5 pore. Regarding the variation in the origin of coke formation with framework alumina content, in a 10-ring structure whose pores cannot accomodate a concentration of aromatics, it was proposed that an increase in acid site density leads directly to an increase in paraffin cracking fragments (carbonium ions) within the pore system and thus to the greater paraffin participation in coke. The key point advanced was that the differences in coke yields was not the result of differing basic origins of the coke, but that the origins arise from structural constraints on the reactions of the same intermediates in the formation of that coke.

Because the Fischer-Tropsch liquids are very complex in their chemical distribution, Table 1 and Groggin, (1958), many articles on the behaviour of various compounds over ZSM-5 are applicable to the work.

One of the first and most comphrensive studies of ZSM-5 catalysts was performed by Chang and Silvestri, (1977). A wide range of feeds were utilized to determine product distributions and possible mechanisms for the conversion of compounds containing to hydrocarbons. The reactions of compounds containing oxygen over the zeolite was characterized as dehydration or decarboxylation with shape selective transformation leading to hydrocarbons having a narrow distribution of molecular weights.

The reactions of alcohols were studied using methanol, t-butanol, and 1-heptanol. The reaction conditions were 644K, LHSV of 6, and 1 atm. The results showed nearly

Table 1. Analysis of the Fischer-Tropsch Liquid Used in this Work

Compound	Weight %	Compound	Weight %
C_5	2.016	Nonane	2.711
Hexane	6.322	5-decene	0.508
Benzene	1.829	1-decene	0.517
Other C_6	10.220	Other C_9	4.595
3-methyl-1-hexene	1.143	Decane	6.333
2,2-dimethyl-1-pentene	1.519	Decanol	3.423
Heptane	4.809	Other C_{10}	4.305
3-ethyl-1-pentene	1.746	Undecane	4.956
2,3-dimethyl-2-pentene	2.646	5-methyl-1-decene	4.130
2,4-dimethyl-2-pentene	1.007	Other C_{11}	8.989
Other C_7	0.871	2,5-dimethyldecane	2.446
2,5-dimethyl-3-hexene	3.007	Other C_{12}	4.390
2,2-dimethyl-3-hexene	1.808	Other C_{13}	4.436
Octane	7.914		
Ethylcyclopentane	0.411		
2-methyl-1-octene	1.723		

Florescence indicator analysis (Performed by PETC)

Aromatic and Diolefin	12%
Olefin	70%
Saturate	18

Simulated Distillation Analysis (Performed by PETC)

Gasoline (400 °F +)	70%
Diesel (400 - 650 °F)	28%
650 °F +	2%

The liquid was made using a CO-ThO_2-ZSM-5 catalyst in a Berty reactor at 553 K.

complete water elimination, and very similiar hydrocarbon distribution. Essentially no hydrocarbons over C_{11} were produced, along with very little C_1 or C_2 hydrocarbons. The predominate compounds in all three cases were iso-compounds along with methyl-substituted aromatics. The total aromatic portion of hydrocarbons ranged from 36 to 41 weight percent. Also included was the sulfur analogue of methanol, methanethiol. Due to great difficulty in conversion the reaction temperature was raised to 755 K. At this temperature and the other previous conditions desulfurization was partial with 27.2% of the feed carbon converted to dimethyl sulfide. The overall hydrocarbon distribution after desulfurization was similiar to the alcohols, with the main difference being more light gas was produced. This was probably due to the higher reaction temperature. Also the aromatic production, though still mainly methyl-substituted, appeared to peak at C_9 rather than C_8, as observed in the alcohol feeds.

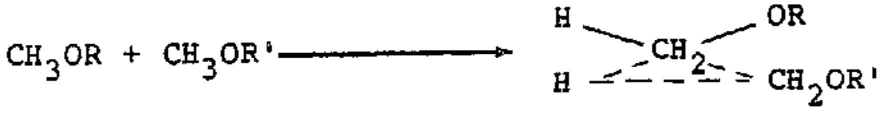
The aldehydes, propanal and methylal, showed differing results. The propanal was efficiently converted to hydrocarbons with a higher selectivity to aromatics than the alcohols. However methylal gave a product similar to the alcohols. Also different in these cases was an obvious dissociation to CO and CO_2.

The carboxylic acid, acetic acid, showed a relatively low conversion, 29.9%, with the major hydrocarbon product being isobutene. The isobutene was probably produced by the zeolite catalyzed ketonization to acetone followed be aldolization and cracking to isobutene. Acetone was detected in the products to support this theory. Contrasting the carboxylic acid is the conversion of n-propyl ester. The deoxygenation of this ester proceeded mainly via water elimination. Propylene was the main hydrocarbon product in this reaction.

Observed in all feeds was a selective production of hydrocarbons which terminated about C_{10}. This distribution resulted from the molecular shape of the zeolite. The aromatics that were formed were mainly methyl substituted benzenes. The xylenes were found to be essentially in thermodynamic equilibrium, however with higher aromatics certain isomers fall short of the thermodynamic equilibrium values. Specifically the isomers were 1,3,5-trimethylbenzene, 1,2,3,4-tetramethylbenzene, and 1,2,3,5-tetramethylbenzene. These were the isomers with the lowest diffusivities, due to steric constraints.

Also studied in the same article was the effect of changing the reaction conditions on the conversion of methanol to hydrocarbons. The effect of temperature was shown in a range from 533 to 811 K. At 533 K the main reaction is the dehydration of methanol to dimethylether (DME). The hydrocarbons formed are predominatly C_2 - C_5 olefins. The conversion of methanol to DME approaches completion around 633 K. During this time the formation of aromatics was constantly increasing. With further temperature increases secondary reactions became more and more evident, with methane and light olefins content increasing. Above 733 K the decomposition of methanol to H_2 and CO became measurable.

From the product distribution, the primary mechanism in methanol to hydrocarbon reactions was proposed to be a concerted bimolecular reaction between a methylene donor and a methanol or methyl ether acceptor. Subsequent protonlysis yields olefins.



$$CH_3OR + CH_3OR' \longrightarrow \begin{array}{ccc} H & & OR \\ & CH_2 & \\ H & \cdots & CH_2OR' \end{array} \qquad (1)$$

$$\longrightarrow CH_3CH_2OR' + HOR \longrightarrow \qquad (2)$$

$$CH_3CH_2OR \xrightarrow{H^+} C_2H_4 + HOR \qquad (3)$$

$$R, R' = H \text{ or alkyl}$$

These olefins can then be reacted to form higher order aromatics, olefins, or paraffins.

In a later sequel the effect of pressure on the conversion of methanol to hydrocarbons over ZSM-5 was studied, Chang et al. (1979). At a constant temperature of 643 K methanol was reacted at 0.04, 1, and 50 atm partial pressures. The reaction path for the conversion of methanol was considered to be (a) the dehydration of methanol to DME, (b) the dehydration of DME to olefins, and (c) the transformation of olefins to aromatics and paraffins. The initial dehydration step was considered to be rapid and reversible with close approach to equilibruim. When the reaction partial pressure is reduced to 0.04 atm the results show the majority of products to be light olefins, with minor amounts of paraffins and aromatics. The effect of lowered pressure was to decouple the dehydration and aromatization steps of the reaction sequence. As expected, at the higher pressure the polymethyl substitution increased. The increase was observed most in the durene (1,2,4,5-tetramethylbenzene) yield. Thus the effect of pressure was to enhance the overlap of the dehydration and aromatization steps, leading to enhanced selectivities of polymethyl benzenes.

In another study performed at Mobil, Leiderman et al. (1978) studied the process variable effects on the conversion of methanol to hydrocarbons. The ranges of process variables were as follows: temperature, 590-755 K, pressure 1-4.40 atm, and WHSV of 0.5 to 4.0, and 35 pounds of methanol per hour per pound of catalyst.

The effect of temperature showed the yields of hydrocarbons were practically unchanged as the temperature increased. More unreacted methanol and DME was observed at lower temperatures. At higher temperatures more isobutane was formed, with propene and light paraffins being largely unaffected. However ethene and durene decreased at the higher temperature. Since the methanol conversion differed at varying temperature an activation energy was calculated. The conversion change corresponded to an activation energy of 12 kcal/mole.

Also studied was the effect of pressure on the reaction. As with increasing temperature, conversion increased with increasing pressure. At the same temperature, the vapor residence time at 4.40 atm is about 4.4 times as great as the value at 1 atm. With first order kinetics, the reaction rate would be expected to increase by a factor of 4.4 in going from 1 to 4.40 atm. However the increase was only about 1.4, which suggested adsorption of methanol by the catalyst.

In testing variables, other than reaction conditions the effects of coke was studied. It was found that after formation of coke on the catalyst, most of the catalyst activity was restored by oxidative regeneration. However, some activity was lost irreversibly from cycle to cycle due to steaming and other factors. This irreversible loss occurred after seven cycles when approximately 2500 pounds of methanol per pound of catalyst had been processed. The catalyst activity had decreased by a factor of two. But surprisingly during the first cycle when conversion fell from 99 to 82 weight percent the catalyst had 50 percent of its surface covered with coke. This showed the extreme activity of the zeolite. As said earlier most of this area was recovered by regeneration. The 50 percent drop in surface area corresponded to an average coke amount of 24 weight percent.

In U.S. Patent 3894106 Chang et al. (1975) tabulated the conversion of several ethers. Studies involving dimethyl ether, di-n-hexyl ether, tetrahydrofuran, and methylal, were conducted at varying pressures, ranging from 1 to 4.40 atm. The aromatic product stayed around 39 weight percent and the C_5 and higher oil was around 35 weight percent. The remainder was C_4 and smaller. The conversion was always greater than 98%.

At a constant pressure and temperature of 1 atm and 644 K, the product distribution for the di-n-hexyl ether was 37.7% aromatics, 13.12% C_5 and higher aliphatics, and the remainder C_4 and smaller. The tetrahydrofuran yielded 66.16% aromatics, not surprising due to the structure of tetrahydrofuran. The methylal yielded 48.08% aromatics and 10.27% C_5 and higher oils.

In looking at Fischer-Tropsch liquids it can be seen that though oxygenates are present, a very large part of the liquid is comprised of what could be considered low octane gasoline or low value chemicals. The conversion over ZSM-5 of many of these components have been studied separately. These studies can be seen as important in describing the catalytic properties of ZSM-5 in upgrading various hydrocarbon mixtures, including Fischer-Tropsch liquids.

A study of the upgrading of low octane hydrocarbons to high octane gasoline was one such study, Garwood et al. (1976). A mixture of equal amounts of methanol and natural gas liquids was passed over ZSM-5. Though product distributions were not given the octane number was raised from 54 to 89.1. The same reaction was also performed using a light reformate (C_6-390 K) in place of the natural gas liquids. The product showed a higher C_5^+ content than the natural gas liquids, and a higher octane rating of 98.1. Also acetone was substituted for the methanol and the same experiment using light reformate was repeated. This experiment yielded a product of 88.2 weight percent hydrocarbons having a research octane number of 95.7. The non-liquid hydrocarbon product was mostly butenes.

The catalytic properties of ZSM-5 with respect to C_5, C_6, and C_7 components, a major part of gasoline, was characterized in part by Chen and Garwood (1978). The results over ZSM-5 were noteworthy in two respects: (1) for the first time it was shown a zeolite can have a pore system which differentiates catalytically between molecules having a straight chain, methyl, and dimethyl substitution, and (2) the relative rate constants for the hexane isomers varied significantly with temperature.

For example, it was found that at 648 K, n-hexane was converted 8.8 times faster than 3-methylpentane. Upon raising the temperature to 783 K, both compounds were converted at the same rate. The relative rate of disapperance of the paraffins were shown to be:

1. With respect to chain length.

   n-C_7 >n-C_6 >n-C_5

2. Among the isomers.

   n-C_7 >2-methyl C_6 >3-methyl C_6 >dimethyl C_5>ethyl C_5
   n-C_6 >2-methyl C_5 >3-methyl C_5 >dimethyl C_4

Shown in Table 2 is the relative cracking rates of C_5 - C_7 paraffins found as a result of this experimentation, Derouane, (1980). Thus the rate of conversion for each group of molecules having about the same critical dimensions increased with increasing molecular chain length, as would be expected from chemical reactivity considerations. The critical dimension of the molecule appears to be more important than the length of the molecule in determining its rate of diffusion through ZSM-5. Or, "the diffusion rate is probably controlled by the matching of the size and shape of the molecule with that of the pore opening rather than by the tortuosity or the channel as in the case of erionite", Chen and Garwood, (1978).

Because ZSM-5 sorbs monocyclic aromatics, the alkylation reaction between benzene/toluene and the cracked fragments have been studied. In most homogeneous and hetereogeneous catalyst systems the relative rate constants of k(toluene)/k(benzene) was 1.4. But the opposite prevails

Table 2. Relative Cracking Rates of C_5 through C_7 Paraffins

Paraffin	Relative Cracking Rate (1)
n-heptane	1.00
2-methylhexane	0.52
3-methylhexane	0.38
2,3-dimethylpentane	0.09
n-hexane	0.71
2-methylpentane	0.38
3-methylpentane	0.22
2,3-dimethylpentane	0.09

(1) T = 613 K, H-ZSM-5, 35 atm, LHSV 1.4

in ZSM-5. This phenomena was attributed to the fact that through sorbtion data ZSM-5 was shown to be accesible to both toluene and benzene, but the methyl group in the toluene molecule apparently decreased the diffusivity of the alkylated molecule to such an extent that the rate of benzene alkylation surpassed the rate of toluene alkylation.

Through these studies the authors concluded the ZSM-5 exhibits molecular sieving effects among large molecules, such as alkylbenzenes, as well as smaller molecules, such as paraffins. This was drastically different from the eight-membered ring zeolites which generally have a sharp molecular sieving effect, which prevents the entrance of certain molecules. Also it was concluded the shape selectivity properties were strongly temperature dependent.

A more extensive study has been performed on the aromatic production, Cattanach, (1973). This patent explored the aromatic production using various feeds including n-hexane, n-heptane, n-octane, and various naphtha cuts. Also the ZSM-5 was ion-exchanged with zinc and nickel. In the absence of added hydrogen and at atmospheric pressure several reactions were conducted at varying temperatures with n-hexane as the feed over H-ZSM-5. At 700 K the aromatic production was about 18 weight percent. However when the temperature was raised to 811 K, the production jumped to almost 50 percent. These results were shown to be virtually independent of space velocity. The reactions showed the vast differences in selectivities with variations in temperature. Again using H-ZSM-5 at 823 K and varying space velocities and pressures a C_6 - 367 K naphtha was converted in the absence of added hydrogen. The product analysis showed the aromatic yield to range from 35 to 47 weight percent. As the space velocity increased the olefin content increased slightly. This increase was small and had little effect on the aromatic production.

Using a C_5 - 383 K light Coastal F.C.C. gasoline the effect of ion-exchange, temperature, and space velocity was compared. This type of feed was specifically used because the high olefin content (40.5 weight percent) enabled reactions at lower temperatures to be carried out. Over the H-ZSM-5 the aromatic production changed from 32.7 weight percent at 663 K to 43.1 weight percent at 823 K. This was due primarily to the fact that at higher temperatures the paraffins also were converted, whereas at the lower temperatures the aromatic content came primarily from the olefins. As the space velocity was greatly increased, the reaction was driven more toward olefins and less towards aromatics. This increase was an extreme change (WHSV of 1 to WHSV of 29). The effect of incorporating zinc in an acid H-ZSM-5 increased the yield of aromatics from 43.1 weight percent to 55.8 weight percent at the same temperature.

Several experiments were conducted utilizing the Zn-ZSM-5 at a pressure of 1 atm and 773 K. With a feed of n-hexane the aromatic formation was 39 weight percent. Using n-heptane and n-octane the aromatic yield was 32.0 and 36.0 weight percent.

Also studied was the minimum temperature needed to obtain at least 30 weight percent aromatic production. The catalysts used were H-ZSM-5 and ZN-ZSM-5, at a WHSV of 2 and no added hydrogen. Three types of feeds were used, a 330-394 K boiling range raffinate, C_6-456 K naphtha, and the F.C.C. gasoline. The minimum temperature for the H-ZSM-5 ranged from 616 to 756 K depending on the content of the feed material. The range of temperatures showed the paraffins required the highest temperatures while the olefins required much lower temperatures. For reasons unknown the Zn-ZSM-5's minimum temperature held constant at about 672 K.

Though Fischer-Tropsch liquids contain few extremely large hydrocarbon molecules, the ability of ZSM-5 to dewax oils by shape selective cracking and hydrocracking has been shown by Chen et al. (1972). Using a zinc exchanged ZSm-5 catalyst at 644 K, a LHSV of 4, and a pressure of 35 atm a lube oil with a pour point of 303 K was 33 percent converted. The most important improvement was a dropping of the pour point to 233 K and a drop in the viscosity index from 108.4 to 76.9.

Up to now, specific compounds and mixtures have been discussed because of their presence in many Fischer-Tropsch products. Now the specific reactions and products of the upgrading of the Fischer-Tropsch liquids can be better shown.

The first Fischer-Tropsch upgrading reaction was conducted by Ireland et al. (1976), where Fischer-Tropsch light oil was fed over the hydrogen form of ZSM-5 and nickel exchanged ZSM-5. At reaction conditions of 600 K and WHSV of 2.0, the resulting products contained 93.6 and 93.1 weight percent gasoline range compounds respectively. The R+O octane number, a criterion for gasoline production, was 90.6 and 82.6 respectively. This was a significant improvement over a charge R+O octane number of 59. An extreme reduction of the oxygenates occurred, which was good due to the detremental effect of oxygenates in gasoline.

Ireland et al. (1976), again shows the upgrading of a Fischer-Tropsch liquid over the hydrogen form of the ZSM-5. This time however the charge is much higher in average molecular weight. Two examples show the catalyst when fresh and after regeneration in air. At process conditions of 596 K and WHSV ot 2.0 the R+O octane numbers are 82.9 and 86 respectively with a charge octane number of 59. The acid content, one type of oxygenates, was reduced from an acid number of 3.5 to less than 0.05.

Kuo et al. (1977) showed that over the hydrogen form of ZSM-5 the fraction of Fischer-Tropsch products too heavy for gasoline were cracked and reformed into the gasoline range.

A charge containing 24.90 weight percent of hydrocarbons with a boiling range of 491 K was reduced to 13.1 weight percent. The R+O octane number was also increased from 55 to 92.

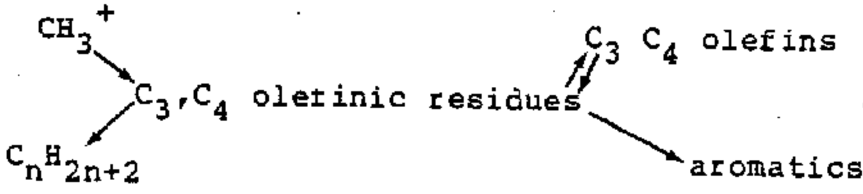
In a study by Stowe and Murchison, (1982) of Dow Chemical U.S.A. the conversion of Fischer-Tropsch liquids over H-ZSM-5 was examined. This study made use of model compounds to simulate the conversion of Fischer-Tropsch liquids. The model compounds were n-hexane, 1-hexene, n-octane, 1-octene, 1-butene, isobutene, a C_4 mixture, and a mixed oxygenate synthetic feed.

Using the synthetic oxygenate mixture the selectivity of aromatics and LPG increased with temperature at the expense of lower olefins and C_5+ oils. The methane selectivity was very low. At a temperature of 573 K the aromatic yield was 5.8 weight percent, while the oil was 29.0 weight percent. However when the temperature was raised 150 K the aromatic yield jumped to 42.5 percent while the oil dropped to 13.6 percent. The difference in yields resulted from the drop in olefins content.

The hydrocarbon feeds showed a wide range of selectivities. All reactions were carried out at 1 atm pressure, 773 K, and steam dilutent with the C_4 feeds. In the C_4 range the isobutene yielded 17.4 percent aromatics, 27.2 percent C_5 and larger oils, and 24.1 percent LPG. The remainder was ethylene, propylene, and a small amount of methane. The 1-butene however yielded 30.1 precent aromatics, 27.3 percent oils and 32.3 percent LPG. The increase in aromatic yield from 1-butene when compared to isobutene was at the expense of the propylene yield. The mixed C_4 feed showed extremely similar results to the results from the 1-butene. This probably was due to the greater amounts of normal butene isomers possible. The higher hydrocarbons showed a greater selectivity to aromatics and LPG than the butenes and oxygenates. The yields ranged from 43.7 percent aromatics and 50.0 percent LPG for the 1-octene to 30.4 percent aromatics and 57.3 percent LPG for n-hexane.

The final experiments were with a Fischer-Tropsch light oil over a range of temperatures. The aromatic yield ranged from 13.6 percent at 673 K to 50.8 percent at 773 K. The aliphatic oil ranged from 61.8 percent to 6.6 percent in the same temperature range. The difference was mainly present in the LPG yield. These experiments again showed the drastic effect of temperature on the selectivity of the catalyst.

The mechanisms for the reactions have also been studied in great detail. Anderson et al. (1979) studied the reactions of n-hexane, 3-methylpentane and 2,2-dimethylpentane over H-ZSM-5. Also studied was the poisoning effects of nitrogenous bases. These studies led to the important conclusion that the Bronsted activity was mainly involved in the catalytic reactions. Any water produced from reactions such as methanol would quench Lewis activity. The results using hydrocarbon feeds led to the conclusion that olefins, and olefinic residues of carbon number greater or equal to 3 are the main intermediates of aromatic production, and that ethylene was not an important intermediate. Several reasons were given for this conclusion. The first was that as the space velocity for the reaction of 3-methylpentane on H-ZSM-5 decreased, the proportion of aromatic products increased and the proportion of cracked products (carbon number less than 6) decreased. The second reason was that as the conversion of 3-methylpentane increased, the olefin/alkane ratio decreased. Bearing in mind that alkanes are very inert relative to olefins this was equivalent to saying the the proportion of olefins in the cracked product decreased as the space velocity decreased. However it was shown that the propylene/propane ratio fell faster than the ethylene/ethane ratio. This suggests propylene is a much more important intermediate than ethylene in subsequent conversion to aromatics. Based on the conclusion of olefinic intermediates the general reaction scheme was proposed:



(4)

where H^+ indicates an acidic site on the catalyst. In this scheme it was understood that saturated hydrocarbon-cracked products were also formed, but were relatively inert, and the connection between the olefinic residues and the corresponding olefins was shown to be reversible but not necessarily in equilibrium.

In order to form olefinic residues from the reactants several reactions must take place. For the case of the alkane reactant the conversion was probably initiated by a hydride abstraction reaction; for instance, in the case of n-hexane,

$$C_6H_{14} + H^+ \longrightarrow C_6H_{13}^+ + H_2$$

or (5)

$$C_6H_{14} + R^+ \longrightarrow C_6H_{13}^+ + RH$$

The cracking reactions can then generate olefinic products by conventional routes. For methanol, and other compounds containing oxygen a different reaction equation was utilized.

$$CH_3OH \rightarrow (CH_3)_2O \rightarrow (\text{olefinic residues}) \rightarrow \text{aromatics} \qquad (6)$$

This reaction did not include a sorbed C_2 residue such as $C_2H_5^+$ because of the low reactivity of ethylene. Nevertheless some ethylene was formed by a reaction similiar to (3).

$$CH_3OH \longrightarrow (CH_3)_2O \rightarrow (C_2\text{residue}) \longrightarrow C_2H_4 \qquad (7)$$

The mode of the initial carbon-carbon bond formation from dimethyl ether (or from methanol itself) was still quite uncertain. The possible generation of a carbenoid species, CH_2 from methanol at an acidic site has been suggested to account for this.

In a later work, Anderson et al. (1980) studied the labeling reactions over ZSM-5. When olefins such as ethylene or propylene are reacted over ZSM-5 the results suggest that once protonation of the olefin occurs at a Bronsted site, further reaction leading to carbon-carbon bond formation is rapid compared with reconversion to the olefin

$$\begin{gathered} C_nH_{2n} + \mathrm{HOZeol} \longrightarrow \\ [C_nH_{2n+1}\underline{\mathrm{OZ}}\mathrm{eol} \longrightarrow C_nH_{2n+1} + \ominus\mathrm{Zeol}] \longrightarrow \qquad (8) \\ \text{Higher Hydrocarbons} \end{gathered}$$

This reactivity of the olefins in the above equation toward carbonium ions generally increases with an increasing degree of olefin substitution. Thus, even with ethylene as the primary reactant, much of the basic reaction may occur preferentially between protonated ethylene and a higher olefin, for instance,

$$\begin{gathered} C_2H_4 + H^+ \longrightarrow C_2H_5^+ \longrightarrow \\ C_2H_5^+ + R_1R_2C{=}CH_2 \longrightarrow R_1R_2C^+{-}CH_2C_2H_5 \longrightarrow \quad (9) \\ R_1R_2C{=}CHC_2H_5 \quad \text{etc} \\ (R_1,\ R_2 = \text{alkyl}, H) \end{gathered}$$

On this basis, one would not expect ethylene conversion to be an oligomerization to linear olefins, instead the products would resemble products from methanol, with the selectivity of the zeolite the fate of a reactant will depend not only on its intrinsic reactivity, but also on its lifetime within the catalyst. Thus, if two reactants were of the same intrinsic reactivity but of different diffusivity the overall result would be that the reactant with the highest diffusivity would have the lower apparent reactivity. This may in part contribute to the apparently low reactivity of ethylene compared to higher olefins.

In the above reaction mechanism the main point addressed was the initial reactions. Not many mechanisms were brought forward linking the aromatics with the olefinic intermediates. Through UV spectroscopy data Vedrine et al. (1980) postulated a mechanism linking olefins to the final formation of aromatics.

The possible mechanism to convert propene to propane and benzene involved an electrolytic conversion of pentadienyl to cyclopentenyl cation and rearrangements of the stable cyclopentenyl cations to the stable cyclohexanyl cation. The key step of this mechanism was a hydride transfer between a carbenium ion and a hydrocarbon. This mechanism is shown in Figure 4. The UV spectroscopy allows one to follow the carbocations which are formed in the aromatization pathways and shows that cyclopentenyl carbocations are formed first, followed by the formation of cyclohexenyl carbocations and further of alkylaromatics. By increasing the temperature polyaromatics and

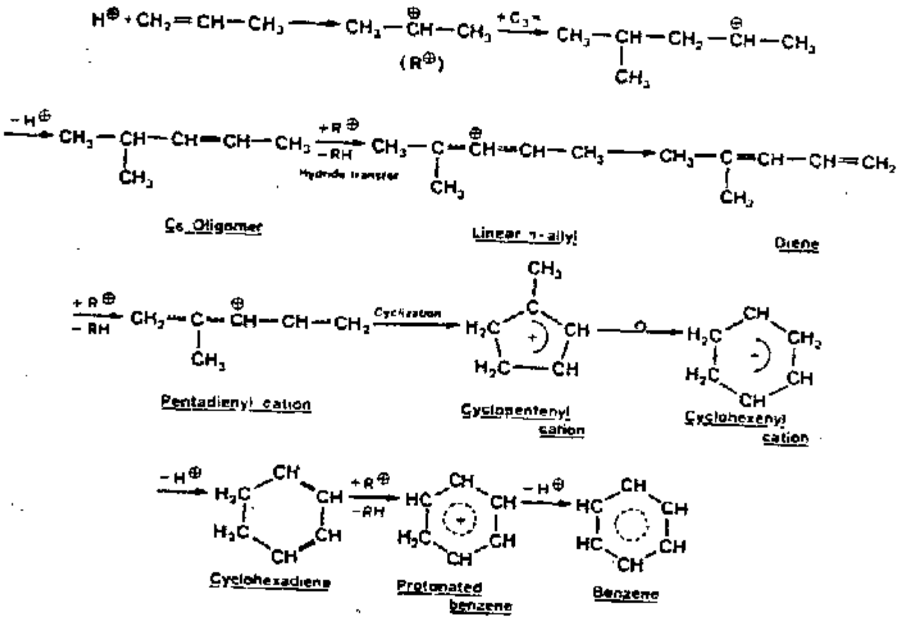


Figure 4. Mechanism of Aromatic Formation (Vedrine et al., 1980)

polyalkylaromatics are further formed. Such carbocations were formed during the intermediate steps and an aromatization mechanism by conjunct polymerization of olefins and carbocations was proposed. This was in good agreement with catalytic data which showed that aromatics and isoparaffins yield increases when the olefin yield decreases.

Dejaive et al. (1980) proposed a carbenium ion mechanism for the upgrading of the hydrocarbon chain and the formation of the hydrocarbon chain and the formation of higher hydrocarbons based on a common initial intermediate. This common initial intermediate could be ethylene, as produced by the dehydration of methanol and/or dimethyl ether, or the cracking of higher hydrocarbons. However ethylene has been proven to be of lower reactivity than of say, propylene, so it is unlikely gaseous ethylene was part of the consecutive reaction network. The ethylene can be protonated by Bronsted acidic sites to form a carbenium like surface species, which can react further with formation of higher molecular weight oligomers. Figure 5a shows a scheme which accounted for the experimental results.

As shown an ethyl-carbenium ion is initially formed, which through surface reactions forms propene or butene species. From these three species higher order paraffins, isoparaffins, olefins, and aromatics can be formed.

The occurance of carbenium ion types can also be

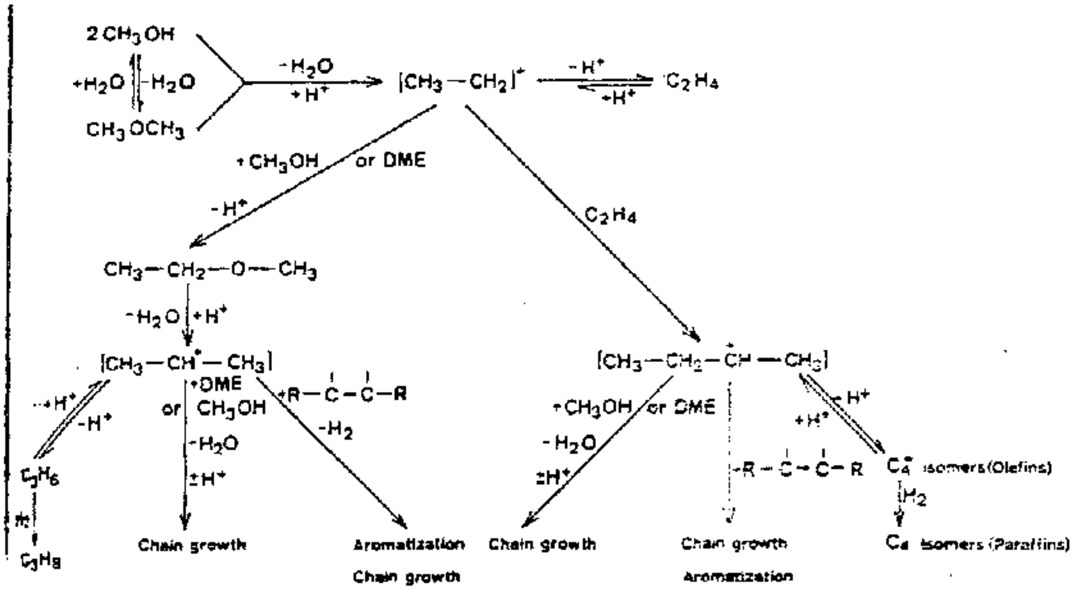


Figure 5a. Mechanism of Methanol to Aromatics (Dejaive et al., 1980)

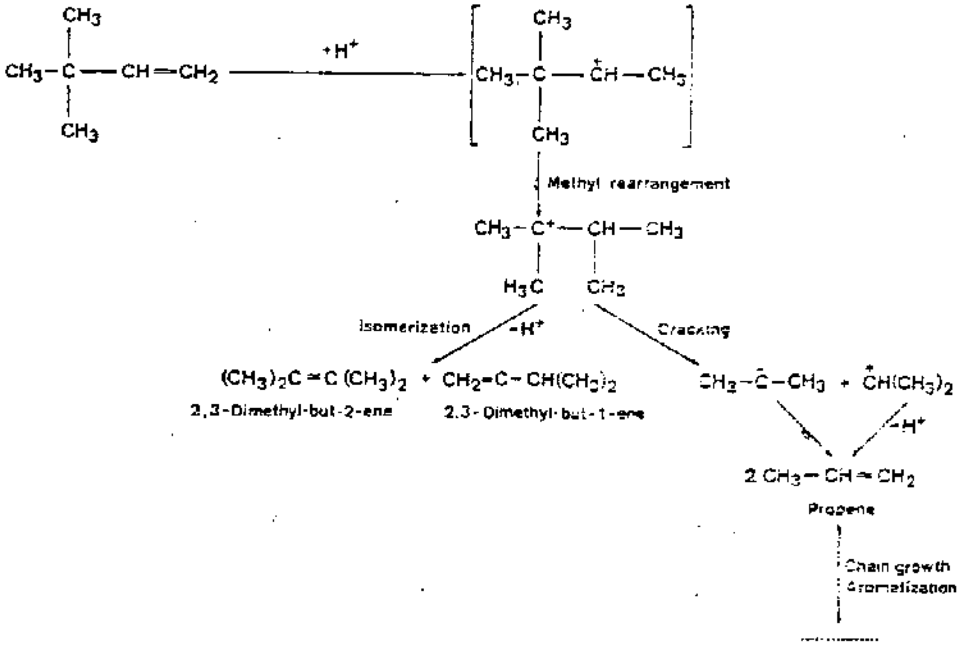


Figure 5b. Mechanism of Hydrocarbons to Aromatics (Dejaive et al., 1980)

ascertained by using other reactants. With 3,3-dimethyl-1-butene, isomerization occured with the reactant going to 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene. These products were cracked to form large amounts of light olefins The reaction mechanism is shown in Figure 5b. The carbenium ion from 3,3-dimethyl-1-butene is rearranged by a methyl shift into a more stable tertiary cation. The latter, by proton release, leads to two olefinic C_6 isomers which crack to propene or undergo aromatization.

The upgrading of both carbenium ion mechanisns can be explained as before, which was by condensation of an olefin and a carbenium ion which by dehydration can form cyclic C_6^+ hydrocarbons. However, competing with this reaction is a hydrogen transfer reaction between the cyclic hydrocarbons and light olefins leading to aromatics and saturated C_2-C_5 hydrocarbons. This pathway is shown in Figure 5c.

These reactions are favored by ZSM-5 because of the catalyst's long, intersecting channels. Dejaive et al. assumed that since the probability for the formation of a given aromatic hydrocarbon was roughly proportional to the number of availiable reaction paths, the major aromatic compounds should be toluene, xylenes, ethyltoluenes, and 1,2,4,-trimethylbenzene. Other aromatics would be present in small amounts due to alkylation. It was found that such a distribution agreed with the experimental observations and

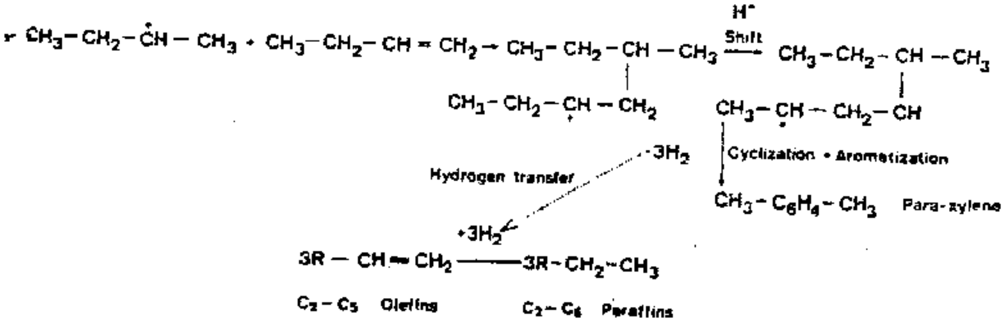


Figure 5c. Mechanism of Formation of Higher Saturated Hydrocarbons and Aromatics (Dejaive et al., (1980)

further reinforces the role played by the molecular sieving properties of the zeolite which were needed to conduct the postulated mechanisms.

The conclusions gathered show in the formation of aromatics a cycloaddition of an olefin and a carbenium ion was favored by the unique structural properties of the zeolite. The predicted distribution for the aromatic hydrocarbons was remarkably well reflected in the experimental data and discrepancies could be explained by probable alkylation.

Also proposed was that some of the unique properties of the acidic forms of the ZSM-5 family of zeolites result from the combination of strongly acidic and molecular sieving properties.