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Selective conversion of methanol into hydrocarbons on chryso-zeolite or zeolite ZSM-5 catalysts

Pierre Lévesque

A Thesis

in

The Département

of

Chemistry

Presented in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy at Concordia University Montréal, Québec, Canada

June 1987

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ABSTRACT

Selective conversion of methanol into hydrocarbons on chrysophase-zeolite or zeolite ZSM-5 catalysts.

Pierre Lévesque, Ph.D.
Concordia University, 1987

Methanol can be converted to hydrocarbons using ZSM-5 type zeolite catalysts. To improve the selectivity of the Methanol - To - Gasoline (MTG) process, new zeolitic materials were prepared. Starting from short chrysotile asbestos fibers, chrysophase-zeolites ZSM-5 were found to be active and very selective - when compared to pure zeolite ZSM-5 - in the methanol conversion to hydrocarbons. Their peculiar catalytic properties were essentially related to the presence of magnesium coming from the asbestos macrostructure. The amount of Mg extracted from the fibers before the zeolite hydrothermal synthesis influenced greatly the crystal particle size and the adsorption/ desorption properties of the catalysts. The presence of a basic site generated by the magnesium led to catalysts with controlled selectivity and high activity under mild reaction conditions.

In addition, the incorporation in a controlled way of metals (zinc, and/or manganese) provided more selective
zeolite or chryso-zedite ZSM-5 catalysts which exhibited higher production of the more commercially valuable hydrocarbons (olefins and aromatics) under normal conditions.

The formation of hydrocarbons on zeolite or chryso-zedite ZSM-5 was suspected to occur through an alkylloxonium intermediate giving propylene as the first desorbed hydrocarbon species.
SONMAIRE

Conversion sélective du méthanol en hydrocarbures sur les catalyseurs chrysozzéolite et zéolite ZSM-5

Pierre Lévêque, Ph.D.
Université Concordia, 198

Le méthanol peut être converti en hydrocarbures en utilisant un catalyseur zéolitique ZSM-5. Afin d'améliorer la sélectivité du procédé MTG (Methanol-To-Gasoline), de nouvelles zéolites ont été préparées. Partant de courtes fibres d'amianté chrysotile, des chryso-zéolites ZSM-5 ont été synthétisées. Ces catalyseurs se sont révélés actifs et très sélectifs lorsque comparés à la zéolite ZSM-5 pure. Leurs propriétés catalytiques sont dues à la présence de magnésium issu des restes de fibres d'amianté. La quantité de Mg extraite avant la synthèse hydrothermale des chryso-zéolites joue un rôle déterminant dans les propriétés d'adsorption / désorption des catalyseurs ainsi que dans la taille des particules de zéolites. La présence
d'un site basique provenant du magnésium donne un catalyseur à activité et sélectivité contrôlées. De plus, l'ajout de métaux (zinc et/ou manganèse) par des méthodes précises permet d'obtenir un rendement plus élevé en hydrocarbures économiquement valable (oléfines et aromatiques).

La formation des hydrocarbures (à partir de méthanol) sur les catalyseurs zéolitiques se fait via un intermédiaire de type oxonium, donnant le propylène comme produit primaire de la réaction.
Remerciements

Je tiens à remercier le Docteur Raymond Le Van Mão pour avoir été l'instigateur de ce projet de recherche. Ses conseils et les discussions que nous avons eus ensemble m'ont grandement aidé.

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À Isabelle,
mes parents
et
Docteur Mao
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INTRODUCTION

The word "catalysis" was used for the first time in 1597 by Libarius. It is only in the second-half of the eighteen Century that catalysis was seriously studied. At the beginning of the nineteen Century, few compounds were prepared by catalysis (and photocatalysis) (1). In 1835, Jacob Berzelius (1779 - 1849) gave the first definition of a catalyst: "une substance qui réveille les affinités assoupies des réactifs ... sans prendre part directement à la réaction chimique." This definition represents well the role a catalyst should play in a chemical reaction.

Heterogeneous catalysis studies the influence of substances on the rates of chemical reaction. The reactants and the catalyst represent two distinct phases (gas/solid for example). The catalyst can alter only the rate of a chemical reaction which is thermodynamically feasible, that is, a reaction which involves a decrease in free energy. The reacting species are chemisorbed on the catalyst and the system may follow a new path with a lower energy of activation (E_a) (see figure A).
Figure A: Potential energy versus reaction coordinate.

a: uncatalyzed reaction
b: case of a good catalyst
c: case of a bad catalyst
$\Delta H$: enthalpy of reaction equal to $E_2 - E_1$
In the early 1960's, new types of porous solid catalysts were developed: shape-selective zeolite catalysts. They improved old synthesis routes, opened up new ones and should be a major factor in catalytic industrial development. At the present time, many groups are doing research on the use of natural and synthetic zeolites in various processes.

Porous solids usually exhibit a large surface area, mainly located inside the solid, and accessible by the pores. The heterogeneous catalytic reaction occurs through a stepwise process, some steps of which are of a physical nature (figure B).

In microporous solids (where the pore diameters are smaller than 10 Å), the internal diffusion of reactants and products species could be influenced by the pore size. The classical theory of diffusion considers two regimes: the normal diffusion regime in which the pore size of the host material is greater than the mean free path of the diffusing molecule and the Knudsen regime for which the diffusivity decreases with the pore dimension. As presented by P.B. Weisz and emphasized by various authors (17), a new diffusion regime exists in the zeolite, i.e., configurational diffusion (figure C). The observed rate of catalytic reaction in zeolites is moderated by an effectiveness parameter $\eta$:

$$k_{\text{obs}} = \eta \cdot k$$
Figure B: Physical and chemical steps in heterogeneous catalysis
1 - external diffusion
2 - internal diffusion
3 - adsorption of reactant A
4 - chemical reaction
5 - desorption of product B
6 - internal counter-diffusion
7 - external counter-diffusion
Figure C: Diffusivity versus pore size in porous materials
where \( k = \) intrinsic rate constant

\( \eta = \) parameter which is function of a diffusivity

coefficient D, radius R and the concentration of

the reactant(s) C.

Reaction characterized by a small \( \eta \) value (formation or transformation of antiselective species) will be selectively retarded with respect to those having a higher effectiveness factor (formation or transformation of proselective species). Since zeolites are microporous solids, their structure will largely influence the product distribution in the synthesis of hydrocarbons.

Another field of interest for many chemists is the chemistry of the various compounds containing one carbon atom \((2, 3, 4)\). Carbon monoxide is well known and currently used in mixture with \( H_2 \) (Fisher-Tropsch synthesis for example). Methanol (\( CH_3OH \)) can be prepared from various sources (natural gas, biomass, coal) via synthesis gas (\( CO + H_2 \)). Methanol is found in various commercial preparations and is part of many Research and Development programs (see figure D).

In the 1970’s, the influence of two events revealed the industrial potential of methanol:

- the discovery by workers at Mobil of the selective catalytic conversion of methanol to hydrocarbons (olefins and high octane gasoline) over a new zeolite catalyst (ZSM-5 type),
- the Arab Oil embargo.

They were key events for the development of alternative
Figure D: Production of chemicals starting from natural resources via synthesis gas.
routes in the petrochemical industry.

Methanol could be used as a motor fuel (directly or blended with gasoline). But, when compared to gasoline, methanol has some disadvantages: easy contamination by water, corrosivity, toxicity, low volumetric energy (5). Therefore, at the present time, it is more commercially attractive to convert CH₂OH into conventional hydrocarbon fuels or chemicals.

In industrialised countries, research is conducted to find alternative non-petroleum materials which can become important source of fuels. The conversion of methanol (a one C atom compound) on new zeolitic materials (ZSM-5 type zeolite) to obtain hydrocarbons (olefins and gasoline) at a relatively low cost is an alternative. The methanol-to-gasoline (MTG) process has some advantages: it is a new efficient way to produce chemical feedstocks starting from an alcohol (methanol) which is easily produced by well established processes. The MTG technology is now available on an industrial scale in New Zealand (6).

Catalysts have become a large and important business marked by a slow but steady growth. U.S. sales of process catalysts (those used in refining and chemical processes) reached 4.86 billion pounds in 1985, valued at $955 millions. Their use is forecast to grow at an annual rate of 2% to 5.4 billion pounds in 1990, worth $1.12 billions
(7). By taking into account all the industrial plants in the world, large amounts of money are invested in catalysts every year.

Many promising areas for future research have been identified in a study on selected catalyst developments (7). These areas include phase-transfer catalysts, catalysts for asymmetric synthesis, multifunctional catalysts, intercalated catalysts and zeolites. The latter, also known as shape-selective catalysts, have a bright future.

In order to be involved in this challenging field, research is done on zeolitic materials in our laboratory. The work described here, which was performed at Concordia University, had for its goal the preparation of a different types of zeolite catalysts and their use in the MTG process. Composite catalysts (asbestos/zeolite) were synthetized starting from asbestos-7 TF 12 grade fibers, and were compared to pure zeolite ZSM-5 (synthesised at Concordia) in the conversion of methanol into hydrocarbons. Metal zeolites were prepared leading to a greater selectivity in the MTG process.
1.1 Zeolite materials

Zeolites are porous, crystalline alumino-silicates composed of AlO$_4$ and SiO$_4$ tetrahedra, interconnected through shared oxygen atoms, forming a three-dimensional framework. The oxygens in the structure are shared by two tetrahedra. The framework will possess a net negative charge located on the Al. This is balanced by an exchangeable cations (M$^{n+}$) on the structure. The general representation is:

$$\frac{Mx}{n} \left[ \frac{(AlO_2)x}{(SiO_2)y} \right] \cdot zH_2O$$

where $n$ is the charge on the cation and $z$ is the water of hydration.

Zeolites, which exist as natural or synthetic solids (15), are defined by some specific characteristics. Two simple factors could be used to identify them: the size and shape of the channels and the silica-alumina ratio (or Y/X). In general, Y/X is greater than or equal to one.

As catalysts, zeolites are unique in their ability to discriminate between reactant molecules and to control product selectivity, depending on molecular size and shape (16). This phenomenon, called "shape-selective catalysis", 

10
is a consequence of the well-defined geometry of zeolite pores, channels, and cages, which are of molecular dimensions (17). Because zeolites can act as sieves for molecules, they are often called "molecular sieves".

Generally speaking, zeolites can be classified into three categories (see figures 1A and 1.2):

- a narrow-pore opening (3 to 5 Å) characterized by 8-rings of oxygen atoms,
- a medium-pore opening (around 6 Å) characterized by 10-rings of oxygen atoms,
- a wide-pore opening (around 7Å) characterized by 12-rings of oxygen atoms.

When the cation M is a proton, the zeolite becomes a strong Brønsted acid. When used as acid catalysts, zeolites are usually in the H⁺ form.

Zeolites play an important role in industry. The three main areas where zeolites are industrially used at present comprise the following processes: adsorption/separation, catalysis, and ion-exchange. Particularly in the catalytic processes, synthetic zeolites, which can be produced with higher purity and less structural defects are practically the only ones in use. Some natural zeolites which can be obtained at very low cost in certain regions of the world have found other bulk applications such as filler in paper, building stones, etc (82).

As adsorbents, the zeolites of type-A which have high
Figure 1.1: Typical zeolite pore geometries.
Figure 1.2: The truncated octahedron (a) and (b) the array of truncated octahedra in the framework of zeolite A.
affinity for water and other polar molecules are currently used for the removal of water and carbon dioxide from natural gas and other hydrocarbons. Their restricted pore diameters can prevent the adsorption of hydrocarbons from the feed and thus minimize the loss of these molecules during the removal process (sieving action).

As catalysts, their great selectivity (zeolite X and Y) sharply reduced the amount of gas oil required to produce gasoline over the classical silica-alumina in the FCC process (Fluid Cracking Catalysis). Today, about 90 percent of all catalytic cracking units employ zeolite catalysts. About 290 million pounds of cracking catalyst with a value of $145 million were produced in 1978 (18). The crystalline ZSM-5 zeolite now plays an important role in industrial plants.

As ion-exchangers, zeolites find commercial applications in the removal and purification of radioisotopes, of ammonium ions, of metals prior to the washing process (detergent builders).
1.2) **ZSM-5 Zeolite (Zeolite Socony-Mobil)**

The pentasil zeolite ZSM-5 catalyst is the key element in the MTG process (19,20). ZSM-5 (21) is a shape-selective synthetic zeolite characterized by the following chemical-structural properties:

- high silica/alumina ratio (from 5 to infinity)
- medium pore size (around 5.5 Å)
- tridimensional framework made of intersecting channels (see figure 1.3),
- constraint index (1 < C.I. < 12).

These properties confer its unique catalytic performance to ZSM-5:

- high thermal resistance due to a high Si/Al ratio,
- high reactivity and selectivity.

The selectivity of the hydrocarbons formed, starting from methanol is due to the 5.5 Å pore opening which is wide enough to produce hydrocarbons up to C_{11} (in the gasoline range). Coke resistance is due to the impeded formation of the bulky fused aromatic rings which are considered as precursors for carbon deposition.

Since the mid-1970's, there are currently six licensed processes based on the ZSM-5 zeolite with more than 25 commercial plants (20):

- Methanol to gasoline (MTG)
- Distillate dewaxing
viewed along [010]

Secondary building units: complex 5-1

Framework density: 17.9 T/1000 A^3

Channels: \{[010] 10 5.4 \times 5.6 \rightarrow [100] 10 5.1 \times 5.5\} \ldots

Fault planes: (100)

Type species: Mobil synthetic zeolite ZSM-5

Na_{n}Al_{n}Si_{86-n}O_{182} \cdot 16 \, H_{2}O \text{ with } n \leq 27 \text{ and typically about 3}

orthorhombic, Pnma, a=20.1 \, b=19.9 \, c=13.4 \, A

5.1-5.5 \, A^\circ

Figure 1.3: Structure and channel system of zeolite ZSM-5.
- Xylene isomerization
- Toluene disproportionation
- Ethylbenzene synthesis
- Lubrication oil dewaxing

All these commercial processes use fixed-bed reactors. For the MTG process, a fluidized-bed reactor is under development.

The conversion of methanol into hydrocarbons can be done on other catalysts (19). However, for the MTG reaction, the ZSM-5 zeolite appears to be the more efficient, due to its shape-selectivity.
1.3 Chrysö-zeolite ZSM-5

Various types of zeolites are used today in many processes (adsorbent, catalyst, ion exchange). They also have a promising future (22). In order to take part in the challenge, a new zeolite was synthesized at Concordia University (23). Because of patent limitations, the zeolite field is restricted. A different approach was taken in order to prepare a zeolite which can be used in the MTG process. A crystalline aluminosilicate with the ZSM-5 structure was prepared from chrysotile asbestos fibers. The name chryso-zeolite ZSM-5 is applied to the mixture of the initial product and the resulting solid after treatment and synthesis.

The asbestos "chrysotile" is available in Quebec. The long fibers are used in many industrial compounds. The short fibers (grade 7) are usually rejected. Therefore, it is possible to modify those low cost fibers for a specific purpose.

The chrysotile fibers contain silica, magnesium oxide, iron oxide and some impurities. By partially leaching out the magnesium, the silica is available for synthesis. To the asbestos remnants, a source of aluminum is added and the chryso-zeolite is synthesized under appropriate conditions.

The zeolite ZSM-5 within an asbestos remnants seems to have some advantages: control of the selectivity in the MTG
process; support available for further improvement of the catalyst. When compared to pure ZSM-5, the main difference in the chryso-zeolite is the presence of MgO. This magnesia left in the asbestos remnants before synthesis plays a role when the chryso-zeolite are used in the MTG process.

Tests were performed on chrysotile asbestos and chryso-zeolite type A to evaluate their toxicity. It was shown that chryso-zeolite was safe. It did not damage the cell membrane of the red blood cell. In addition, the viability and the leakage of two marker enzymes were tested on cultured pulmonary macrophages. It was observed that chrysotile asbestos fibers induced cytotoxic responses, whereas an equivalent amount of chryso-zeolite resulted in essentially no significant response (see table 1.1 and 1.2) (24).

The starting material may represent a health hazard if not used under proper conditions, but the final product was found to be safe. The same results should be valid for chryso-zeolite ZSM-5.

Chrysotile asbestos fibers are included in many products (concrete, friction pads, fire proof equipment). At the present time, the industrial processes use large amounts of asbestos. The preparation and commercialisation of chryso-zeolite products of various structures will not consume as much asbestos as the other well known processes but the chryso-zeolites are products of high commercial value.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Percentage of hemolysis (60 min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.0</td>
</tr>
<tr>
<td>Chrysotile</td>
<td>95.0</td>
</tr>
<tr>
<td>Chryso-zeolite</td>
<td>0.0</td>
</tr>
</tbody>
</table>

* 1.0 µg of each solid

Table 1.1: Hemolytic response to chrysotile versus chryso-zeolite.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Viability (% control)</th>
<th>Enzyme leakage (% liberation)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ATP (1)</td>
<td>LDH (2)</td>
</tr>
<tr>
<td>Control</td>
<td>100.0</td>
<td>2.1</td>
</tr>
<tr>
<td>Chrysotile</td>
<td>28.4</td>
<td>62.6</td>
</tr>
<tr>
<td>Chryso-zeolite</td>
<td>98.9</td>
<td>7.6</td>
</tr>
</tbody>
</table>

* 250 ug of each solid

(1) ATP : Adenosine triphosphate
(2) LDH : Lactit dehydrogenase
(3) β-GAL : β-Galactosidase

Table 1.2: Pulmonary macrophage response to chrysotile versus chryso-zeolite.
Chapter 2: Alcohols

2.1 Synthesis of alcohols

As stated earlier, methanol can be prepared from various sources via synthesis gas. Raw materials like coal, methane (natural gas), biomass, oils in presence of oxygen, steam (gasification on Ni catalyst) yield synthesis gas (carbon monoxide CO and hydrogen H₂ in various ratios). Starting from syngas (or synthesis gas), methanol can be prepared using zinc and/or copper on alumina or chromium oxide (in presence of alkali) according to the reaction:

\[ \text{CO} + 2 \text{H}_2 \xrightarrow{\text{catalyst}} \text{CH}_3\text{OH} \]

\[ P = 50 - 100 \text{ atm.} \]
\[ \text{temp} = 250^\circ \text{C} \]

Using syngas, higher alcohols could be synthesised, but the process is less efficient at the present time. However, some techniques for the synthesis of C₂-C₄ alcohols from synthesis gas have been developed. They are good prospect since C₂-C₄ alcohols can be used as blending stock or cosolvent for the blending of methanol to gasoline. Mixtures of alcohols can be prepared (from C₁ to C₅) for further transformation in hydrocarbons.
This process where methanol is synthesised from syngas, is of great interest for Canada (and others countries) since large reserves of natural gas, biomass and coal are available at low cost (4). The methanol (or mixture of alcohols produced) can then be converted to hydrocarbons using the MTG technology.

2.2 Conversion of light alcohols to hydrocarbons

Alcohols could be catalytically dehydrated into olefins in presence of acids (sulfuric acid), solid acids (alumina, zeolites) or acid-base catalyst (titania-magnesia, alumina-zinc oxide). Chang et al (9) studied the conversion of methanol and other oxygenated compounds (butanol, heptanol, ethers for example) over zeolite catalysts. The conversion of ethanol to hydrocarbons was studied by various groups (10-13) on different catalysts (zeolites, modified zeolites). Ethanol yielded liquid aliphatic hydrocarbons, aromatics or ethylene depending upon the catalyst and the experimental conditions (temperature, pressure, reactant/catalyst ratio). Dehydration of ethanol and high yield in ethylene were obtained (10-12). Higher alcohols (propanol, butanol) when converted to hydrocarbons on acid catalysts (zeolite ZSM-5) gave more liquids than methanol but the content in aromatics decreased (14).
2.3) The Methanol-To-Gasoline (MTG) process

The MTG process is based on the simplified reaction:

\[ n \text{CH}_3\text{OH} \rightarrow [\text{CH}_2]_n + n\text{H}_2\text{O} \]

ZSM-5

Even if the reaction seems very simple, it took many years to solve some limitations. Even now, with an industrial plant existing in New-Zealand, some problems are unresolved. The reaction is highly exothermic. The heat of reaction being 1740 kJ/Kg of methanol (20) at 400°C (i.e. capable of provoking a temperature rise of about 600°C under adiabatic conditions - producing a phenomenon known as "hot spot" within a fixed catalytic bed). It is essential to provide efficient heat removal to the reaction system. A complete conversion of methanol is necessary. Any unconverted methanol will be lost by dissolution in the aqueous phase formed during the reaction. ZSM-5 undergoes two types of aging under MTG reaction conditions:

- reversible deactivation due to coke formation on the catalyst,
- irreversible deactivation due to a gradual loss of zeolite crystallinity (slow process) under the combined effects of steam and high temperature.

In this reaction, for each mole of methanol converted, one mole of water is produced. This water which is discarded, represents 56% of the weight of methanol. A maximum
of 44 grams of hydrocarbons is obtained with each 100 grams of methanol used.

In the industrial fixed-bed reactor, a large amount of catalyst is necessary to minimize regeneration cycles following a carbon build-up in the ZSM-5. This problem is avoided in a fluidized bed reactor. The fixed-bed process developed by Mobil uses two reactors in series. In the first one, the crude methanol containing about 17% of water is dehydrated to a methanol—dimethyl ether—water mixture which is sent to the conversion reactor where the hydrocarbons are formed. Typical operating conditions are:

- 1st reactor: $T_{\text{inlet}} = 315^\circ C$
  $T_{\text{outlet}} = 400^\circ C$
  $P_{\text{inlet}} = 13 - 24 \text{ atm}$
  space velocity $= 20 \text{ h}^{-1}$ (WHSV)

- 2nd reactor: $T_{\text{inlet}} = 340^\circ C$
  $T_{\text{outlet}} = 455^\circ C$
  $P_{\text{inlet}} = 13 - 23 \text{ atm}$
  space velocity $= 1 - 5 \text{ h}^{-1}$ (WHSV)
  molar recycle ratio $= 3 - 4$ (based on total fresh feed)

Using two reactors, the temperature is more easily regulated. Gases are recycled in order to control the reaction temperature and to increase the yield of hydrocarbons.

During the conversion, an aromatic compound, durene (1,2,4,5-tetramethylbenzene) is produced in considerable amount. If in too high concentration, durene will cause
serious problems to the gasoline user. This aromatic compound has an excellent research octane number (110 RON) and boils within the gasoline distillation range (197 °C). However, its freezing point is relatively high (79 °C), and tends to crystallize and cause carburetor "icing" in cold temperature. It is generally desirable to keep its concentration under 2% by weight. In the MTG process, durene is mostly formed by alkylation of lower molecular weight aromatics with methanol and/or ether. Lower methanol partial pressure and higher reaction temperature tend to reduce the durene level. However, under these reaction conditions, the conversion to liquid hydrocarbons is much lower.

In the MTG process, about 75% of the hydrocarbons produced are in the C5+ gasoline fraction. A significant amount of additional gasoline can be produced by alkylation of C3 and C4 olefins with isobutane. The resulting mixture is rich in isoparaffins and aromatics giving a high octane number. This quality is far superior to that obtained from a classical Fischer-Tropsch reactor.

<table>
<thead>
<tr>
<th>Product</th>
<th>Fischer-Tropsch</th>
<th>MTG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fixed bed</td>
<td>Fluidized bed</td>
</tr>
<tr>
<td>Light gases (C1+C2)</td>
<td>11</td>
<td>23</td>
</tr>
<tr>
<td>LCO  (C3+C4)</td>
<td>11</td>
<td>29</td>
</tr>
<tr>
<td>Gasoline (C5-C11)</td>
<td>25</td>
<td>14</td>
</tr>
<tr>
<td>Fuel Oil (C11)</td>
<td>51</td>
<td>5</td>
</tr>
<tr>
<td>Oxygenates</td>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td><strong>Octane of gasoline</strong></td>
<td><strong>75</strong></td>
<td><strong>95</strong></td>
</tr>
<tr>
<td></td>
<td><strong>100</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

26
Other processes are known such as the Methanol-To-Olefins (MTO) and Mobil-Olefins-to-Gasoline and Distillate (MOGD). Light olefins will play a dominant role in any future methanol-based chemicals economy. Olefins are initial products in the conversion of methanol to hydrocarbons over zeolite catalysts. To improve the selectivity in olefins, several approaches have been reported (80):

- shape-selective catalysis (small pore zeolites),
- partial conversion with recycle (recovering of the intermediate olefins and recycling of unreacted feed),
- reaction at subambient partial pressure (less aromatization at high conversion),
- high temperature conversion (olefins selectivity is increased at high temperature),
- reaction over modified zeolites and other catalysts (addition of metals or of phosphorous compounds).

Propylene and butylene (prepared from methanol) can be polymerized to gasoline and middle distillate (MOGD process).

Other approaches were studied. In the mid-1970s, Dow Chemical launched a major effort to develop processes for obtaining chemicals from coal via gasification, liquefaction, and Fischer-Tropsch synthesis on a molybdenum catalyst (high production of LPG materials). The products of the F-T synthesis were upgraded by using a ZSM-5 zeolite in series. This last step represented a major improvement in the overall value of the process (81).
Having the two reactions underway simultaneously in one reactor is an unresolved problem. The F-T synthesis is done at low temperature and high pressure while the conversion on ZSM-5 is normally done at high temperature and low pressure.
3.1) Synthesis of zeolite ZSM-5

The zeolites prepared and used as catalysts were of the ZSM-5 zeolite type. They were synthesised in our laboratory according to a technique developed by Argauer and Landolt (21).

Hydrothermal synthesis of zeolite ZSM-5

The usual procedure for the synthesis of a zeolite ZSM-5 is the following. Silica gel was mixed with an aqueous solution of sodium hydroxide (Fisher) and tetrapropylammonium bromide (TBA Br) (Aldrich). This gel mixture was heated for one hour at 80°C. To this, an aqueous solution of sodium aluminate (Fisher) was added. The mixture was stirred another 10 minutes at 80°C. The overall mixture was transferred to a teflon container and loaded into an autoclave. The synthesis in the autoclave was done at 170°C for ten days under a pressure close to eight atmospheres (water vapor pressure at 170°C). After ten days in the autoclave, the solid formed was filtered, washed with water, dried at 120°C/12 hrs and calcined at 550°C for 12 hrs in air (see table 3.1).

Ion exchange was done with the zeolite ZSM-5 prepared
<table>
<thead>
<tr>
<th>Catalyst precursor</th>
<th>Silica gel (g)</th>
<th>Na aluminate (g)</th>
<th>TPA bromide (g)</th>
<th>NaOH (g)</th>
<th>Added water (mL)</th>
<th>Synthesis Temperature (°C)</th>
<th>Synthesis Time (days)</th>
<th>Product (g)</th>
</tr>
</thead>
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<td>P-38</td>
<td>44*</td>
<td>1.5</td>
<td>40</td>
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<td>160</td>
<td>170</td>
<td>10</td>
<td>22.4</td>
</tr>
<tr>
<td>P-68</td>
<td>25**</td>
<td>1.8</td>
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<td>170</td>
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<td>P-71</td>
<td>52**</td>
<td>4.0</td>
<td>80</td>
<td>5.0</td>
<td>320</td>
<td>170</td>
<td>10</td>
<td>48.5</td>
</tr>
<tr>
<td>P-CAN-13</td>
<td>110**</td>
<td>10.5</td>
<td>110</td>
<td>7.0</td>
<td>390</td>
<td>170</td>
<td>10</td>
<td>112.0</td>
</tr>
</tbody>
</table>

(*) Silica gel Baker: 60% in SiO₂
(****) Silica gel Baker: 90% in SiO₂
Product dried at 120 C/12 hr and 550 C/12 hr

Table 3.1: Preparation of pure zeolite ZSM-5 starting from silica gel.
to obtain the acid form. The zeolite was immersed in an aqueous NH₄Cl solution (5% by weight) for one hour at 80 °C (10 ml for each gram of solid). A fresh solution of NH₄Cl was added to the zeolite every hour. The exchange lasted five hours. The solid was filtered, washed with water, dried at 120 °C/12 hrs and activated in air at 550 °C/12 hrs. (NH₄⁺ is exchanged with the Na⁺ inside the zeolite particle. During activation, NH₃ is released and the acid form (or H⁺ form) of the catalyst is obtained.)

At this stage, the catalyst was characterized using several techniques (see characterization, section #3.4).

The acid form of the catalysts was intimately mixed with bentonite (mechanically mixed, between 20 to 65% by weight of bentonite, usually 20%), and made into paste with water. The paste was pressed into an extrudate. Little catalyst pellets were obtained. This form of catalyst was easy to handle (easier than powder) and used in the fixed bed reactor (to avoid excessive pressure drops as is usually observed with finely divided powders).
3.2 Synthesis of the chryso-zeolite ZSM-5

The chryso-zeolite ZSM-5 were prepared according to a technique described by Le Van Mao et al (23).

a) Magnesium leaching of the asbestos fibers

The first step in the synthesis was the magnesium leaching of chrysotile (asbestos) fibers. Mineral and organic acids were used as leaching agents. The asbestos fibers (.7 TF 12 short fiber grade) were digested with mineral acid solution (usually HCl) at 80°C for several hours. After dilution with cold water, the suspension was allowed to settle for twelve hours, then filtered, washed with water and finally dried at 120°C. The experimental parameters for the preparation of the leached asbestos (Alix) are reported in table 3.2.

b) Hydrothermal synthesis of the chryso-zeolites ZSM-5

The resulting solid materials (Alix) were mixed with an aqueous solution containing tetrapropylammonium bromide (TPA Br) and NaOH. The suspension was mixed at 80°C for one hour. An aqueous solution of sodium aluminate was added (see table 3.3) and mixed for 10 minutes at 80°C. The resulting suspension was loaded in a autoclave and heated at 170°C for 10 days.

After unloading, the suspension was filtered and the solid was washed thoroughly with deionized water, dried (120°C / 12 hrs), and finally calcined in air at
<table>
<thead>
<tr>
<th>Alix</th>
<th>Amount of 7TF-12 asbestos (g)</th>
<th>HCl solution</th>
<th>Heating time (80 °C)</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>N</td>
<td>mL</td>
<td>(Dehyd)</td>
</tr>
<tr>
<td>001/2</td>
<td>100</td>
<td>3.0</td>
<td>1000</td>
<td>7.0 h</td>
</tr>
<tr>
<td>013</td>
<td>100</td>
<td>2.4</td>
<td>1000</td>
<td>4.5 h</td>
</tr>
<tr>
<td>025</td>
<td>200</td>
<td>3.0</td>
<td>2000</td>
<td>5.0 h</td>
</tr>
<tr>
<td>020/2</td>
<td>100</td>
<td>2.4</td>
<td>1000</td>
<td>4.0 h</td>
</tr>
<tr>
<td>024</td>
<td>120</td>
<td>2.4</td>
<td>1200</td>
<td>3.5 h</td>
</tr>
<tr>
<td>018/1</td>
<td>100</td>
<td>2.4</td>
<td>1000</td>
<td>3.5 h</td>
</tr>
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<td>1000</td>
<td>3.5 h</td>
</tr>
<tr>
<td>027</td>
<td>150</td>
<td>2.4</td>
<td>1500</td>
<td>2.5 h</td>
</tr>
<tr>
<td>030</td>
<td>150</td>
<td>2.4</td>
<td>1500</td>
<td>2.5 h</td>
</tr>
<tr>
<td>017</td>
<td>100</td>
<td>2.4</td>
<td>1000</td>
<td>2.5 h</td>
</tr>
<tr>
<td>016</td>
<td>100</td>
<td>2.4</td>
<td>1000</td>
<td>1.25 h</td>
</tr>
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<td>032</td>
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<td>2.4</td>
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<td>066</td>
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<td>6000</td>
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<tr>
<td>071</td>
<td>1200</td>
<td>2.4</td>
<td>12000</td>
<td>1.5 h</td>
</tr>
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</table>

Table 3.2: Magnesium leaching of asbestos fibers. Preparation of Alix, precursors of the chryso-zeolite.
<table>
<thead>
<tr>
<th>Catalyst precursor</th>
<th>Alix Sample</th>
<th>Na' aluminate (g)</th>
<th>TPA bromide (g)</th>
<th>NaOH (g)</th>
<th>Added water (mL)</th>
<th>Synthesis T (°C)</th>
<th>Time (days)</th>
<th>Product (g)</th>
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</thead>
<tbody>
<tr>
<td>A-39</td>
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<td>170</td>
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<td>A-45</td>
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<td>10</td>
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<td>170</td>
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<td>110.0</td>
<td>7.0</td>
<td>390</td>
<td>170</td>
<td>10</td>
</tr>
</tbody>
</table>

(1) Dried product at 120 °C/12 hr and 550 °C/hr.

Table 3.3: Preparation of the chryso-zeolite ZSM-5.
550°C for 12 hours.

The sol was subjected to NH₄⁺ ion exchange using a 5% by weight NH₄Cl aqueous solution. The NH₄⁺ forms when activated in air at 550°C for at least 12 hours, released NH₃, and yielded the acid forms (or H⁺ form) of the catalyst. These catalysts were characterized.

The acid form of the catalysts were intimately mixed with bentonite (in general 20% by weight) and made into paste with water. The paste was pressed and extruded into small pellets.

3.3 Preparation of metal catalysts

Two different metals were introduced in (or on) the catalyst. Zinc was included by ion exchange. Zn had an aromatizing effect (36). Manganese was added by impregnation ("wet" or "dry"). Mn favored the formation of light olefins (37).

a) Zinc loading

Zn ions were incorporated in the H-forms of the pure zeolite or chryso-zeolite material by treating the solids with an aqueous solution of ZnCl₂ under "ion-exchange conditions".

The catalysts were immersed in a 2% by weight aqueous
solution of ZnCl₂ (Mallinckrodt), using 10 ml of solution per gram of compounds. The suspension was heated at 70–80°C under reflux with moderate stirring. After a few hours of heating, the suspension was allowed to cool, then filtered and the solid was washed with an excess of deionized water. The Zn catalysts were dried at 120°C for twelve hours and activated in air at 550°C for twelve hours.

Changes in the concentration of the aqueous zinc solution, the volume added, or the time during which the solid was in contact with the solution, were factors to vary the Zn concentration in the catalysts.

Table 3.4 reports the preparation conditions of the Zn loaded samples: the Zn content was measured by atomic absorption.

b) Mn loading ("wet" and "dry")

Samples were prepared starting from catalysts with or without Zn. Two different techniques of impregnation were used: "wet" and "dry".

- "Wet" impregnation of Mn

The catalyst / Mn ("wet") samples were prepared according to the "wet" impregnation method (38). Zeolite or chryso-zeolite ZSM-5 (with or without Zn) were added to an aqueous solution of MnCl₂ (3% by weight). The mixture was allowed to stand overnight at ambient temperature,
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Weight of acid catalyst (g)</th>
<th>ZnCl₂ solution</th>
<th>Temp. (°C)</th>
<th>Time (hr)</th>
<th>Composition of the Zn loaded catalyst ( % w/w )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP-68/Zn2</td>
<td>10</td>
<td>1</td>
<td>80</td>
<td>0.5</td>
<td>0.14</td>
</tr>
<tr>
<td>HP-68/Zn3</td>
<td>13</td>
<td>2</td>
<td>80</td>
<td>3.0</td>
<td>0.37</td>
</tr>
<tr>
<td>HP-68/Zn1</td>
<td>10</td>
<td>2</td>
<td>80</td>
<td>7.0</td>
<td>0.55</td>
</tr>
<tr>
<td>HA-62/Zn</td>
<td>22</td>
<td>1</td>
<td>80</td>
<td>0.5</td>
<td>0.23</td>
</tr>
<tr>
<td>HA-69/Zn4</td>
<td>9</td>
<td>0.5</td>
<td>25</td>
<td>0.25</td>
<td>0.32</td>
</tr>
<tr>
<td>HA-69/Zn1</td>
<td>14</td>
<td>1</td>
<td>25</td>
<td>0.5</td>
<td>0.53</td>
</tr>
<tr>
<td>HA-69/Zn2</td>
<td>14</td>
<td>1</td>
<td>25</td>
<td>1.0</td>
<td>0.62</td>
</tr>
<tr>
<td>HA-69/Zn3</td>
<td>9</td>
<td>1</td>
<td>80</td>
<td>0.5</td>
<td>1.25</td>
</tr>
<tr>
<td>HA-58/Zn2</td>
<td>8</td>
<td>2</td>
<td>80</td>
<td>0.5</td>
<td>0.88</td>
</tr>
<tr>
<td>HA-58/Zn1</td>
<td>10</td>
<td>2</td>
<td>80</td>
<td>1.0</td>
<td>1.36</td>
</tr>
</tbody>
</table>

Table 3.4: Preparation of the Zinc loaded catalyst.
after which the water was removed in an oven. The resulting material was calcined at 550°C for twelve hours. Changing the volume or the concentration of the Mn solution was used to change the Mn content. The final forms of the catalyst were obtained by extruding the solid catalyst with bentonite (20% or 35% by weight) in the presence of water. The weight percentage metal content was evaluated by atomic absorption.

"Dry" Impregnation of Mn

The catalyst Mn (dry) samples were prepared according to a technique developed at Concordia (39). The acid or Zn bearing catalysts were intimately mixed with bentonite (20% or 35% by weight) and made into pastes with an aqueous solution of Mn with an appropriate concentration of MnCl₂·4H₂O (Baker). The amount of aqueous solution of Mn (which replaced the water for the extrusion) was just sufficient to wet the mechanical mixture of catalyst and bentonite. The catalysts were dried at 120°C/12 hours and activated in air at 550°C for twelve hours. The content of Mn was evaluated by atomic absorption (see table 3.5).
<table>
<thead>
<tr>
<th>Final catalyst</th>
<th>Zn loaded cat.</th>
<th>Bentonite weight</th>
<th>MnCl₂ solution</th>
<th>Mn content (metal % w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn content w/w</td>
<td>(%)</td>
<td>Conc. (%, w/w H₂O)</td>
<td>Volume added (mL)</td>
</tr>
<tr>
<td>HP-68/Zn2-Mn2</td>
<td>0.14</td>
<td>4</td>
<td>6</td>
<td>3.7</td>
</tr>
<tr>
<td>HP-68/Zn3-Mn2</td>
<td>0.37</td>
<td>4</td>
<td>6</td>
<td>3.8</td>
</tr>
<tr>
<td>HP-68/Zn1-Mn2</td>
<td>0.55</td>
<td>4</td>
<td>6</td>
<td>3.7</td>
</tr>
<tr>
<td>HA-62/Zn-Mn1</td>
<td>0.23</td>
<td>4</td>
<td>4</td>
<td>3.2</td>
</tr>
<tr>
<td>HA-62/Zn-Mn2</td>
<td>0.23</td>
<td>4</td>
<td>6</td>
<td>3.5</td>
</tr>
<tr>
<td>HA-62/Zn-Mn3</td>
<td>0.23</td>
<td>4</td>
<td>10</td>
<td>3.6</td>
</tr>
<tr>
<td>HA-62/Zn-Mn4</td>
<td>0.23</td>
<td>4</td>
<td>15</td>
<td>3.6</td>
</tr>
<tr>
<td>HA-69/Zn4-Mn2</td>
<td>0.32</td>
<td>4</td>
<td>6</td>
<td>4.0</td>
</tr>
<tr>
<td>HA-69/Zn1-Mn2</td>
<td>0.53</td>
<td>4</td>
<td>6</td>
<td>4.0</td>
</tr>
<tr>
<td>HA-69/Zn1-Mn4</td>
<td>0.53</td>
<td>4</td>
<td>15</td>
<td>4.2</td>
</tr>
<tr>
<td>HA-58/Zn2-Mn1</td>
<td>0.88</td>
<td>4</td>
<td>6</td>
<td>3.6</td>
</tr>
<tr>
<td>HA-58/Zn1-Mn1</td>
<td>1.36</td>
<td>4.5</td>
<td>6</td>
<td>4.4</td>
</tr>
<tr>
<td>HA-58/Mn</td>
<td>1.36</td>
<td>4.5</td>
<td>6</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Table 3.5: Incorporation of Manganese in the catalyst by dry impregnation (with or without Zn).
3.4) **Physico-chemical characterization of the catalysts**

Elemental analysis, X-ray powder diffraction pattern determination, scanning electron microscopy (SEM), surface measurement (BET technique), the adsorption of water and n-hexane, the adsorption / temperature programmed desorption of ammonia and of oxygenated species (methanol, dimethyl ether), and Si MAS-NMR, were techniques used to characterize the samples.

3.4.1) **Elemental analysis**

Conventional techniques of atomic absorption were used for Si, Al, Na, Mg, Fe, Zn and Mn concentration measurements. A sample of 0.1 gram was weighted in a platinum crucible, calcined at 750 °C for one hour, and reweighed to obtain the dry weight. A fusion mixture was mixed with the zeolite material (0.9 gram of potassium carbonate / lithium tetraborate in a 2:1 ratio), and placed at 750 °C for forty-five minutes. The resulting solid was dissolved in acid (HCl concentrated and H₂SO₄ 10%), and oxidized by addition of hydrogen peroxide (30%). The resulting mixture was diluted to 100 ml and atomic absorption was run (further dilutions were occasionally needed). The content in metal oxides was calculated from external standards.

From the atomic absorption, two derived quantities
were particularly significant.

The first, the magnesium leaching degree (MLD) of the chryso-zeolite samples is defined as:

$$ \text{MLD} = \left( \frac{\text{MgO}}{100} \right) \times 100 \% $$

where \(( \text{MgO} )_i\) is the initial magnesium content in the asbestos fibers and \(( \text{MgO} )_f\) is the magnesium contents in the Alix or catalyst samples (based on the dried oxide).

The second is the \(( \text{Mat} / \text{Al} )\) atom ratio:

$$ \left( \frac{\text{Mat}}{\text{Al}} \right) = \frac{( \text{Si} ) + ( \text{Al} ) + ( \text{Na} ) + ( \text{Mg} ) + ( \text{Fe} )}{( \text{Al} )} $$

where \(( \text{Si} )\), \((\text{Al})\), \((\text{Na})\), \((\text{Mg})\) and \((\text{Fe})\) are numbers of atoms of each element in a dehydrated sample. In the case of the chryso-zeolite catalysts, this ratio could be seen as proportional to the reciprocal of the aluminum atom concentration, and thus acid site concentration.

$$ \left( \frac{\text{Mat}}{\text{Al}} \right) = \frac{\text{constant}}{( \text{Al}^- )} \sim \frac{\text{constant}}{( \text{H}^+ )} $$

The \(( \text{Mat} / \text{Al} )\) atom ratio is equivalent to the atomic ratio \(( \text{Si} / \text{Al} )\) commonly used for pure zeolites.

3.4.2 X-ray powder diffraction

The ZSM-5 zeolitic structure was identified by means of its characteristic diffraction pattern \((21, 25)\) (Figure 3.1 and 3.2). The catalysts (zeolite or chryso-
Figure 5.1: X-ray diffraction pattern of pure zeolite ZSM-5.
Figure 3.2: X-ray diffraction pattern of chrysoc-zeolite ZSM-5.
zeolite) were ground, mechanically mixed with NaCl (internal standard), in a ratio of 2:1 (by weight). The solid was evenly spreaded on a sample holder and the X-ray diffraction pattern recorded. An X-ray powder diffractometer was used (model: Philips PW 1050 / PW 1360, Cu Kα radiation, λ = 1.54178 Å, Ni filter) with an integration system. The counts recorded during a scanning of the peaks were used to evaluate the degree of crystallinity.

The degree of crystallinity (DC) of the ZSM-5 zeolite structure of the sample (pure and chryso-zeolite) was determined by a procedure similar to that of Kulkarni et al (26). To ensure that the measurement did not depend on sample preparation, NaCl was used as internal standard; this compound exhibits a strong diffraction peak at 2θ = 31.0 - 32.5. The pure ZSM-5 zeolite samples (HP-38, HP-68, HP-71 and HP-CAN 13) which had similar crystallinity, were assigned a 100% value of crystallinity.

3.4.3 Scanning Electron Microscopy (SEM)

Using a Hitachi Model S-20 SEM, the ZSM-5 particle was seen in the pure sample (HP sample). With the chryso-zeolite, the morphological change of our samples was followed: original asbestos fibers --> leached fibers (Alix) --> chryso-zeolite ZSM-5 catalyst. From the SEM observations, the size of the ZSM-5 particles was evaluated. These
observations also showed the overall aspect of the chrysotile zeolite samples. The SEM was necessary for ascertaining that the samples synthesized were not simply a mechanical mixture of "ZSM-5" and "unconverted asbestos".

3.4.4) Surface measurement (BET)

An important parameter in heterogeneous catalysis is the surface area of the catalyst (solid). Physical adsorption of nitrogen in a static system at liquid nitrogen temperature was used as proposed by Brunauer, Emmett and Teller (27). This technique was known as the BET method.

a) BET theory

The BET theory was based on several assumptions:
- homogeneous surface which could accommodate one adsorbate molecule per site,
- multilayer adsorption and no lateral interaction between adsorbed molecules,
- an adsorption – desorption equilibrium.

The physical and mathematical treatment of these hypothesis lead to the BET equation (28, 29):

\[
\frac{P}{V (P_0 - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \frac{P}{P_0}
\]

where \( P \) = pressure of the \( N_2 \) gas in equilibrium with the surface.
\( P_0 = \text{saturated vapor pressure of } N_2 \text{ at liquid } N_2 \) 
\( \text{temperature (77.3 K) with } P_0 = 760 \text{ mm Hg} \)

\( V = \text{volume of } N_2 \text{ (STP) adsorbed by the sample} \)

\( V_m = \text{volume of } N_2 \text{ (STP) corresponding to the} \)
\( \text{formation of a monolayer} \)

\( C = \text{constant varying with the adsorbent-adsorbate} \)
\( \text{interactions. It is related to the differential} \)
\( \text{heat of adsorption } E_A \text{and to the heat of} \)
\( \text{liquefaction } E_L \text{by the following relation:} \)

\[
C = \exp \left[ \frac{E_A - E_L}{RT} \right]
\]

where \( R = \text{ideal gas constant} \)
\( T = \text{absolute temperature} \)

From a plot of \( P/V(P_0 - P) \) versus \( P/P_0 \) at low partial pressure (0.05 < \( P/P_0 < 0.35 \)), a value of \( V_m \) could be deduced.

\[
V_m = \frac{1}{\text{(slope + intercept)}}
\]

This value of \( V_m \) (cm\(^3\) per gram) was used to evaluate the specific area of the solid:

\[
\text{area} = \frac{V_m}{22414} \times N \times A_m \times 10^{-20} \text{ (m}^2/\text{g)}
\]

where \( N = \text{Avogadro's number} \)

\( A_m = \text{area occupied by a nitrogen molecule. The most} \)
\( \text{widely accepted value 16.2 } \)Å\(^2\) (28) was used.
b ) Experimental set-up

The set-up (figure 3.3) was a classical apparatus used for static volumetric BET adsorption. It contained:
- a good vacuum source: mechanical pump with a diffusion pump (pressure < $10^{-3}$ mm Hg)
- a sample holder
- a volumetric part where volume of gas and pressure were measured
- a mechanical pump to change the level of mercury in the volumetric part of the apparatus.

c ) Experimental technique

1./ sample degassing: at 300°C for three hours under vacuum (P < $10^{-3}$ mm Hg)

2./ calibration of the dead-volume: helium was introduced in the BET apparatus. The sample chamber was closed. By changing the mercury level in the volumetric column, the corresponding pressure was recorded.

The dead volume X was calculated from:

\[ P_5 (V_5 + X) = P_6 (V_6 + X) \]

\[ X = \frac{P_5 V_5 - P_6 V_6}{P_6 - P_5} \]

where $P_5$ and $P_6$ are the pressures recorded (mm Hg) when the mercury was above the level 5 or 6.

$V_5$ and $V_6$ are the volumes above the level 5 or 6.
Figure 3.3: BET apparatus.
All the volumes measured were converted to STP assuming ideal behaviour.

The sample chamber was opened, and the mercury levels were changed. The pressure was recorded at each level. From these measurements, the free space was obtained (space available in the sample holder, between the zeolite particles at various pressures).

3. Nitrogen adsorption isotherm

The helium was evacuated from the system and was replaced by nitrogen. By keeping the sample chamber closed, the total nitrogen introduced was evaluated by measuring the pressure at various volumes. After the opening of the sample chamber, nitrogen was adsorbed on the sample which was cooled in liquid nitrogen (-195.8°C). The pressure was measured at various volumes and the partial pressures (P/Po) were evaluated as well as adsorbed volumes of nitrogen. From these results, the slope and the intercept of a P/(Po - P)V versus P/Po plot gave V_m, the volume of a monomolecular layer. The specific surface area of the different zeolite and chrysó-zeolite was calculated from V_m.
d) Results

The experimental readings were analysed using a computer program (BASIC language) in an Olivetti M24 computer (see appendix 1).

e) Pore filling and evaluation of external surface

In order to evaluate the external surface of the catalysts, the pore-filling method (30) was used. Benzene vapors were in contact with the zeolitic catalysts. These vapors entered in the porous solid and filled the cavities and the channels. Next, the samples were frozen to $-196 \degree$C (in liquid nitrogen) and left under vacuum for few hours in order to evacuate the benzene outside the particles. The benzene blocked the pores and stopped the penetration of $\text{N}_2$. The external surface was evaluated using the BET apparatus.

3.4.5) Adsorption of water and n-hexane

Doubly deionized water and n-hexane (Fisher reagent grade) were adsorbed on the samples. The technique adopted has been described by Le Van Mao et al. (31,32). After three hours of degassing at $300 \degree$C under vacuum, the samples were cooled to $25 \degree$C and brought into contact with the vapors (water or n-hexane) until equilibrium was reached. The sampling tubes were weighed and the equilibrium adsorption capacity (weight of adsorbed vapor per weight of
activated zeolite) was calculated. The operating conditions were reported in table 3.6.

Adsorption measurements were done on the catalysts in their H⁺ forms (zeolite and chryso-zeolite) and on the magnesium leached asbestos (Alix) which were used for the catalyst preparation. The relative affinity index (RAI) defined as the volume ratio of adsorbed n-hexane to adsorbed water in zeolites (pure and composite) was calculated. This index indicates the hydrophobic character of the ZSM-5 based materials (RAI > 1).(31-34)

3.4.6 Adsorption / temperature programmed desorption of ammonia (A/TPD)

To study the strength and density of the acid sites in the samples, ammonia was adsorbed on the H⁺ form of the catalysts (zeolite, chryso-zeolite and Alix samples) at room temperature or at 100 °C, and then desorbed by increasing the temperature (up to 450 °C, heating rate was 5 °C/min). This procedure was similar to that described by Hidalgo et al. (35).

Ammonia was chemisorbed on the acid site of the catalysts. To reduce the physisorption which occurred simultaneously (mainly at room temperature), a rigorous flushing with dry nitrogen was carried out prior to the desorption phase. During the NH₃ desorption operation, the nitrogen
<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Critical diameter (Å)</th>
<th>Vaporization temperature (°C)</th>
<th>Vapor pressure (mm Hg)</th>
<th>Adsorption temperature (°C)</th>
<th>Time required (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexane</td>
<td>4.9</td>
<td>0</td>
<td>45</td>
<td>25</td>
<td>3</td>
</tr>
<tr>
<td>water</td>
<td>2.8</td>
<td>22</td>
<td>22</td>
<td>25</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 3.6: Operating condition for the n-hexane or water adsorption.
stream, which carried the desorbed ammonia, was bubbled into a solution of diluted HCl. After the desorption step, this HCl solution was titrated with NaOH and the amount of NH\textsubscript{3} desorbed was calculated knowing the NaOH titer and the original HCl concentration. The amount of ammonia adsorbed at 100°C and then desorbed was believed to be related to acid sites of medium and strong character (35). The NH\textsubscript{3} adsorbed at room temperature corresponded to the overall acidity which should include weak sites.

3.4.7 Temperature programmed desorption of reactive species and detection by mass spectrometry (TPD/MS)

Temperature programmed desorption of methanol, dimethyl ether and light olefins was studied using a programmable furnace coupled to a mass spectrometer.

The catalysts were:

- pure zeolite: HP-CAN 13
- chryso-zeolite: HP-CAN 15 MLD = 99 %
  : HA-72 MLD = 92 %
  : HA-CAN 14 MLD = 86 %

These catalysts were saturated with either methanol (vapor at 15°C), dimethyl ether (1 % in He) or propylene (10 % in He) at room temperature.

The compounds were desorbed by increasing the temperature from 25 to 600°C (rate up to 150°C/min) in the
presence of an inert carrier gas (He). The various species were detected by MS. The temperature at which they desorbed was measured.

3.4.8) Si Magic Angle Spinning NMR

NMR spectra were obtained on a Varian VXR 300 FT-NMR spectrometer operating at 59.592 MHz, equipped with a superconducting solenoid magnet. A computer system (model VXR 4000) was used for data acquisition and as amplifiers for final rf pulse generation. $^{29}$Si MASS - NMR spectra were obtained with Kel-F Doty probes (Doty Scientific) at a spinning speeds of 451 KHz. All $^{29}$Si line positions (chemical shifts) were referred to TMS (tetramethylsilane).

The samples used for analysis were:
- pure zeolite ZSM-5 (HP-CAN 10).
- pure zeolite ZSM-5 + Mg added by wet impregnation (HP-CAN 13 / Mg)
- pure zeolite ZSM-5 + Mg solution added to the silica gel before the synthesis (HP-96)
- chryso-zeolite, MLD = 76 % (HA-95)
- chryso-zeolite, MLD = 86 % (HA-CAN 14)
Catalytic tests were performed by injecting methanol (without any further purification or dehydration) with the help of injection syringe (50 ml) on an infusion pump (Sage Instrument, pump model 341 A) into a methanol vaporizer gas mixer (set at 150°C). Dry Nitrogen gas was supplied to the methanol vaporizer and gas mixer from a cylinder connected in-line with a flowmeter. The vaporized methanol was then carried by the nitrogen gas through a fixed catalyst bed set in a catalytic reactor contained inside an oven which was thermoregulated. A chromel-alumel thermocouple in conjunction with a digital thermometer unit was placed in the catalyst to monitor the temperature of the bed. The gaseous mixture flowing out of the catalytic reactor was run through a series of condensers maintained at 5–10°C, to a liquid collector immersed in an ice bath followed by a cylinder from which gas sampling was carried out (figures 3.4 and 3.5).

Catalytic tests were performed at atmospheric pressure in this experimental set-up. Some runs were done at higher pressure (up to 450 psi or 30 atm) with an apparatus designed specially for reactions above atmospheric pressure (figure 3.6).

During a run, the liquid products were collected in a flask and the gases were analysed periodically by gas
Figure 5.4: Experimental set-up for reaction at atmospheric pressure.
Figure 3.5: Configuration and size of the reactor.
Figure 3.6: Experimental set-up for high pressure reaction (up to 1000 psi).
chromatography with a 2.5 m long column (Chromosorb P AW-DMCS coated with 20% by weight of squalane). The GC was a dual FID Hewlett-Packard model 5790, coupled to a 3392 A HP integrator. The gas chromatograph was also equipped with a capillary column (PONA type fused silica coated with a crosslinked methyl silicane liquid phase, 50 m long) used for accurate analysis of the liquid fractions (organic and aqueous) after a run was completed. The composition of the aqueous layer was determined from a methanol in water external standard.

- Catalytic testing

Table 3.7 reports the reaction conditions used in the first two parts of the research:

- preparation and catalytic testing of zeolites or chryso-zeolite ZSM-5 catalysts.
- preparation and catalytic testing of metallic catalysts (zeolites or chryso-zeolite ZSM-5 containing Zn and/or Mn).

In table 3.8, the reactions conditions were reported when the various reaction parameters were studied.

From the chromatograms, the conversion of methanol, the conversion to hydrocarbons and the selectivities were calculated using a carbon atom basis. The routine calculations were done using a computer program (BASIC language) and an Olivetti M24 P.C. (see appendix 2).
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst (weight)</td>
<td>4 g (dry)</td>
</tr>
<tr>
<td>Temperature</td>
<td>350 - 500 °C</td>
</tr>
<tr>
<td>Total pressure</td>
<td>1 atm.</td>
</tr>
<tr>
<td>Methanol pressure</td>
<td>0.9 atm.</td>
</tr>
<tr>
<td>Inert carrier gas</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>W.H.S.V. *</td>
<td>2.4 h⁻¹</td>
</tr>
<tr>
<td>Reaction duration</td>
<td>4 hrs</td>
</tr>
</tbody>
</table>

*W.H.S.V.: Weight hourly space velocity

\[
g \text{ of methanol injected per hour} \div g \text{ of catalyst}
\]

Table 3.7: Reaction parameters used in the catalytic testing.

<table>
<thead>
<tr>
<th>Parameter studied</th>
<th>Parameter set</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp (°C)</td>
</tr>
<tr>
<td>Temp</td>
<td>300-500</td>
</tr>
<tr>
<td></td>
<td>400</td>
</tr>
<tr>
<td>L.H.S.V.</td>
<td>400</td>
</tr>
<tr>
<td>P_{MeOH}</td>
<td></td>
</tr>
</tbody>
</table>

* L.H.S.V.: Liquid hourly space velocity

\[
\text{volume of liquid methanol injected per hour (mL/hr)} \div \text{volume of catalyst (mL)}
\]

Table 3.8: Experimental setting to study the effect of reaction parameters.
- **Durene evaluation using GC/MSD**

The production of durene (1,2,4,5-tetramethylbenzene) was evaluated at various pressures (ranging from atmospheric to 450 psi). In order to determine the durene content, external standards and organic liquid phases obtained from various reactions were injected in a GC-MSD (Hewlett-Packard 5890 GC and mass selective detector 5970) equipped with a PONA capillary column. The exact durene content was obtained from a calibration curve.

- **Influence of the external diffusion**

In order to evaluate the influence of the external mass transfer, reactions were performed using different sizes of catalyst (HA-ÇAN 14). The sizes of the pellets were in the range:
- large = up to 8 mesh,  
- medium = 10 to 20 mesh,  
- small = 30 to 60 mesh.

The experimental conditions used were:

\[
\text{WHSV} = 2 \text{ h}^{-1}
\]

\[
\text{PMeOH} = 0.9 \text{ atm}
\]
- **Activation energy**

To evaluate the apparent activation energy ($E_{app}$), catalytic runs were performed with two catalysts:

- HP-CAN 13 (pure zeolite ZSM-5)
- HA-CAN 14 (MLD = 86%)

In order to evaluate the initial rate ($r_0$), the space time ($\tau = \frac{w}{F}$ = weight catalyst / feed mole methanol per hour) was varied keeping the partial pressure of the reactant constant. The conversion to hydrocarbons was evaluated at different temperatures (minimum of 2). $r_0$ was obtained from the slope at low $\tau$ using computer fitting program to a polynomial curve (see appendix 3).

- **Identification of primary products of the reaction**

To determine the initial product(s), reactions were performed under conditions where low conversion was obtained:

- temperature: 250°C
- methanol partial pressure: 0.1 to 0.2 atm
- residence time: between 0.05 to 0.1 min.

The ratio of ethylene / propylene was determined at various times of the reaction.
Chapter 4: Results and discussion

4.1 Preparation of Aliz

Starting from short chrysotile asbestos fibers, crystalline alumino-silicate materials can be prepared. Prior to the synthesis of the zeolitic structure, the asbestos fibers were submitted to a leaching process.

The chrysotile asbestos material has a well organized structure, made of sheets of Si and Mg as shown in figure 4.1. This magnesium silicate has the following theoretical chemical composition:

\[ \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 \]

It also contains some impurities such as iron oxide (FeO, Fe_2O_3 or Fe_3O_4) which can account for 10% of the weight in some cases. Other metals can be present in trace amount (Al, Ni for example) (table 4.1).

As can be seen in figure 4.1, free magnesium hydroxide (brucite) are inserted in the Mg layer and coexist with the Mg atoms which are bound to the tetrahedrally coordinated silicon atoms through oxygen bridges. These magnesium hydroxide molecules constitute the weak points for the acid attack in the Mg leaching
Figure 4.1: Structure of the chrysotile asbestos fiber.
### Chemical composition (dried oxide basis)

<table>
<thead>
<tr>
<th></th>
<th>% wt/wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>42.8</td>
</tr>
<tr>
<td>MgO</td>
<td>50.2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>6.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.1</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.1</td>
</tr>
<tr>
<td>Others</td>
<td>0.2</td>
</tr>
</tbody>
</table>

*As FeO and Fe₃O₄

**Table 4.** Chemical composition of 7 TF 12 asbestos fiber (dried oxide basis).
process. This leaching process increases the total surface area of the fibers by creating some micropores in the asbestos (see figure 4.2) (41).

In the present case, the acid was HCl. Other acids such as H2SO4 or CH3COOH can be used as leaching agents (41, 42). By varying the acid concentration or the contact time, it was possible to change the amount of Mg extracted from the chrysotile fibers (see table 3.2).

During the Mg leaching, some SiO2 can be released, along with the Mg, to the acid medium. After the leaching operation, the acid medium was diluted with water and left to settle for several hours. During this step, a slow deposition of free SiO2 on the asbestos remnants occurred. No loss of silicon was measured during the leaching operation. In addition, scanning electron microscopy analysis of the Alix samples did not show silica aggregates (see figure 4.3) except for very high MLD values. This redeposition of SiO2 can be the starting point for the zeolite crystallization.

In order to produce chryso-zeolite ZSM-5 which are efficient in the MTG process under normal conditions (temperature, contact time), a MLD of 75 to 80 % or higher, was necessary. Below that MLD, poor activity of the chryso-zeolite catalyst is observed. The presence of a zeolitic structure with acid sites (active sites) is essential to obtain a conversion into hydrocarbons. The
Figure 4.2: Surface area of leached asbestos (Alix) versus MLD.
Figure 4.3: Scanning electron micrograph of an Alix sample (Alix.013, MLD: 92%).
(magnification x'700)
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Alix 018 (80%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol conversion</td>
<td>12%</td>
</tr>
<tr>
<td>Products:</td>
<td></td>
</tr>
<tr>
<td>$\text{C}_1$ - $\text{C}_4$ paraffins</td>
<td>33% *</td>
</tr>
<tr>
<td>$\text{C}_2$ - $\text{C}_4$ olefins</td>
<td>8%</td>
</tr>
<tr>
<td>liquids</td>
<td>4%</td>
</tr>
<tr>
<td>dimethyl ether</td>
<td>55%</td>
</tr>
</tbody>
</table>

*mainly methane

Table 4.2: Catalytic activity of an Alix sample.
( temp: 400°C; WHSV: 2.4 h⁻¹ )
Alix sample showed no catalytic activity. A dehydration of methanol to dimethyl ether was observed at normal temperature (400 °C) (see table 4.2).

4.2) Zeolite and Chryso-zeolite ZSM-5 Catalysts

The catalytic behavior of the zeolite ZSM-5 depended on their chemical composition, structure and surface properties. All these influence the ability of a catalyst to convert methanol into hydrocarbons.

4.2.1) Chemical composition

Tables 4.3 and 4.4 report the chemical characteristics of the samples studied. The label HP represents the catalysts (in the H⁺ form) made from silica gel (pure zeolite ZSM-5). HA stands for catalysts (under the H⁺ form) prepared from leached 7 TF 12 asbestos fibers. These catalysts had similar Mat/AL (or Si/Al) molar ratios, which were in the 15-35 range.

The content in sodium had to be low (Na₂O < 0.4 wt %) to obtain an active catalyst.

The main difference between the two types of zeolite catalysts was the presence of magnesium (and iron) in the chryso-zeolite catalysts. By using the above mentioned leaching techniques, the amount of Mg left in the asbestos
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>SiO₂ (%)</th>
<th>Al₂O₃ (%)</th>
<th>Na₂O (%)</th>
<th>Mat/Al</th>
<th>Si/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP-38</td>
<td>98.14</td>
<td>3.03</td>
<td>0.09</td>
<td>28.1</td>
<td>27.5</td>
</tr>
<tr>
<td>HP-68</td>
<td>97.17</td>
<td>2.57</td>
<td>0.17</td>
<td>32.7</td>
<td>32.1</td>
</tr>
<tr>
<td>HP-71</td>
<td>96.98</td>
<td>2.89</td>
<td>0.13</td>
<td>29.6</td>
<td>28.5</td>
</tr>
<tr>
<td>HP-CAN-13</td>
<td>96.79</td>
<td>3.01</td>
<td>0.20</td>
<td>28.4</td>
<td>27.3</td>
</tr>
</tbody>
</table>

MgO and Fe₂O₃ not detected.

Table 4.3: Chemical composition of the pure zeolite ZSM-5 samples.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Alix sample</th>
<th>MLD</th>
<th>SiO₂ (Z)</th>
<th>Al₂O₃ (Z)</th>
<th>Na₂O (Z)</th>
<th>MgO (Z)</th>
<th>Fe₂O₃ (Z)</th>
<th>MLD</th>
<th>Mat/Al</th>
<th>Si/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA-39</td>
<td>001/2</td>
<td>98</td>
<td>95.11</td>
<td>2.94</td>
<td>0.08</td>
<td>1.33</td>
<td>0.54</td>
<td>97.4</td>
<td>28.7</td>
<td>27.5</td>
</tr>
<tr>
<td>HA-45</td>
<td>013</td>
<td>92</td>
<td>90.92</td>
<td>2.40</td>
<td>0.12</td>
<td>3.12</td>
<td>3.44</td>
<td>93.8</td>
<td>34.9</td>
<td>32.2</td>
</tr>
<tr>
<td>HA-62</td>
<td>025</td>
<td>94</td>
<td>91.26</td>
<td>3.23</td>
<td>0.27</td>
<td>3.10</td>
<td>2.13</td>
<td>93.8</td>
<td>26.0</td>
<td>24.0</td>
</tr>
<tr>
<td>HA-56</td>
<td>020/2</td>
<td>93</td>
<td>90.06</td>
<td>3.82</td>
<td>0.12</td>
<td>3.65</td>
<td>2.33</td>
<td>92.7</td>
<td>22.0</td>
<td>20.0</td>
</tr>
<tr>
<td>HA-58</td>
<td>024</td>
<td>88</td>
<td>86.03</td>
<td>2.91</td>
<td>0.17</td>
<td>5.99</td>
<td>4.90</td>
<td>88.1</td>
<td>28.8</td>
<td>25.1</td>
</tr>
<tr>
<td>HA-49</td>
<td>018/1</td>
<td>87</td>
<td>84.32</td>
<td>3.49</td>
<td>0.14</td>
<td>6.29</td>
<td>5.80</td>
<td>87.5</td>
<td>23.9</td>
<td>20.5</td>
</tr>
<tr>
<td>HA-54</td>
<td>018/2</td>
<td>88</td>
<td>83.53</td>
<td>3.02</td>
<td>0.17</td>
<td>6.85</td>
<td>6.43</td>
<td>86.4</td>
<td>27.6</td>
<td>23.5</td>
</tr>
<tr>
<td>HA-64</td>
<td>027</td>
<td>81</td>
<td>85.66</td>
<td>2.78</td>
<td>0.16</td>
<td>7.50</td>
<td>4.43</td>
<td>85.1</td>
<td>36.8</td>
<td>31.9</td>
</tr>
<tr>
<td>HA-69</td>
<td>030</td>
<td>82</td>
<td>81.70</td>
<td>3.41</td>
<td>0.15</td>
<td>7.90</td>
<td>6.84</td>
<td>84.2</td>
<td>24.5</td>
<td>20.4</td>
</tr>
<tr>
<td>HA-48</td>
<td>017</td>
<td>80</td>
<td>82.98</td>
<td>3.55</td>
<td>0.14</td>
<td>7.95</td>
<td>5.38</td>
<td>84.2</td>
<td>23.8</td>
<td>19.9</td>
</tr>
<tr>
<td>HA-60</td>
<td>016</td>
<td>80</td>
<td>81.15</td>
<td>2.23</td>
<td>0.35</td>
<td>9.87</td>
<td>6.20</td>
<td>80.4</td>
<td>38.1</td>
<td>30.9</td>
</tr>
<tr>
<td>HA-72</td>
<td>032</td>
<td>92</td>
<td>87.87</td>
<td>3.38</td>
<td>0.15</td>
<td>3.90</td>
<td>4.70</td>
<td>92.2</td>
<td>25.5</td>
<td>22.1</td>
</tr>
<tr>
<td>HA-73</td>
<td>034</td>
<td>85</td>
<td>84.84</td>
<td>3.41</td>
<td>0.10</td>
<td>8.59</td>
<td>3.06</td>
<td>82.9</td>
<td>26.0</td>
<td>21.1</td>
</tr>
<tr>
<td>HA-CAN-14</td>
<td>071</td>
<td>82</td>
<td>82.11</td>
<td>4.60</td>
<td>0.37</td>
<td>6.68</td>
<td>6.24</td>
<td>86.7</td>
<td>19.0</td>
<td>15.2</td>
</tr>
<tr>
<td>HA-CAN-15</td>
<td>066</td>
<td>95</td>
<td>91.36</td>
<td>2.94</td>
<td>0.16</td>
<td>0.62</td>
<td>4.92</td>
<td>98.8</td>
<td>28.8</td>
<td>26.4</td>
</tr>
</tbody>
</table>

Table 4.4: Chemical composition of the chryso-zeolite ZSM-5 samples.
remnants (Alix) or the others elements present could be controlled. During the synthesis of the chryso-zeolite, the MLD could change and increase by few percent. It was possible that during the leaching process, some Mg was extracted but not washed out when filtered. During the synthesis, this Mg was released in the solution. Except for small changes observed in the magnesium content, the chemical composition stayed constant (see table 4.5) and could be controlled.

This free magnesium present in the synthesis suspension did not interfere with the growth of the ZSM-5 particles. A zeolite catalyst was synthesized (starting from silica) in the presence of Mg$^{2+}$. The degree of crystallinity of the final product was high. The content in Mg was low (0.32 wt % MgO). The magnesium was probably ion exchanged into the zeolite. The excess of Mg in solution was washed out by rinsing after the synthesis.
<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Na₂O</th>
<th>MgO</th>
<th>Fe₂O₃</th>
<th>MLD</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlIX 025</td>
<td>90.6</td>
<td>0.32</td>
<td>0.14</td>
<td>2.95</td>
<td>2.57</td>
<td>94</td>
</tr>
<tr>
<td>HA-62</td>
<td>91.3</td>
<td>3.23</td>
<td>0.27</td>
<td>3.10</td>
<td>2.13</td>
<td>94</td>
</tr>
<tr>
<td>AlIX 030</td>
<td>83.7</td>
<td>0.22</td>
<td>0.16</td>
<td>8.99</td>
<td>6.98</td>
<td>82</td>
</tr>
<tr>
<td>HA-69</td>
<td>81.7</td>
<td>3.41</td>
<td>0.15</td>
<td>7.90</td>
<td>6.84</td>
<td>84</td>
</tr>
</tbody>
</table>

Table 4.5: Comparison of the chemical composition of the AlIX (precursor) and of the chyso-zolite catalyst.
4.2.2 ) Physical properties

Physical properties such as the crystallinity and the particle size may influence the catalytic performance of the solids. Therefore, it is necessary to measure those parameters in order to better understand the behaviour of the catalysts.

a ) Zeolite ZSM-5

Table 4.6 reports the physical properties of the HP catalysts (pure zeolite ZSM-5). The general aspect is seen in figure 4.4.

The surface area of the ZSM-5 synthesized at Concordia was in the 410 m²/g range which was the expected value (30). Because the material was porous, this surface was mainly located inside the particles. The outside represented only 1 to 2% of the total surface.

The degree of crystallinity was assumed to be 100%. HP catalysts were used as external standards to evaluate the crystallinity of the chryso-zeolite synthesized in the laboratory. The samples of pure zeolite ZSM-5 had a similar degree of crystallinity when compared with each other.

The particle size was obtained by scanning electron microscopy. The general aspect of the ZSM-5 particles was seen at high magnification.

The crystallization of the zeolite ZSM-5 was influenced by many factors (43, 44). The formation of a
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Degree of crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP-38</td>
<td>set at 100</td>
</tr>
<tr>
<td>HP-68</td>
<td></td>
</tr>
<tr>
<td>HA-39</td>
<td>86</td>
</tr>
<tr>
<td>HA-45</td>
<td>91</td>
</tr>
<tr>
<td>HA-62</td>
<td>100</td>
</tr>
<tr>
<td>HA-56</td>
<td>86</td>
</tr>
<tr>
<td>HA-58</td>
<td>88</td>
</tr>
<tr>
<td>HA-69</td>
<td>90</td>
</tr>
<tr>
<td>HA-54</td>
<td>86</td>
</tr>
<tr>
<td>HA-64</td>
<td>96</td>
</tr>
<tr>
<td>HA-69</td>
<td>99</td>
</tr>
<tr>
<td>HA-48</td>
<td>84</td>
</tr>
<tr>
<td>HA-60</td>
<td>83</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Degree of crystallinity</th>
<th>Total surface area (m²/g)</th>
<th>External surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP-71</td>
<td>set at 100%</td>
<td>414</td>
<td>-</td>
</tr>
<tr>
<td>HP-CAN-13</td>
<td></td>
<td>432</td>
<td>5 (1)</td>
</tr>
<tr>
<td>HA-72</td>
<td>92 *</td>
<td>393</td>
<td>-</td>
</tr>
<tr>
<td>HA-73</td>
<td>67 *</td>
<td>320</td>
<td>-</td>
</tr>
<tr>
<td>HA-CAN-14</td>
<td>63 **</td>
<td>316</td>
<td>60 (2)</td>
</tr>
<tr>
<td>HA-CAN-15</td>
<td>75 **</td>
<td>394</td>
<td>14</td>
</tr>
</tbody>
</table>

* degree of crystallinity based on pure ZSM-5 HP-71
** degree of crystallinity based on pure ZSM-5 HP-CAN-13

(1) density : 2.04 g/cm³
(2) density : 2.09 g/cm³

Table 4.6: Physical properties of zeolite and chrysanthemite used as catalysts.
Figure 4.4: SEM of a pure zeolite ZSM-5 (HP-38).
(magnification x 10000)
pure phase product occurred only in a narrow interval of reagents. Romannikov et al. studied the effect of the molar ratio on the crystallization of ZSM-5:
- OH / SiO₂ should be low to get ZSM-5. At higher ratio, other zeolitic structures were detected like mordenite (a large pore zeolite).
- the templating organic cation tetrapropylammonium bromide (TPA Br) did not interfere with the selectivity of the synthesis. Only ZSM-5 was obtained. But TPA influenced the rate of crystallization and the particle size (44).
- an increase in the SiO₂ / Al₂O₃ ratio increased the rate of crystallization.

The time required for the synthesis of ZSM-5 depends on the initial molar ratio of the reactants which influenced the rate. Since the aluminum content in the catalysts was high, a long period of time (10 days) in autoclave was used to obtain a complete crystallization during the hydrothermal synthesis.

The synthetic zeolite ZSM-5 has an exceptional structure and activity. The only weak point is the cost of production. The templating agent which gave the unique structure was expensive. Some attempts have been made to find new routes for the synthesis of ZSM-5 (45, 46) and this problem is still under investigation.
b) Chryso-zeolite ZSM-5

The properties of the chryso-zeolite catalysts are reported in table 4.6. The general appearance of the chryso-zeolite can be seen in figures 4.5 and 4.6.

The degrees of crystallinity of the chryso-zeolite ZSM-5 were obtained from HP catalysts as external standards. The crystallinities were close to the standards. No fixed trend was observed for the synthesis of chryso-zeolite but a lower degree of crystallinity was measured at low MLD. By reducing the attack of the acid, the Alix samples showed smaller surface areas. Therefore, it is possible to suppose that less Si is free and accessible for synthesis.

This is also seen with the surface of the chryso-zeolite catalysts. When the MLD decreased, a smaller total surface area was measured. But, the external surface increased due to the presence of the asbestos remnants, representing between 15 to 20% of the total surface. The surface is expressed in m² per gram of solid. In the chryso-zeolite catalyst, some unleached asbestos is still present. These remnants, containing Mg, could change the configuration of the solid, limited the crystallization by giving smaller particles, therefore lowering the total surface of the catalysts. In order to get a trend, more measurements on chryso-zeolites are needed. Unfortunately, the amount of chryso-zeolite initially synthesized was limited.
Figure 4.5: SEM of a chryso-zeolite ZSM-5.
(HA-39, MLD = 97%)
(magnification x20000.)
Figure 4.6: SEM of a chryso-zeolite ZSM-5 (HA-49, MLD = 87%). (magnification x 20000)
Scanning electron microscopy studies showed that the leached asbestos (Alix) retained the fibrous form of the original chrysotile asbestos even at a high magnesium leaching degree (41). Nevertheless, the Alix samples should bear some holes or cracks (be more porous) since a larger surface area was measured by BET when the MLD increased. After the synthesis, the composite ZSM-5/asbestos samples had a degraded structure. Submicron ZSM-5 zeolite particles were embedded in the asbestos remnants, which looked like blocks of a few microns in size. These submicron zeolite particles decreased in size as the magnesium leaching degree decreased (see table 4.7).

In order to produce chryso-zeolite ZSM-5, the ratios of the initial reactants should be within a certain range (23). The influence of each reactant on the synthesis of chryso-zeolite ZSM-5 was not specifically studied. They should have the same effects as with pure ZSM-5.

4.2.3) Surface properties of zeolites and chryso-zeolites

The sorption capacities of the catalysts for water and n-hexane and the acidity (adsorption of ammonia) were evaluated.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>MLD (%)</th>
<th>Zeolite particle size (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP-68</td>
<td>-</td>
<td>1 - 2</td>
</tr>
<tr>
<td>/ HA-62</td>
<td>94</td>
<td>0.1</td>
</tr>
<tr>
<td>HA-58</td>
<td>88</td>
<td>0.05</td>
</tr>
<tr>
<td>HA-69</td>
<td>84</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 4.7: Zeolite particle size of pure zeolite and chryso-zeolite ZSM-5 catalyst (obtained by SEM).
\[ a) \text{ Adsorption of water and } n\text{-hexane} \]

The sorption capacity of the catalysts HP and HA for \( H_2O \) and \( n\text{-C}_6\text{H}_6 \) was evaluated (see table 4.8).

With the relative affinity index (RAI), the hydrophobicity of the HP and HA catalysts, which had similar Si/Al ratio, was determined. According to Le Van Mao (31), a hydrophobic ZSM zeolite (ZSM-5 or ZSM-11) was defined by a RAI equal or greater to one. With the chryso-zeolite, the RAI values decreased at lower MLD. This suggested that the hydrophobicity of the composite catalyst was closely dependant upon the magnesium content. At lower MLD, the chryso-zeolite were more hydrophilic. A similar behavior observed with the Alix samples strongly supported this statement. Adsorption of water could occur on the asbestos remnants.

\[ b) \text{ Adsorption of ammonia} \]

To evaluate the acidity of the various zeolites used as catalysts, the adsorption/desorption of ammonia was studied (table 4.9).

With the composite samples, the \( \text{NH}_3 \) adsorption was higher at lower magnesium leaching degree both for room temperature and 100°C operation, while the Alix samples exhibited low adsorption of ammonia.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>MLD (%)</th>
<th>n-Hexane (wt/wt)</th>
<th>Water (wt/wt)</th>
<th>RAI</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP-68</td>
<td></td>
<td>5.35</td>
<td>8.04</td>
<td>1.01</td>
</tr>
<tr>
<td>HA-39</td>
<td>97</td>
<td>8.86</td>
<td>7.03</td>
<td>1.91</td>
</tr>
<tr>
<td>HA-45</td>
<td>94</td>
<td>9.24</td>
<td>7.94</td>
<td>1.91</td>
</tr>
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<td>HA-56</td>
<td>98</td>
<td>7.88</td>
<td>7.91</td>
<td>1.51</td>
</tr>
<tr>
<td>HA-58</td>
<td>88</td>
<td>8.30</td>
<td>9.24</td>
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<td>10.28</td>
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<td>1.59</td>
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<tr>
<td>Alix 013</td>
<td>92</td>
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<td>5.48</td>
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<tr>
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<td>80</td>
<td>7.63</td>
<td>8.12</td>
<td>1.42</td>
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</table>

* RAI: Relative Affinity Index  
  n-hexane / water (vol/vol) of relative adsorption affinity index

Table 4.8: Water and n-hexane sorptive capacities of the HP and HA samples.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>MLD (%)</th>
<th>$Z_a :$ amount of NH$_3$ adsorbed $^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>room temp $Z_a (x \times 10^4)$</td>
</tr>
<tr>
<td>HP-68</td>
<td>97</td>
<td>1.36 0.27</td>
</tr>
<tr>
<td>HA-39</td>
<td>94</td>
<td>0.99 0.17</td>
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</tr>
<tr>
<td>Alix 016</td>
<td>80</td>
<td>0.79 0.60</td>
</tr>
</tbody>
</table>

$^*$ Expressed in $10^{-6}$ mol of NH$_3$/g of catalyst.

$^{**} Z_a/Z_{Al}$ is the ratio of the molar amount of NH$_3$ adsorbed to the molar amount of Al present in 1 g of catalyst.

n.b.: With HP and HA samples, circa 95% NH$_3$ desorbed at 423 - 473 K and circa 5% at 673-723 K.

Table 4.9: Ammonia adsorption / temperature programmed desorption studies.
c) Influence of the composition on the surface properties

The behavior of the chryso-zeolite catalysts (hydrophobicity and adsorption of NH$_3$) could be related to the presence of basic sites (from MgO) along with the acid sites (from the zeolite) (34). The simultaneous presence of basic and acidic sites within the catalyst favored the lower hydrophobicity and the greater adsorption of NH$_3$. With the Alix samples, the adsorption of NH$_3$ was not dependent on the MLD. The presence of both types of active sites, MgO and H$, could give a different adsorption of the species (ammonia or methanol) on the chryso-zeolite (34). The influence of MgO will be discussed later, with the results of the catalytic testing.

4.2.4) Effect of physico-chemical properties of the catalysts in the conversion of methanol to hydrocarbons

The conversion of methanol to hydrocarbons is an acid-catalysed reaction. It occurs on solid acid catalysts like zeolite ZSM-5. Therefore, the acidic properties of the catalysts will have a large influence on the conversion of the alcohol and the synthesis of hydrocarbons.
a) Effects of the chemical properties

Acidic properties will depend on the chemical composition. The presence of a proton neutralizing the negative charge generated on the Al in the zeolite is at the origin of the Bronsted acidity. Therefore, by changing the content in Al, the acidity will change. The Mat/Al (or Si/Al) as an influence on the activity and selectivity. Chang et al. (47) studied the effect of zeolite SiO₂/Al₂O₃ keeping the other reaction parameters constant (temperature, pressure, contact time). By varying the silica to alumina molar ratio from 35 to 1670 (therefore lowering the acid density), they observed a reaction path similar to the one established by changing the contact time (9) (see figures 4.7 and 4.8).

In the present case, the catalysts (zeolite and chryso-zeolite) had a Mat/Al ratio in the 15-35 range. At this ratio, the conversion towards final products (aromatics and paraffins) was favored. Only catalysts in that Mat/Al (or Si/Al) range were studied. Varying the Mat/Al ratio of the chryso-zeolite by changing the Al content, while the other reaction parameters are held constant, should have the same effects than those observed with pure zeolite by Chang et al.

Lin et al. (48) studied the distribution of the silicon to aluminum ratios in the zeolite ZSM-5. They measured the
Figure 4.7: Methanol conversion over HZSM-5. Hydrocarbon selectivity. (temp = 371°C, 1 atm, 1 LHSV)

\[
\frac{n}{2} \left( 2 \text{CH}_3\text{OH} \right) \leftrightarrow \text{CH}_3\text{QCH}_3 + \text{H}_2\text{O}
\]

\( - \text{H}_2\text{O} \)

\( \text{C}_n\text{H}_{2n} \) (olefins)

\( \downarrow \)

\( n \left( \text{CH}_2 \right) \)

where \( \text{(CH}_2 \) \) is the average formula of aromatic-paraffins mixture

Figure 4.8: Reaction path of the conversion of methanol.
variation of the Si / Al ratio by using electron microprobe analysis (EPMA) and Auger electron spectroscopy (AES). They concluded that the dispersion of the Si / Al ratio across an individual single crystal was homogeneous. Their results were valid for surface measurements obtained by Auger spectroscopy.

As observed by other workers (Dwyer, von Ballmoos, Derouane, see reference 48) the inhomogeneity of aluminum concentration lay between the crystal rather than within a single crystal. They observed a gradient in the Al content which depended on the synthesis method. Silicon rich layers (low Al content) were observed surrounding zeolite particles. They occurred by deposition of Si on the crystals upon cooling. In other cases, as the Si / Al initial molar ratio increased, the variation of the aluminum content between the zeolite particles also increased. During their study, they concluded that the rate of crystallization of the zeolite ZSM-5 in an Al rich environment was slower than in an Si rich environment. Their results were in agreement with those published by Romannikov et al (44).

The hydrophobicity of the zeolite was also related to the silicon to aluminum ratio. Zeolite A or X which had a low Si / Al ratio (equal to 1 or 2) were hydrophilic. ZSM-5 with a high Si / Al was rather hydrophobic. Therefore, the water vapor formed during the conversion of
methanol should not have a noticeable effect on the catalysts. Over a long period of time, a steaming and a dealumination of the zeolite ZSM-5 should occur. This phenomenon was called the irreversible band aging.

With the chryso-zeolite catalysts at low MLD, a more rapid decrease in activity was observed. When a large amount of water vapor was present, it was preferentially adsorbed on the catalyst. The presence of MgO could enhance the adsorption of water (and other species like ammonia or methanol), as shown in tables 4.8 and 4.9. This greater adsorption could favor a dealumination, and be responsible for a more rapid decay of the catalyst (table 4.10).

The coordination of some aluminum located inside the zeolite particle was changed from a tetrahedral to an octahedral in presence of water (66) and therefore altered its catalytic properties.

The acidity could also be changed by varying the amount of sodium exchanged on the catalysts (47). A high concentration of Na⁺ means a lower concentration of H⁺, a lower acid density. A high selectivity toward light olefins was observed with sodium rich zeolite.

In some zeolite and chryso-zeolite catalysts prepared in the laboratory, the Na⁺ content was high even after ammonium exchange and activation in air. These catalysts exhibited low conversion (presence of dimethyl ether in the gas phase) and a high selectivity toward light olefins as hydrocarbon products at normal temperature (400°C). In
<table>
<thead>
<tr>
<th>Run</th>
<th>Conversion of ReOH. to HC</th>
<th>Selectivity</th>
<th>C&lt;sub&gt;1&lt;/sub&gt;-C&lt;sub&gt;4&lt;/sub&gt;</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;4&lt;/sub&gt; ole.</th>
<th>Arom.</th>
<th>C&lt;sub&gt;5&lt;/sub&gt; alkyls</th>
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<tr>
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<td>47.3</td>
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<td>8.0</td>
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<td>11.4</td>
<td>42.4</td>
<td>4.2</td>
<td>20.0</td>
</tr>
</tbody>
</table>

Table 4.10: Influence of steaming on the catalyst activity and selectivity.
(catalyst: HA-CAN 14 (50% zeolite), MLD=86 %
temp: 400°C,
WHSV: 2.5 h⁻¹)
order to avoid variation in activity and selectivity due to a different acidity when the two types of zeolite were compared, an acceptable sodium content in the catalysts was set at 0.4% by weight of Na₂O (or lower) as measured by atomic adsorption.

To control the selectivity of zeolite catalysts, several groups tried various ways to change the acidity of pentasil zeolite. The presence of phosphorous compounds (trimethyl phosphite, orthophosphoric acid) (49, 50) on the zeolite acid sites could neutralize them, lowered the acidity of the catalysts, increased the shape-selectivity and therefore favored the production of light olefins. Bórön pentasil zeolites showed lower acidity than Al in ZSM-5. The introduction of B in the zeolitic structure and reduction of the Al content gave catalysts with high selectivity for light olefins in the conversion of methanol. More simply, a dealumination in presence of water vapor or acid gave a lower acidity, increasing the selectivity toward primary products (olefins).

Building of coke on the catalysts influenced the selectivity. When the conversion of methanol was done over an extended period of time (many days), a significant carbon build-up occurred on the surface of the zeolite catalysts. This carbon deposit (or coke) was found inside and outside the zeolite particles (51, 52). It could block the access of methanol to the acid sites (pore
Figure 4.7: Conversion of methanol to hydrocarbons versus the time of the reaction (regeneration after 940 min).
(catalyst: HA-CAN+4 (80% zeolite), 400°C, WHSV = 2.5 h⁻¹)
blockage), lower the acidity and cause deactivation of the catalyst (see figure 4.9). As the conversion to hydrocarbons decreased, the formation of primary products was favored at the expense of liquids (mainly aromatics).

Several techniques exist to evaluate the acidity of the various zeolites: infrared spectroscopy (53), microcalorimetry (54), adsorption/desorption of a base. In the present work, the latter was used to measure the acidity of the zeolite and chryso-zeolite ZSM-5. The results were reported in table 4.9. Greater adsorption of ammonia was observed at low MLD or at high content of MgO. This should corresponded to a more acidic catalyst. But MgO is known to be basic and should lower the acidity. In the chryso-zeolites, the MgO present could neutralize the active sites and change the adsorption/desorption of the species (bases or reactants) from the catalysts.

b) Effects of the physical properties

The physical properties of the catalysts (degree of crystallinity, crystal size, zeolite structure) had an important influence on the catalytic properties. This effect could be in some way related to the molecular shape-selectivity.

The degree of crystallinity might influence the conversion. A low crystallinity implied the presence of amorphous
phase in the sample which could create a pore blockage, limited the diffusion of reacting molecules and products, and increased the shape constraints. Similarly, the structure of the zeolite had an effect (55). Different products were expected depending on the zeolite used (sieving effect). Small molecules were obtained with small pore zeolites (like chabazite, erionite). Larger molecules (hexamethylbenzene for example) were produced when large pore sized zeolites like X, Y, mordenite were used. In the present work, only one zeolitic structure was used: ZSM-5. It was identified by its characteristic X-ray diffraction pattern.

The particle size influenced the selectivity as observed by Derouane (55). Smaller crystallites with larger outer surface were expected to be less shape-selective than larger crystals. In the case of alkylation of toluene to xylene (dimethylbenzene) in presence of methanol, the products will spend less time diffusing inside the small zeolite particles, giving a higher yield in ortho or meta substituted xylene. Larger particles gave more para-xylene. This compound is not the thermodynamically favored isomer, but it had a smaller critical diameter and diffused more easily.

With methanol, the particle size had another influence. In shorter channels, the primary products (light olefins) had less chance of being readSORBED and
forming final products (aromatic hydrocarbons). A smaller "residence time" inside the pores limited the reaction path, favoring the selectivity in light olefins. This phenomena was observed with the chryso-zeolite catalyst. As the MLD decreased, the particles size also decreased giving a higher selectivity for light olefins. Therefore, the presence of Mg in the asbestos remnant restricted the crystallization process, enhanced the formation of smaller zeolitic particles. This influenced the selectivity in the conversion of methanol.

Some techniques could increase the shape-selectivity of the zeolite particles. Impregnation of metals or deposition of P compounds in the pores limits the diffusion and influences the selectivity.

The pores diameter of the zeolite ZSM-5 are in the molecular range:
- 5.4 x 5.6 Å for the [010] channel,
- 5.1 x 5.5 Å for the [100] channel.

Durene (1,2,4,5- tetramethylbenzene) has a critical diameter of 6.1 Å (19). The selectivity is largely influenced by diffusion. Disubstituted aliphatic hydrocarbons (neo-hexane for example) are not favored products. The formation of fused ring aromatic molecules, which are coke precursors, is restricted. Therefore, the catalyst is active over a longer period of time since carbon deposits formation is limited.
4.3) Chryso-zeolite versus zeolite in the MTG process

The two types of zeolites were tested in the methanol to gasoline (MTG) process. Starting from methanol, hydrocarbons were produced.

4.3.1) Selectivity versus MLD

Tables 4.11, 4.12 and figure 4.10 report the catalytic conversion and products selectivity of various catalysts at 400°C. In table 4.11, the catalytic data of two pure ZSM-5 catalysts and a series of chryso-zeolite ZSM-5 having a MLD ranging from 80 to 97% are reported. At 400°C, all the catalysts were active and converted methanol into hydrocarbons. The trend of the selectivity for hydrocarbons obtained at 400°C starting from methanol is shown in figure 4.10. Table 4.12 reports the conversion and selectivity of two catalysts at various temperatures: one pure ZSM-5 (MP-38) and one chryso-zeolite (HA-60, MLD = 80%). The selectivity in commercial valuable products (olefins and liquids) was higher with the chryso-zeolite over the temperatures studied.

The methanol conversion was based on the amount of methanol recovered in the products (liquid phases):

\[
\text{Conversion} = \frac{(\text{MeOH})_{\text{rec}}}{(\text{MeOH})_{\text{inj}}} \times 100 \, (\%) \\
\]

where \((\text{MeOH})_{\text{rec}}\) and \((\text{MeOH})_{\text{inj}}\) were the amounts of
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>MLD (%)</th>
<th>Methanol conversion to HC (%)</th>
<th>Product selectivity (Z C atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$C_1-C_4$ para. $C_2-C_4$ ole.</td>
</tr>
<tr>
<td>HP-38</td>
<td>-</td>
<td>99</td>
<td>35</td>
</tr>
<tr>
<td>HP-68</td>
<td>-</td>
<td>99</td>
<td>31</td>
</tr>
<tr>
<td>HA-39</td>
<td>97</td>
<td>99</td>
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<tr>
<td>HA-60</td>
<td>80</td>
<td>98</td>
<td>12</td>
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</table>

Table 4.11: Catalytic data for the HP and HA catalyst

(400 °C, WHSV : 2.5 h⁻¹)
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp (°C)</th>
<th>Conversion to HC (%)</th>
<th>Product selectivity (% C atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$C_1$-$C_4$</td>
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<tr>
<td>HP-38</td>
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</tr>
<tr>
<td>HA-60</td>
<td>375</td>
<td>80</td>
<td>9</td>
</tr>
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<td>400</td>
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<td>35</td>
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<td>HA-60</td>
<td>400</td>
<td>98</td>
<td>12</td>
</tr>
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<td>HP-38</td>
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</tr>
<tr>
<td>HA-60</td>
<td>500</td>
<td>99</td>
<td>4</td>
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</tbody>
</table>

Table 4.12: Catalytic data for the HP-38 (pure zeolite ZSM-5) and HA-60 (chryso-zeolite ZSM-5, MLD: 80%) at various reaction temperatures. (WHSV: 2.4 h$^{-1}$)
Figure 4.10: Selectivity in hydrocarbons versus the MLD of the chrysso-zeolite catalysts (400°C, WHSV = 2.5 h⁻¹).
At 100%, the triangles, square and circle represent the selectivity obtained with the pure zeolite ZSM-5.
methanol recovered and injected, respectively.

The conversion in hydrocarbons was based on the C atom yield:

\[
\text{Conversion} = \frac{(C_{\text{prod}})}{(C_{\text{feed}})} \times 100 \text{ (\%)}
\]

where \((C_{\text{prod}})\) and \((C_{\text{feed}})\) were the numbers of C atoms in the products (hydrocarbons) and feed (methanol), respectively. The products included gases (\(C_1\) - \(C_4\) paraffins, \(C_2\) - \(C_4\) olefins) and liquids (\(C_5^+\) aliphatics and aromatics). The remainder included:

- mainly dimethyl ether (if present)
- volatile gases (\(CO\) and \(CO_2\))
- C deposited on the catalyst

The last two products containing carbon (volatile gases and C deposit) were produced in very small amount under normal experimental conditions and were neglected. The C deposit represented about 1/3 of the weight of the catalysts after a 4 hours reaction.

The product selectivity, based on the number of C atoms, was expressed as follows:

\[
P.S. (\%) = \frac{\sum i \, Ci}{\sum C} \times 100
\]

where \(\sum C\) and \(\sum i \, Ci\) were the sums of all hydrocarbons produced and of the selected products, respectively.

Table 4.11 and figure 4.10 show that when the MLD was higher than 90%, the chryso-zeolite catalysts exhibited catalytic properties quite similar to those of a pure ZSM-5 based catalyst. However, when the MLD was less than 90%,
more light olefins were produced at the expense of the paraffins (primarily) and the aromatics. This trend was observed over various temperatures for the two extreme catalysts (see table 4.12). A possible explanation could be the effect of the smaller zeolite particles embedded together which were observed at low MLD. They could influence the diffusion and limit the formation of bigger molecules (aromatics compounds) at the expense of the light olefins. However, it seems unlikely that a small change in crystallite size could bring about such a large variation in the product spectrum.

Thus, a possible explanation should be found in the presence of Mg in the chryso-zeolite catalysts. Basic sites (MgO) and Brønsted acid sites should co-exist in the catalysts. The presence of a basic site could cause a "partial neutralization" of an acid site with a subsequent decrease in the acidity which is responsible for the aromatization and H-transfer steps. But the adsorption of NH₃ changed and increased with the content of Mg in the chryso-zeolite. Therefore, it is possible to have a different adsorption phenomenon in presence of both acidic and basic sites.
4.3.2) Selectivity and activity at various reaction parameters

The chemical composition could influence the selectivity. Another way of changing the product distribution was achieved by varying the reaction parameters like temperature, liquid hourly space velocity (contact time) and pressure.

a) Temperature

The effect of temperature on the catalyst selectivity and activity at low space velocity (L.H.S.V. = 1 hr⁻¹) is shown in figures 4.11 to 4.13. The pure zeolite catalyst (HP-71) and the chryso-zeolite (HA-72 and HA-73) shown similar trends. At low temperature, the main reaction was methanol dehydration to dimethyl ether. With increasing temperature, light olefins were formed (major initial products). The yield in liquid hydrocarbons (C₅⁺ aliphatics and aromatics) increased with the temperature, to reach a maximum in the 375-400 °C range, at atmospheric pressure. At high temperature (above 450 °C), the production of light olefins and methane became significant, as a result of secondary cracking of larger hydrocarbon molecules. These results corresponded to those obtained by Mobil (19). Only the amount of C atoms in each group of hydrocarbons changed. More light olefins were produced with the HA-73 catalyst.
Figure 4.11: Effect of the temperature on the selectivity for gaseous products.
(catalyst: 65% zeolite)
Figure 4.12: Effect of the temperature on the selectivity for liquid hydrocarbons.
Figure 4.13: Effect of the temperature on the conversion to hydrocarbons.
The main difference between the chryso-zeolite and the zeolite ZSM-5 was the temperature at which the catalyst became active (selective toward hydrocarbons). The temperature at which light olefins were produced increased when the MLD decreased. This phenomenon is shown in figure 4.13. HP-71 was active above 325°C while HA-73 (MLD = 83%) was active only above 375°C. The temperature at which the catalysts were active for the production of hydrocarbons changed but not the general reaction path:

\[ 2 \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \]

- \( \text{C}_2 - \text{C}_5 \) olefins
- paraffins
- aromatics
- cycloparaffins
- \( \text{C}_6^+ \) olefins

The same phenomena was observed by temperature programmed desorption of methanol. The presence of magnesium in the chryso-zeolite was invoked to explain these differences (56).

Most of the catalytic runs were performed at 400°C, where all the catalysts showed a complete conversion of methanol. No noticeable amount of CO, CO\(_2\) or H\(_2\) was produced at that temperature (9).
b) **Liquid hourly space velocity.**

To study the effect of contact time, runs were performed with a liquid hourly space velocity (L.H.S.V.) increasing from 1 to 50. The product selectivity changed with the contact time (see figures 4.14 and 4.15). When the amount of reactant (methanol) increased with respect to the amount of active sites on the catalyst, the selectivity was shifted toward the light olefins (primary products of the reaction (47)) and dimethyl ether. The reactant/active sites ratio could be changed in order to evaluate the reaction path. Another way to vary the methanol to catalyst ratio was by diluting the catalyst with an inert material (like bentonite) (see table 4.13).

When the two types of zeolites ZSM-5 were compared, the same phenomenon was observed as with the temperature. By decreasing the magnesium leaching degree of the chrysso-zeolite, the catalysts lost their activity more rapidly under severe conditions. At higher L.H.S.V., the chrysso-zeolite exhibited a lower conversion to hydrocarbons than the pure zeolite (see figure 4.16).

c) **Methanol partial pressure**

Table 4.14 shows the effect of lowering the methanol partial pressure. Any significant change in the reactant partial pressure affected the relative rates of the olefin forming and aromatization steps on the catalysts. A lower
Figure 4.14: Effect of the liquid hourly space velocity on the gaseous products. (temp: 400°C)
Figure 4.15: Effect of the liquid hourly space velocity (LHSV) on the liquid hydrocarbons.

N.B. at low conversion, dimethyl ether peak on the chromatogram interferes with the C5 peaks in the gas phase.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% zeolite</th>
<th>Conversion</th>
<th>Product selectivity (% C atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>of MeOH</td>
<td>to HC</td>
<td>C&lt;sub&gt;1&lt;/sub&gt;-C&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
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<td>99</td>
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</tr>
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<td>HA-72A</td>
<td>80</td>
<td>99</td>
<td>93</td>
</tr>
<tr>
<td>HA-72B</td>
<td>65</td>
<td>99</td>
<td>99</td>
</tr>
<tr>
<td>HA-72C</td>
<td>50</td>
<td>90</td>
<td>82</td>
</tr>
<tr>
<td>HA-72D</td>
<td>35</td>
<td>57</td>
<td>37</td>
</tr>
<tr>
<td>HA-73A</td>
<td>80</td>
<td>99</td>
<td>95</td>
</tr>
<tr>
<td>HA-73B</td>
<td>65</td>
<td>96</td>
<td>96</td>
</tr>
<tr>
<td>HA-73C</td>
<td>50</td>
<td>87</td>
<td>76</td>
</tr>
<tr>
<td>HA-73D</td>
<td>35</td>
<td>51</td>
<td>27</td>
</tr>
</tbody>
</table>

Table 4.13: Effect of zeolite / bentonite concentration.
(400°C, WHSV = 2.4 h⁻¹, P<sub>MeOH</sub> = 0.9 atm)
Figure 4.16: Effect of the liquid hourly space velocity on the conversion to hydrocarbons.
methanol partial pressure led to higher production of light olefins and this could be achieved at complete conversion of methanol. In order to vary the $P_{\text{MeOH}}$, the amount of reactant was reduced and the amount of carrier gas increased. In this case, two effects had to be considered: lower methanol partial pressure and lower contact time (higher flow rate). This could explain why only a partial conversion of methanol to hydrocarbons was observed at low $P_{\text{MeOH}}$.

The methanol partial pressure could be lowered by diluting the feed. But no inert substance was found to dilute the methanol without causing problems of vaporisation, competitive adsorption, diffusion or pore blockage. By using water, the $P_{\text{MeOH}}$ was decreased but $P_{\text{water}}$ increased, giving more light olefins. A competitive adsorption on the strong acid sites occurred between the water and the light olefins, limiting the formation of aromatics and the hydrogen transfer reactions (5). A large amount of water increased the irreversible aging of the catalyst by steaming.

By using liquid hydrocarbons, problems of vaporisation and coke deposit could occur.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( P_{\text{MeOH}} ) (atm)</th>
<th>Conversion (%)</th>
<th>Product selectivity (% C atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>of MeOH to NC</td>
<td>( C_1-C_4 )</td>
<td>( C_2-C_4 )</td>
</tr>
<tr>
<td>HP-71B</td>
<td>0.9</td>
<td>99</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>92</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>92</td>
<td>54</td>
</tr>
<tr>
<td>HA-72B</td>
<td>0.9</td>
<td>97</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>84</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>80</td>
<td>30</td>
</tr>
<tr>
<td>HA-73B</td>
<td>0.9</td>
<td>99</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>77</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>74</td>
<td>15</td>
</tr>
</tbody>
</table>

*interference of dimethyl ether at low conversion*

Table 4.14: Effect of the methanol subatmospheric partial pressure.
(400 °C, LHSV = 1 h⁻¹)
d) **High pressure**

As stated earlier, changing the pressure affected the relative rate of the products formation. An increase in pressure enhanced the overlap of the olefin-forming and aromatization steps. Therefore, higher methanol conversion and increased liquid yield were obtained when the pressure increased (see figures 4.17 and 4.18). More liquids were produced when the pressure was increased from atmospheric to 150 psi. Above, the yield was constant. The same trend was observed for the yield in aromatics in the liquid phases (see figure 4.19). Varying the pressure affected the aromatics' distribution. More C9 and C10 were formed at higher pressure (figure 4.20 and 4.21).

The catalyst activity is shown to be modified at higher pressure. Two factors could be responsible (5):
- greater adsorption of reactants or products on the surface of the catalysts,
- mass transport (diffusion) limitations.

The greater adsorption was favored by the higher partial pressure of the various species present in the catalytic bed. The diffusion limitations were caused by a greater selectivity in polymethyl aromatic compounds. As observed in the present work, and confirmed by Chang et al (9, 19), when the pressure was increased, the dehydration and the polymerization steps overlapped, yielding a higher degree of aromatic substitution.
Figure 4.17: Selectivity of the catalyst HP-CAN 13 at high pressure.
(400 °C, WHSV = 2.4 h⁻¹)

- : C₁-C₄ paraffins
- : C₂-C₄ olefins
- : C₅⁺ aliphatics
- : aromatics
Figure 4.18: Selectivity of the catalyst HA-ÇAN 14 at high pressure.
(400 °C, WHSV = 2.4 h⁻¹)
- same symbols as in figure 4.17
Figure 4.19: Selectivity towards aromatics compounds in the liquid phase at various pressure.
Figure 4.20: Selectivity in C₉ aromatics at high pressure. It represents the influence of pressure on the alkylation reactions. The maximum yield in C₉ aromatics is at 200 psi.
Figure 4.21: Percentage of durene in the liquid phase at various pressure.
The alkylation reaction was strongly influenced by the pressure. By varying P from atmospheric to 450 psi, the selectivity changed, favoring the larger aromatic hydrocarbons like C₉ and C₁₀ (see figure 5.7 and 5.8, pages 181 and 182). As the pressure increased, the methylation of benzene also increased giving a higher yield in durene. Alkylaromatics cannot be converted further in zeolite ZSM-5 (by dehydrocyclization and subsequent alkylation) and are the largest molecules formed. Durene, which is not the thermodynamically favored tetramethylbenzene isomer (19), was preferentially formed. At 371°C, the thermodynamic equilibrium is 33% for durene over the tetramethylbenzene isomers. In presence of ZSM-5, durene represents 50% or more of tetramethylbenzenes formed at atmospheric pressure.

It possesses a critical diameter most compatible with the zeolite ZSM-5 channel dimension. It is the bulkiest isomer able to move with relative ease through the zeolite channel system, and is therefore more easily formed than the other C₁₀ aromatics within the zeolite. This phenomena was related to the shape-selectivity properties of the ZSM-5 zeolite. If larger pore zeolites were used (mordenite for example), the C₁₀ thermodynamic equilibrium is attained (19).

Since ZSM-5 is shape-selective, the yield in durene was favored over the other C₁₀ aromatics. By increasing the pressure, the selectivity for the undesirable durene was also increased (see figure 4.22). A striking effect was that the chryso-zeolite catalysts were more shape-selective.
Figure 4.22: Percentage of durene in the tetramethylbenzene isomers versus the pressure.
than pure zeolites. Even at low pressure, high selectivity in durene versus the other tetramethylbenzenes was obtained. The yield in aromatic compounds being lower, the amount of durene in the liquid phase was smaller with a chryso-zeolite. Many factors could be responsible for a greater shape-selectivity:
- larger particles,
- pore blockage and diffusion restriction,
- smaller pores.

In the present case, the chryso-zeolite catalyst, prepared in the laboratory, had a lower degree of crystallinity than the pure zeolite ZSM-5. In addition, the general physical aspect of the chryso-zeolite (small particles attached together to form blocks which were embedded in the asbestos remnant) could restrict the diffusion and increase the shape-selectivity. These two aspects together could favor the formation of durene.

The selectivity of a pure zeolite could be enhanced by impregnating the catalyst with metals (see table 4.15). Mg impregnation in a pure zeolite could improve the selectivity by limiting the mass transfer, and increasing the shape-selectivity.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA-CAN 15 (MLD 99%)</td>
<td>15.4</td>
</tr>
<tr>
<td>HA-CAN 14 (MLD 86%)</td>
<td>15.7</td>
</tr>
<tr>
<td>HP-CAN 13 2% Mg</td>
<td></td>
</tr>
<tr>
<td>HP-CAN 13 5% Mg</td>
<td>3.4</td>
</tr>
<tr>
<td>HP-CAN 13 10% Mg</td>
<td>19.5</td>
</tr>
</tbody>
</table>

Table 4.15: Influence of the Mg impregnation on the selectivity. Difference in % of durene in the tetramethylbenzene isomers compared to HP-CAN 13. (400 °C, atmospheric pressure)
e) **General aspect of the conversion of methanol on chryszo-zeolite**

Even if the samples of zeolite and chryszo-zeolite had similar Si / Al ratio, some physical and chemical differences arise. Physical properties such as particles size and degree of crystallinity might have an influence on the selectivity but not to such a significant extent as observed in the present work. The differences in selectivity and especially in activity, which were measured under different reaction conditions, were probably due to chemical factors. The composite catalysts contained MgO, a basic active site. The magnesium, which came from the asbestos fibers, could affect the Brønsted acid sites by partially neutralizing them. In addition, the presence of Mg affected the adsorption - desorption capacity of the catalyst. As the content of magnesium increased, the temperature at which the catalyst became active also increased (see figure 4.13).
4.4 Temperature programmed desorption from the catalysts

It has been proposed that the magnesium oxide acts as a basic site and creates a different adsorption (34). In order to evaluate the adsorption properties of the catalysts, a temperature programmed desorption of reactive species was done. After saturation of the catalyst with methanol (exothermic process), the temperature was increased and the desorbing species were detected. Knowing the reaction path, it was possible to predict which species should be present. It was expected that products like aromatics or paraffins would not be formed. The species to identify were methanol, dimethyl ether, water and light olefins (ethylene, propylene and butene). As hydrocarbons formed upon desorption of the reactive species, ethylene and propylene were detected. More propylene was produced than ethylene.

As the temperature increased, various species were desorbed. When methanol was used as adsorbate, a large amount was physisorbed or weakly chemisorbed and desorbed below 200°C, without reacting. Above 200°C, dimethyl ether and water were detected, followed by a rapid desorption of light olefins (mainly propylene) and water at temperature above 300°C. The same pattern was observed with all the catalysts studied. Only the temperature at which the species were desorbed changed with the catalyst. The release of dimethyl ether occurred at higher temperature.
DME appeared at 210 °C with the HP catalyst and between 220 °C and 250 °C with the composite catalysts.

Hydrocarbons desorbed at higher temperature when a chrysoc-zeolite was used as catalyst (see table 4.16). In addition, as the MLD increased, the temperature of desorption of dimethyl ether and propylene increased. When dimethyl ether was used as adsorbate, the same phenomena was observed. Weakly adsorbed dimethyl ether was released at low temperature. Hydrocarbons were formed above 300 °C. This is the most important step in the synthesis of hydrocarbons. The first olefins were detected at higher temperature suggesting that it was the limiting step. Then, the simultaneous presence of olefins and oxygenated species yielded the formation of larger molecules. The temperature of formation of propylene changed with the catalyst used. When propylene was adsorbed on the catalysts, the maximum desorption temperature was lower (below 300 °C).

The reaction should occur between the species adsorbed on the catalyst. When the concentration of the reactive species was high in the gas phase, the formation of the hydrocarbon products was favored. By using a step desorption or a slow temperature climb rate, dimethyl ether was desorbed. At higher temperature, only a small amount of propylene was detected. If a large amount of dimethyl ether was present in the gas phase, more propylene was formed.

If propylene and methanol were both adsorbed on the catalyst (sequential adsorption), they were released
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Diff. in temp. of desorption of olefins (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP-CAN 13</td>
<td>-</td>
</tr>
<tr>
<td>HA-CAN 15</td>
<td>3</td>
</tr>
<tr>
<td>(MLD 99%)</td>
<td></td>
</tr>
<tr>
<td>HA-72</td>
<td>35</td>
</tr>
<tr>
<td>(MLD 92%)</td>
<td></td>
</tr>
<tr>
<td>HA-CAN 14</td>
<td>56</td>
</tr>
<tr>
<td>(MLD 86%)</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.16: Difference in the temperature of desorption of the light olefins compared to the HP-CAN 13 catalyst.
simultaneously. Noticeable amounts of butenes were detected in the 270 - 350 °C range, at temperatures where no olefins were detected when methanol was used alone. This observation supported the hypothesis of an alkylation reaction between the oxygenates and the light olefins (57).

From the general appearance of the desorption pattern (figure 4.23), it was possible to believe that the first hydrocarbon to be desorbed (propylene) was only formed at a specific temperature. As soon as this species was present on the surface, the desorption of propylene occurred. In order to give propylene, a carbon-carbon bond must be formed. This is the most important step in the synthesis of hydrocarbons. This reaction took place at a specific temperature suggesting that it was the limiting step. A rapid chain elongation to give a C_3^+ specie followed the formation of the first C-C bond. Propylene desorbed and probably gave ethylene by a secondary reequilibration of the primary olefinic product(s). Then, the simultaneous presence of olefins and oxygenated compounds in the gas phase led to the formation of larger molecules (6).

The differences of temperature between the catalysts, as observed by TPD, were consistent with the results obtained earlier when the effect of temperature was studied. The HA samples were found active but at higher temperature. The magnesium content should be responsible for such a change in activity.
Figure 4.23: General aspect of the desorption of the species from the catalyst. Similar patterns were observed for all the catalysts. Only the temperature at which the species desorbed changed.
4.5) **Apparent Activation Energy**

When a heterogeneous catalytic reaction occurs, several physical and chemical processes take place in proper sequence. Hill (58) presented these seven steps:

- mass transfer of reactants from the main body of the fluid to the exterior surface of the catalyst particles,
- molecular diffusion of reactants from the exterior surface of the catalyst particle into the interior pore structure,
- chemisorption of the reactant on the catalyst surface,
- reaction on the surface (may involve several steps),
- desorption of (chemically) adsorbed species from the surface of the catalyst,
- transfer of products from the interior catalyst pores to the external surface of the catalyst by molecular diffusion,
- mass transfer of products from the exterior surface of the particles into the bulk of the fluid.

In order to evaluate the apparent activation energy, some assumptions were made. Firstly, the mass transfer of species between the catalyst particles and fluid was not a limiting step in the process and could be neglected. By changing the size of the pellets, the conversion and the selectivity did not change.
<table>
<thead>
<tr>
<th>size</th>
<th>conv. to HC (%)</th>
<th>selectivity</th>
<th>light para</th>
<th>light ole</th>
<th>C\textsubscript{5} alip</th>
<th>arom</th>
</tr>
</thead>
<tbody>
<tr>
<td>large</td>
<td>100</td>
<td>22.8</td>
<td>35.8</td>
<td>26.9</td>
<td>14.5</td>
<td></td>
</tr>
<tr>
<td>medium</td>
<td>100</td>
<td>21.4</td>
<td>34.0</td>
<td>27.9</td>
<td>16.7</td>
<td></td>
</tr>
<tr>
<td>small</td>
<td>100</td>
<td>20.5</td>
<td>34.5</td>
<td>28.7</td>
<td>16.3</td>
<td></td>
</tr>
</tbody>
</table>

conditions: catalyst = HA-CAN 14 (80% zeolite)
T = 400°C, WHSV = 2 h\textsuperscript{-1}, P_{MeOH} = 0.9 atm

Secondly, since the two types of catalysts had the same active structure (zeolite ZSM-5), the molecular diffusion, which was not negligible, was assumed to be small and similar in both cases. The reactants and products obtained at low conversion were of small size (methanol, dimethyl ether and light olefins). They should diffuse relatively easily in the pores compared to aromatic molecules. Therefore, the molecular diffusion was not taken into account. The process depended on the adsorption, the reaction and the desorption steps. The activation energy was equal to:

$$E_{\text{app}} = E_{\text{ads}} + E_{\text{rxn}} - E_{\text{des}}$$

The adsorption and reaction processes were exothermic; while the desorption was endothermic.

For the present work, a simple kinetic model was used, similar to a model proposed by Chang et al (47):
where \( A \) = oxygenated species (the methanol/dimethyl ether species in equilibrium)

\( B \) = olefins

\( C \) = aromatics and paraffins.

At low conversion, the second step was neglected. The oxygenates were lumped together, as were olefins. The general rate expression was:

\[
 r = r_C w
\]

where \( r \) = rate of the reaction (moles of hydrocarbons formed/hour on a carbon atom basis),

\( r_C \) = rate of the catalytic reaction (moles of hydrocarbons formed/hour \( g \) of catalyst),

\( w \) = weight of catalyst (g),

\[
 r_C = \frac{r}{w} = \frac{1}{w} \frac{\Delta C}{1/F} = \frac{\Delta C}{\Delta \tau}
\]

where \( C \) = conversion to hydrocarbons

\( F \) = feed (mole/hour)

\( \tau \) = space time = \( w/F \) (g, hour/mole)

The rate of the catalytic reaction was therefore determined from a plot of conversion to hydrocarbons versus the space time. The general form of the rate equation was:

\[
 r_C = k_1 P_A^x
\]

with the rate constant written in the Arrhenius form:

\[
 k = a e^{-E/RT}
\]

where \( a \) is the pre-exponential factor.
E is the activation energy
R is the gas constant
T is the absolute temperature

The rate equation was: \( r_C = a e^{-E/RT} P_A^x \)

By keeping the partial pressure of the oxygenated species constant, \( r_C \) became:

\[ r_C = k' e^{-E/RT} \text{ where } k' = a \cdot P_A^x \]

By knowing the rate at various temperatures, the apparent activation energy was determined.

It was possible to keep the partial pressure of the oxygenates constant, only when the oxygenated species did not react with the catalyst particles. Otherwise, intermediate and products were formed, changing \( P_A \) in the catalytic bed. No conversion occurred when the reactants were not in contact with the catalyst. In order to get \( \tau \rightarrow 0 \), the weight of the catalyst \( (\dot{w}) \) should be equal to zero or the feed in methanol should be infinite. In the present work, the conversion into hydrocarbons was evaluated at various \( \tau \), and extrapolated to zero. When \( \tau = 0 \), the conversion equals zero.

To express the conversion in terms of \( \tau \), a polynomial equation was used:

\[ C = a + b \tau + c \tau^2 + \ldots + n \tau^n \]

where \( a = 0 \) since \( C = 0 \) when \( \tau = 0 \)

\( b \) to \( n \) are constant

The initial rate \( r_0 \) (when \( \tau \) is close to zero) is: 

135
\[
    r_0 = \lim_{\tau \to 0} (r_0) = \lim_{\tau \to 0} \left( \frac{\delta C}{\delta \tau} \right)
\]
which gives \( r_0 = b \).

The results are reported in tables 4.17 and 4.18.

For the HP catalyst, two temperatures were used and the activation energy was calculated using:

\[
    \ln \frac{r_0 a}{r_0 b} = \frac{E}{R} \left[ \frac{1}{T_b} - \frac{1}{T_a} \right]
\]

This method was less accurate for determining \( E \) than the graphical technique employed for the HA catalyst. Some problems encountered during the catalytic experiments limited the temperature range over which it was possible to perform a reaction with the HP catalyst. Nevertheless, the value of apparent activation energy obtained (\( E_{\text{app}} = 23.5 \text{ kcal/mole} \)) for the formation of light olefins could be compared with the value of 19.3 kcal/mole obtained by Chang et al. (47).

With the chryso–zeolite catalyst, the apparent activation energy determined graphically (figure 4.24) was equal to 14.4 kcal/mole. This lower value of \( E_{\text{app}} \) was due to a greater energy of desorption. As observed earlier, the HA catalysts with a low MLD were active in the conversion of methanol but at higher temperature. A stronger adsorption in presence of Mg which caused a desorption of olefins at a higher temperature (as observed by TPD of methanol) could explain this smaller apparent activation energy.
<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>$\tau$ / (g.h/mole)</th>
<th>Conv. to HC (%)</th>
<th>$r_o$ *</th>
</tr>
</thead>
<tbody>
<tr>
<td>523</td>
<td>0</td>
<td>0</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>4.17</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.44</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>563</td>
<td>0</td>
<td>0</td>
<td>26.9</td>
</tr>
<tr>
<td></td>
<td>4.25</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.50</td>
<td>71</td>
<td></td>
</tr>
</tbody>
</table>

* $r_o$ obtained by extrapolation when $\tau \to 0$

(expressed in mole of hydrocarbons formed per hour per gram of catalyst)

Table 4.17: Conversion of methanol into hydrocarbons at various space time on the catalyst HP-CAN 13 (80% zeolite).
<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>( \kappa ) (gsh/mole)</th>
<th>Conv. to HC (%)</th>
<th>( r_o ) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>603</td>
<td>0</td>
<td>0</td>
<td>4.89</td>
</tr>
<tr>
<td></td>
<td>2.23</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.48</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.65</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18.86</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25.33</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>623</td>
<td>0</td>
<td>0</td>
<td>7.63</td>
</tr>
<tr>
<td></td>
<td>2.13</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.48</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.71</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.65</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.76</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18.86</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>19.05</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25.33</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>643</td>
<td>0</td>
<td>0</td>
<td>10.44</td>
</tr>
<tr>
<td></td>
<td>2.22</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.48</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.65</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18.86</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25.33</td>
<td>84</td>
<td></td>
</tr>
</tbody>
</table>

* \( r_o \) obtained by extrapolation to \( \kappa \rightarrow 0 \)

(expressed in mole of hydrocarbons formed per hour per gram of catalyst)

**Table 4.18** : Catalytic conversion of methanol on the catalyst HA-CAN 14 (80% zeolite) at various temperatures and space time.
Figure 4.24: Arrhenius plot of the initial rate for the conversion of methanol on the catalyst HA-CAN 14.

\[
\text{slope} = -7.251 \times 10^{-3} \\
\text{corr. factor} = -0.998
\]
4.6) **Influence of magnesium on the properties of the chryso-zeolite catalyst**

Chryso-zeolite catalysts exhibited different catalytic activities when compared to a pure zeolite ZSM-5. Some physical differences existed between the two catalysts. In general, the chryso-zeolite had a lower degree of crystallinity and smaller particle size. A small crystal size might favor the formation of molecules of reduced size like gaseous olefins or paraffins. The shorter path inside the catalyst particles could cause a limited reaction sequence. The light olefins had less chance of being readSORBED and polymerized to give aromatic compounds.

The results observed with the two types of catalysts were rather different. It seemed unlikely that a small change in crystallite size could cause such a large variation in the product spectrum (see figure 4.10).

A possible explanation should be found in the chemical composition of the catalysts rather than in the physical aspects. The chryso-zeolite catalysts contained some metals (magnesium and iron) which were not detected in the pure zeolite ZSM-5.

During the synthesis of ZSM-5, aluminum can be replaced by iron provided that component is soluble in the synthesis gel (basic medium) to give a ferrosilicate (59,60). Such catalysts were found to be active in the conversion of methanol to hydrocarbons. High yields in light olefins were obtained with catalysts where the Fe
content was very low. These results could be compared to a silicalite (Si rich ZSM-5). However, the iron in the Alix samples existed in the oxide form. During the hydrothermal synthesis, it will not form a gel with the silica. The chances that iron precipitated with the Si to give a ferrosilicate with the ZSM-5 structure were rather small.

The content of iron was not consistant in the chryso-zeolite and could not be related to the results obtained. Fe should be present as impurities in the asbestos remnants.

No zeolite containing magnesium in their structure has been reported. According to Breck (15), the hydrothermal treatment of magnesium aluminosilicate glasses or similar oxide mixture did not result in the formation of a magnesium zeolite. Mg could be incorporated in zeolite as a cation, following an exchange with Na+. Mg has very little chance of being included in the zeolite structure since it did not have the appropriate valence. A pure zeolite ZSM-5 was synthetized in presence of Mg$^{2+}$. The final content in magnesium was very low. This Mg could act as a cation neutralizing the negative charge on the aluminum.

Before the hydrothermal synthesis of the ZSM-5/asbestos compounds, it was possible to control the amount of Mg in the Alix samples (by leaching techniques). This influenced the content of magnesium in the chryso-zeolite catalyst. The catalytic results obtained in this work could be related to the Mg contents.
In the chryso-zeolite, magnesium could have two effects that would influence the activity of the catalyst.

Firstly, Mg could influence the synthesis of the ZSM-5 structure. Smaller chryso-zeolite particles were obtained at low MLD. Those favored the formation of light olefins.

Secondly, Mg could be present as an oxide (MgO) and exhibit some basic character. According to Tanabe (62), the mixed oxides SiO$_2$ - MgO (and Al$_2$O$_3$ - MgO) with MgO as a minor component, acted as solid bases. A certain amount of magnesium should be located in the asbestos remnants. Some Mg could also be in contact with the Si of the zeolite particles. The regular distribution of the MgO sites facing the SiO$_2$ sites in the original asbestos fibers could be assumed to remain essentially unchanged, in some cases, when the Brønsted acid sites (Al$^+$ - O$^-$) were introduced into the zeolite particles following the crystallization as represented in figure 4.25. These dual acid-base sites could influence the adsorption of the species.

The coexistence of those sites could result to a partial neutralization, causing a subsequent decrease in the acidity of the chryso-zeolite (see figure 4.26), increasing the formation of light olefins.

Based on the data obtained, chryso-zeolites which were very selective in light olefin formation (MLD lower than 90%) also exhibited a higher adsorption of the species. Ammonia adsorption was high both at room temperature and 100°C. The Alix samples did not show any important
Figure 4.25: Presence of acidic and basic sites in the chryso-zeolite catalysts.

Figure 4.26: Possible interaction between adjacent acidic and basic sites in the Mg containing catalyst.
adsorption properties for ammonia. On the other hand, the chrysodezolite catalysts were found more hydrophilic at low MLD (see table 4.8). Methanol and dimethyl ether adsorption/desorption exhibited a release of propylene at higher temperature. This phenomena could be explained by a stronger adsorption of the species in presence of dual acid-basic sites. These dual sites could cause a dissociative adsorption of ammonia (see figure 4.27).

The oxygenated species (methanol, dimethyl ether) also could be strongly adsorbed on the catalyst. As presented in the book by Chang (19) and by Figueras et al (67), the coexistence of acidic and basic sites could play a role in the adsorption and reaction of alcohols. The presence of both sites facilitated the bond dissociation of the alcohol. This is represented in figure 4.27. The presence of Mg enhanced the basic character of the alumino-silicate.

The presence of an electron pair donor in the catalyst could also influence the desorption of the products. A positively charged intermediate could be more strongly adsorbed in presence of the -MgOH group (see figure 4.28). This will explain the difference observed by TPD in the desorption of light olefins starting from methanol.

By having intermediates strongly adsorbed on the surface, the accessibility to the active acid sites was reduced, limiting the reaction sequence.
Figure 4.27: Effects of simultaneous presence of acidic (zeolite) and basic sites (MgO) on NH₃ and methanol adsorption.

Figure 4.28: Interaction and stabilization of the trimethyloxonium intermediate in presence of a basic site.
The greater adsorption capacity could have a negative effect. Water which could be present in the reactant or formed during the reaction, will be adsorbed by the chrysos-zeolite, favoring a more rapid aging of the catalyst.

As stated earlier, the Mg was not included inside the zeolite structure. Pure zeolite catalysts were synthesized and brought in contact with a magnesium solution (impregnation). The selectivity changed with the Mg content (see table 4.19). The trend of the HP catalysts with an increasing amount of Mg was similar to those observed for an HA catalyst. In this case, the magnesium affected the shape-selectivity of the catalyst, limiting the diffusion of larger molecules, and favoring the light paraffins and olefins.

The HP catalysts with Mg introduced by impregnation showed similar activity at various temperatures when compared to a pure zeolite. Therefore, the Mg did not interact with the structure and did not affect the adsorption behavior as observed with the HA catalysts. It only increased the shape-selectivity of the ZSM-5 (61).

As observed by solid state NMR, when Mg was introduced by impregnation on the pure zeolite ZSM-5, it did not interact with the Si. A spectrum similar to a pure zeolite was obtained (see figure 4.29).

On the other hand, when Mg was incorporated in the synthesis gel of the ZSM-5 zeolite, a signal was detected, indicating a possible bonding between Si and Mg. A peak at -98 ppm was observed with the chrysos-zeolite and the pure
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(%)</td>
</tr>
<tr>
<td>HA-CAN 15</td>
<td>0.62</td>
</tr>
<tr>
<td>HA-CAN 14</td>
<td>6.55</td>
</tr>
<tr>
<td>HA-95</td>
<td>11.74</td>
</tr>
<tr>
<td>HP-CAN 13</td>
<td>2</td>
</tr>
<tr>
<td>&quot; 2XMg</td>
<td>0.14</td>
</tr>
<tr>
<td>&quot; 5XMg</td>
<td>0.34</td>
</tr>
<tr>
<td>&quot; 10XMg</td>
<td>0.68</td>
</tr>
<tr>
<td>&quot; Mg wi</td>
<td>0.66</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Conversion (%)</th>
<th>Product selectivity ( % C atom )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃OH to HC</td>
<td>C₄⁺-C₆⁺ para</td>
</tr>
<tr>
<td>99</td>
<td>34.0</td>
</tr>
<tr>
<td>99</td>
<td>21.7</td>
</tr>
<tr>
<td>99</td>
<td>15.2</td>
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<tr>
<td>99</td>
<td>42.0</td>
</tr>
<tr>
<td>99</td>
<td>45.7</td>
</tr>
<tr>
<td>99</td>
<td>39.3</td>
</tr>
<tr>
<td>99</td>
<td>30.6</td>
</tr>
<tr>
<td>99</td>
<td>17.7</td>
</tr>
</tbody>
</table>

Table 4.19: Influence of the presence of Mg in zeolites and chryso-zeolites on the selectivity.
(400°C, WHSV = 2.5 h⁻¹, PMeOH = 0.9 atm)
Figure 4.29: Si solid state NMR of zeolite and chrysocolla.

a) HP-CAN 13
b) HP-CAN 13 / Mg (w.i.)
c) HP-96 (Mg introduced before the synthesis)
d) HA-CAN 14 (MLD = 86%)
e) HA-95 (MLD = 75%)
zeolite ZSM-5 when Mg was present before the synthesis. A bonding Si-O-Mg- was suspected (figure 4.29). In addition, the chryso-zeolite samples exhibited a shoulder between -90 and -100 ppm, probably due to the asbestos remnants, where Si was surrounded by two entities of Mg. The 7 TF.12 asbestos fibers exhibited strong peaks in the Si NMR (figure 4.30). Upon leaching, the peaks at -80 - -100 ppm decreased while the Si-Si peak (-105 ppm) increased (41).

From the solid state NMR results, it was possible to postulate the existence of close interactions between the zeolite structure (Si-Al) containing the acid sites (catalytically active sites) and magnesium (Mg-O-) basic sites.
Figure 4.30: Si solid state NMR of 7 TF 12 chrysotile asbestos fibers.
4.7 Zn and/or Mn Catalysts

Attempts were made to incorporate Zn ions into the zeolite structure and Mn ions into the outermost part of the composite catalyst. Zn ions were introduced by ion-exchange into the H-form of catalyst while Mn ions were impregnated into the catalyst by means of a procedure developed at Concordia (83). Zn and Mn are claimed to be capable of increasing the production of aromatics (36) and light olefins (37) respectively.

The objective of the present work was the preparation of a catalyst which would provide a high cumulative production of light olefins and aromatics. In addition, the catalyst should give a variable ratio of light olefins to aromatics according to the dopant contents of the catalysts.

4.7.1 Effect of Zinc

With the pure ZSM-5 zeolite sample (HP-68), extremely severe conditions of Zn loading were necessary to obtain a 0.1 - 0.6 % (wt/wt of catalyst) Zn content. Zn\(^{2+}\) ions were expected to enter into the zeolite structure, mainly to replace some H\(^{+}\) acid sites.

With the chryso-zeolite ZSM-5 catalysts, the introduction of Zn was easier. When the magnesium leaching degree was higher than 90 %, similar conditions to the HP sample were used for the Zn loading (contact time, }
heating). When the MLD was lower than 90%, milder conditions of loading were necessary to obtain an appropriate Zn content. In these cases, most of the Zn ions were expected to be firmly bound to the asbestos remnants while few of these ions had the chance to enter into the zeolite particles.

Tables 4.20, 4.21 and 4.22 report the catalytic data of the ZSM-5 and of the composite catalysts at 400°C.

The content of Zn introduced by ion exchange should not exceed 0.6% wt/wt. A large amount of zinc in the catalyst gave a smaller yield in hydrocarbons. The main side-product in these cases was dimethyl ether formed by methanol dehydration. ZnO had its own acidic properties (62) and should favor the formation of ether which did not undergo further transformation due to the lack of sufficiently strong acid sites in the zeolite.

On both ZSM-5 zeolite and chryso-zeolite catalysts, the Zn loading introduced by "ion-exchange" and not exceeding 0.6% (wt/wt) provided a significant increase of the aromatic yield mostly at the expense of the light paraffins (see figure 4.31). The same trend was observed at different temperatures, only the amount of each group of hydrocarbons changed under the influence of T as presented in section 4.3.2 (a).
<table>
<thead>
<tr>
<th>Zn (%)</th>
<th>Mn (%)</th>
<th>Conv. to HC (%)</th>
<th>Product selectivity (% C atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>( C_1-C_4 )</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>99</td>
<td>30.9</td>
</tr>
<tr>
<td>0.14</td>
<td>-</td>
<td>99</td>
<td>27.9</td>
</tr>
<tr>
<td>0.14</td>
<td>1.24</td>
<td>99</td>
<td>18.9</td>
</tr>
<tr>
<td>0.37</td>
<td>-</td>
<td>99</td>
<td>21.9</td>
</tr>
<tr>
<td>0.37</td>
<td>1.17</td>
<td>99</td>
<td>11.1</td>
</tr>
<tr>
<td>0.55</td>
<td>-</td>
<td>99</td>
<td>18.0</td>
</tr>
<tr>
<td>0.55</td>
<td>1.72</td>
<td>94</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Table 4.20: Catalytic data of the ZSM-5 based catalysts (series HP-68) at 400 °C.
<table>
<thead>
<tr>
<th>Zn (%)</th>
<th>Conv. to HC (%)</th>
<th>C1-C4 para</th>
<th>C2-C4 ole</th>
<th>Arom.</th>
<th>C5 alip</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23</td>
<td>99</td>
<td>27.9</td>
<td>24.0</td>
<td>21.0</td>
<td>19.2</td>
</tr>
<tr>
<td>0.23</td>
<td>99</td>
<td>20.1</td>
<td>31.9</td>
<td>33.9</td>
<td>19.2</td>
</tr>
<tr>
<td>0.23</td>
<td>99</td>
<td>9.9</td>
<td>24.0</td>
<td>24.0</td>
<td>27.0</td>
</tr>
<tr>
<td>0.23</td>
<td>97</td>
<td>9.9</td>
<td>24.0</td>
<td>24.0</td>
<td>21.0</td>
</tr>
<tr>
<td>0.23</td>
<td>98</td>
<td>7.0</td>
<td>47.1</td>
<td>19.2</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.21: Catalytic data of the chrysanthemic acid catalysts (series HA-62; MLD: 94, %) at 400 °C.
<table>
<thead>
<tr>
<th>Zn (%)</th>
<th>Mn (%)</th>
<th>Conv. to HC (%)</th>
<th>Product selectivity (Z C atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C$_1$-C$_4$ para</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>99</td>
<td>17.1</td>
</tr>
<tr>
<td>0.32</td>
<td>-</td>
<td>98</td>
<td>7.0</td>
</tr>
<tr>
<td>0.32</td>
<td>1.60</td>
<td>91</td>
<td>5.0</td>
</tr>
<tr>
<td>0.53</td>
<td>-</td>
<td>90</td>
<td>6.1</td>
</tr>
<tr>
<td>0.53</td>
<td>1.38</td>
<td>79</td>
<td>6.1</td>
</tr>
<tr>
<td>0.53</td>
<td>3.67</td>
<td>75</td>
<td>6.1</td>
</tr>
</tbody>
</table>

Table 4.22: Catalytic data of the chryso-zeolite

ZSM-5 catalysts (series HA-69, MLD: 84%)
at 400 °C.
Figure 4.31: Effect of zinc incorporation on the yield distribution of hydrocarbons per 100 g of methanol.

- □: light paraffins
- ●: aromatics
- ○: C₅+ non-aromatics

Yield (g.)
4.7.2 Effect of Manganese

The incorporation of Mn sharply decreased the formation of C<sub>1</sub> - C<sub>4</sub> paraffins whereas the production of light olefins (C<sub>2</sub> - C<sub>4</sub>) was dramatically increased (see tables 4.20 to 4.22 and figure 4.32).

The yield in liquid hydrocarbons remained nearly constant. However, with the common "wet" impregnation technique, a significant decrease in aromatic production was observed. With the catalyst prepared by the "dry" impregnation technique, the same content in aromatics was produced in the liquid hydrocarbon products (see table 4.23). The incorporation of Zn into the zeolite structure enhanced to a very large extent the production of aromatics. The "dry" impregnation technique could maintain a high formation of aromatics while it increased significantly the production of light olefins.

The ZSM-5 zeolite particles had an average size of around a few microns. Therefore, the main surface (and thus acid sites) of these zeolite crystals was located within the zeolite pores. The Zn<sup>2+</sup> ions being located inside the pores will influence the aromatization step. The Mn as introduced by the "wet" impregnation technique will disturb both the Zn ions (mostly) and the acid sites which were responsible for the aromatization. This was not the case for the Mn incorporated with the "dry" technique: such Mn ions should remain at the external part of the zeolite particles and affected only the production of light...
Figure 4.32: Effect of the Mn loading on the yield distribution (HA-62 samples at 400°C) (symbols as in figure 4.31).
Table 4.23: Catalytic data of the ZSM-5 catalysts (with or without Zn) and of a similar loading of Mn introduced by two different techniques of impregnation (wet and dry).
olefins.

Zn-Mn-loaded catalysts (using ion exchange and "dry"
impregnation) showed a higher production in light olefins
and in aromatics. Therefore, the preparation of a catalyst
which could provide high yield in hydrocarbons heavily used
by the industries appeared to be very interesting.

4.8 ) Conversion of other light alcohols

The main purpose of this work was to study the
conversion of methanol into hydrocarbons. In order to
obtain a general trend for the light alcohols (C₁ to C₄),
a series of catalytic tests was performed using these
alcohols and their mixture as feeds. The yield depended on
the experimental conditions and on the catalyst. A pure
zeolite ZSM-5 gave similar conversion of C₁ – C₄ alcohols
feed. The selectivity changed by few percent depending on
the alcohol converted. With butanol, more liquid
hydrocarbons were obtained than with methanol. In presence
of a ZSM-5 with Zn and Mn, the selectivity changed due to
the effect of the metals added. This was noticed for all
the alcohols except ethanol, which formed mainly ethylene
(see table 4.24). The same phenomenon was observed when
an "aged" catalyst was used. An "aged" catalyst was a
sample which had over 40 ... reaction cycles behind it
(reaction and regeneration).
These cycles produced a steaming of the catalyst, lowering the acidity by changing the aluminum coordination. The presence of Zn$^{2+}$ on the catalyst replacing the proton will affect the acidity and could also stabilize the catalyst structure (14).

Very high selectivity in ethylene starting from ethanol was observed by Heinze et al on pentasil-type borosilicate catalyst (11).

When compared to C$_1$ - C$_4$ alcohols, the different selectivity using an ethanol feed could be explained by different intermediates in the reaction (different mechanisms) (11,13,14). With the methanol and the dimethyl ether, a trimethyloxonium ion was proposed as intermediate. The first hydrocarbon formed was propylene. With the ethanol, the adsorption of the ether on a weaker acid site and the desorption of ethylene was suspected. With C$_3$ and C$_4$ alcohols, an adsorption of alkyl ether followed by a rearrangement (chain growing) or a desorption of the olefins was suggested as mechanism.
<table>
<thead>
<tr>
<th>Feed</th>
<th>Conversion (%)</th>
<th>Product selectivity (% C atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>of OH</td>
<td>to HC %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeOH</td>
<td>94</td>
<td>85</td>
</tr>
<tr>
<td>EtOH</td>
<td>99</td>
<td>92</td>
</tr>
<tr>
<td>PrOH</td>
<td>99</td>
<td>84</td>
</tr>
<tr>
<td>n-BuOH</td>
<td>99</td>
<td>88</td>
</tr>
<tr>
<td>i-BuOH</td>
<td>99</td>
<td>86</td>
</tr>
</tbody>
</table>

* 82 % was ethylene

Table 4.24: Conversion of C$_1$ to C$_4$ light alcohols on a ZSM-5/Zn-Mn catalyst at 400 °C.
Chapter 5: Reaction Mechanism

The reaction path of acid-catalysed hydrocarbon formation from methanol is composed of three key steps:
- ether formation
- initial C-C bond formation
- oligomerization, aromatization with H-transfer, alkylation, cracking (figure 5.1).

5.1) Ether formation

The mechanism of ether formation from alcohols over oxide catalysts, particularly Al\textsubscript{2}O\textsubscript{3}, usually involves \( \beta \) hydrogen from the alcohol. In the case of methanol, the etherification bears some similarities to that of higher alcohols even if it lacked a parent olefin. The formation of dimethyl ether over a zeolite might be represented by the figure 5.2.

This dehydratation of methanol into dimethyl ether occurs at a lower temperature than the formation of hydrocarbons. Ether is formed in the 200 – 300 °C range, on acid sites of medium strength. The presence of basic sites (MgO) influences the adsorption of oxygenated species and favors the dissociation.
Figure 5.1: Reaction sequence in the methanol conversion over ZSM-5 zeolite catalysts.
Figure 5.2: Dehydration of methanol into dimethyl ether on ZSM-5 catalyst.
5.2 Hydrocarbons formation

5.2.1 First C-C bond

Although considerable research efforts have been done to elucidate the mechanism of the first carbon-carbon bond formation, this question remains unsolved at the present time. Many hypotheses have been proposed but nobody has won this "mechanism sweepstake".

Reactions through alkoxyls (−O-CH₃), carbene and carbenoid (:CH₂), oxonium (R₃O⁺) or methylcarbenium ion (CH₃⁺) have been proposed to explain the formation of the first C-C bond (19, 63). From those, a trimethyloxonium ylide and a surface-bound carbene species have emerged as being the most likely reaction intermediates (64).

- Carbene or carbenoid intermediates

The hypothesis of carbene intermediacy was proposed by Chang and Silvestry (9). Carbene intermediates are produced by -elimination of water from methanol due to the cooperative action of acidic and basic sites or to methylene transfer occurring between two R-O-CH₃ species. These processes have a low probability because of the low active site density in ZSM-5 or the constraints imposed on the bimolecular transition complex explaining the methylene transfer.
But these carbene species might play a role in a carbene-like species insertion into a $sp^3$ C-H bond or might have a greater probability of formation in zeolitic systems where external basic sites could coexist with the zeolite acid sites (chryso-zeolite for example).

An $\alpha$-elimination mechanism involving a carbenoid intermediate was also proposed by Chang (8).

\[ CH_3OH \xrightleftharpoons{H^+} CH_3OH^+ \xrightleftharpoons{-H^+} CH_3OH_2^+ \]

**GAS PHASE**
\[ CH_3^+ + H_2O \leftrightarrow CH_2^+ + H_3O^+ \]

**ZEOLITE**
Oxonium intermediates

Keadling and Butter (49) suggested an intermolecular reaction between a surface dimethyl oxonium species and the methyl group of an incoming DME molecule, aided by a basic site on the catalyst surface.

\[
\begin{align*}
\text{CH}_3 & \quad \text{O} \quad \text{CH}_3 \\
\text{H} & \quad \text{O} \quad \text{CH}_3 \\
\text{Al} & \quad \text{O} \\
\text{O} & \quad \text{Al} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{O} \quad \text{CH}_3 \\
\text{O} & \quad \text{CH}_3 \\
\text{H}_2 \text{C} & \quad \text{Al} \quad \text{O} \\
\text{O} & \quad \text{Al} \\
\end{align*}
\]

Van den Berg et al (65) proposed a mechanism where the key step (the formation of the first C-C bond) was the intramolecular (Stevens-like) rearrangement of a trimethyloxonium ion formed by the bimolecular addition of a methanol molecule to a dimethyloxonium cation.

\[
\begin{align*}
\text{CH}_3 & \quad \text{O} \quad \text{CH}_3 \\
\text{H}_3 \text{C} & \quad \text{O} \quad \text{CH}_3 \\
\text{Al} & \quad \text{O} \\
\text{O} & \quad \text{Al} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{O} \quad \text{CH}_3 \\
\text{H}_3 \text{C} & \quad \text{O} \quad \text{CH}_3 \\
\text{Al} & \quad \text{O} \\
\text{O} & \quad \text{Al} \\
\end{align*}
\]

169
This mechanism appeared attractive since it explained the changes observed in the light olefinic products distribution as function of reaction conditions.

Again, this reaction pathway requires the availability and role of basic sites on the zeolite surface. This is possible since mixed oxides of SiO₂ and Al₂O₃ have some acidic and basic characters in low density (62).

Van den Berg presented two possible schemes leading to ethylene from DME. Route A was through a trialkyloxonium and B was with a carboxonium (see figure 5.3). Route A was favored in terms of kinetic, thermodynamic and theoretical consideration (see figure 5.4).

5.2.2) Initial product(s).

Some mechanism have been proposed but the nature of the initial olefinic product(s) remained controversial. Reacting methanol at low conversion could, in principle, give a hint into the nature of the primary product(s). Propylene has most often been suggested as the first olefin desorbed (19, 63). Haag et al indicated that the primary olefins formed could be affected by the diffusion. The C₂ precursor species to ethylene could be forced to undergo further transformation leading to sequential reaction products rather than to desorbed ethylene. A rake-type mechanism for the conversion of methanol and dimethyl ether into hydrocarbons was proposed (see figure 5.5). As
Figure 5.3: Trialkyloxonium (A) versus carboxonium route (B) for C-C bond formation.
Figure 5.4: Energy diagram for routes A and B (see figure 5.3).
Figure 5.5: Rake-type mechanism for the conversion of methanol and dimethylether into hydrocarbons.
presented by Haag, a $C_2$ species should be formed initially from which ethylene was obtained. Results obtained by some groups, including the present work, favored propylene as the first olefin desorbed from the catalyst. The diffusion, as mention by Haag, did not influence the yield in ethylene.

The first step of the synthesis of hydrocarbons was the formation of the trimethyloxonium ion. A rearrangement should occur to give the first C–C bond. At this point, the intermediate MeOC₂ could give ethylene by desorption or react with an oxygenated molecule and go through a second rearrangement to give a methylpropyloxonium intermediate MeOC₃ (see the rake-type mechanism, figure 5.5). A $C_3^+$ species could desorb to give propylene.

As observed by Dessau (40), the amount of propylene produced in the methanol conversion increased on lowering the contact time. Higher selectivity for propylene was obtained in the present work as function of the reaction time (see table 5.1). These results support the proposal that propylene is the first hydrocarbon desorbed. Ethylene is formed by reequilibration of the higher olefins (propylene, butenes).

The trimethyloxonium mechanism proposed by Van den Berg was more appropriate in explaining the presence of propylene as the first hydrocarbon desorbed. A carbene intermediate, as presented by Chang, should favor the formation of ethylene as the first hydrocarbon formed and
<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Propylene/Ethylene ratio *</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>5.04</td>
</tr>
<tr>
<td>75</td>
<td>3.53</td>
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<tr>
<td>120</td>
<td>3.09</td>
</tr>
<tr>
<td>160</td>
<td>2.81</td>
</tr>
<tr>
<td>205</td>
<td>2.52</td>
</tr>
</tbody>
</table>

* C atom basis

Reaction conditions: catalyst: HA-CAN 11
T: 250°C
\( P_{\text{MeOH}} \): 0.2 atm
diluent: \( N_2 \), 500 cc/min
WHSV: 1.77 h⁻¹

Table 5.1: Propylene / ethylene ratio at various times in the reaction.
desorbed. Chain growing by rearrangement of a trialkyloxonium ion up to the desorption of a \( C_3^+ \) species, which will give propylene, was consistent with the experimental results obtained. One step should be added to the mechanism of by Van den Berg: the addition of another carbon to the chain in order to get a \( C_3^+ \) species.

Such a pathway had been recently presented by Van Hoooff and Van den Berg. Reactions were performed starting from dimethyl ether, methyl-ethylether and diethylether. A low concentration of methyl ethylether on the catalyst and in the gas phase favored a rearrangement reaction into a MeO\( C_3 \) in presence of dimethyl ether. The formation of propylene was explained by a E1 mechanism.

5.2.3) Autocatalytic conversion of methanol

In the MTG conversion, the consumption of methanol rapidly increased as the hydrocarbon product concentration (olefins and aromatics) increased. A reaction could occur between species adsorbed and species in the gas phase (Rideal-Eley mechanism):

\[
\text{CH}_3\text{OH} - \text{DME} \rightarrow \text{C}_3^+, \text{C}_2^+
\]

and

\[
\text{CH}_3\text{OH} - \text{DME} + \cdot \text{C}_n^- \rightarrow \text{C}_{n+1}^- + \text{H}_2\text{O}
\]
The autocatalytic nature of the methanol conversion has been discussed by various authors (57, 69-71). A jump in the conversion of methanol was observed by varying the operating conditions (temperature or space velocity). The reactant concentration decreased when methanol was involved in aliphatic chain growth or aromatic ring alkylation reactions (63). These reactions occurred on medium strength acid sites.

5.2.4) Formation of aromatic compounds

Light olefins formed could be readsorbed on free acid sites. By polymerization (oligomerization and/or cyclization), C$_2$ or C$_3$ olefins are converted to napthenes (C$_5$ or C$_6$ olefins). This reaction, which occurs between two species adsorbed on medium strength acid sites, follows a Langmuir-Hinshelwood mechanism.

C$_2$ - C$_6$ olefins act as precursors of aromatic compounds. Reaction pathways consisted in the dehydrogenation of napthenes into aromatics by hydrogen transfer reactions:

\[
\text{naphthene} + \text{olefins} \rightleftharpoons \text{aromatic} + \text{paraffins}
\]

As the aromatic content increases in the products, the amount of paraffins also increases (table 5.2).

The aromatization pathways of olefins, using propylene
### Table 5.2: Selectivity in light paraffins and aromatics. Evidence of H transfer.

<table>
<thead>
<tr>
<th>C&lt;sub&gt;1&lt;/sub&gt; - C&lt;sub&gt;4&lt;/sub&gt; paraffin</th>
<th>aromatic</th>
</tr>
</thead>
<tbody>
<tr>
<td>34.2</td>
<td>28.3</td>
</tr>
<tr>
<td>20.9</td>
<td>19.6</td>
</tr>
<tr>
<td>13.3</td>
<td>16.4</td>
</tr>
<tr>
<td>16.1</td>
<td>13.6</td>
</tr>
<tr>
<td>16.1</td>
<td>11.6</td>
</tr>
</tbody>
</table>
as a model reactant, is represented by the figure 5.6. In this case, the reaction which proceeds through a carbenium ion, occurs on strong acid sites (72,73).

Restricted transition state shape-selectivity plays an essential role in the product distribution. It could explain the high iso/normal paraffins ratio in the aliphatic products and the cut-off at C_{10-11} in the aromatic distribution (63). The C_{4-6} olefins, which were obtained by oligomerization and/or alkylation of the primary olefins or by cracking of higher olefinic products, could go through an oligomerization and dehydrocyclization step. This would take place at the channel intersection of the ZSM-5, where molecular shape-selectivity constraint act on the formation of the intermediate complex structure. Steric inhibition, limiting the accommodation of iso-aliphatics at these intersections and precluding the accommodation of bimolecular transition complexes of more than ten or eleven carbon atoms, appears as a decisive parameter (63).

The alkylation reaction is largely influenced by the pressure. By varying P from atmospheric to 450 psi, the selectivity changes, favoring the larger aromatic hydrocarbons (see figure 5.7 and 5.8). As the pressure increases, the methylation of benzene also increases giving a higher yield in durene. Alkylaromatics cannot be converted further in zeolite ZSM-5 (by dehydrocyclization and subsequent alkylation). It explains the low coking activity and the high stability of ZSM-5 as a methanol conversion catalyst.
Figure 5.6: Typical intermediates in the conversion of olefins to naphthenes and aromatics.
Figure 5.7: Aromatic selectivity of the catalyst HP-CAN 13 at different pressures. (evidence of alkylation at high P)
Figure 5.8: Aromatic selectivity of the catalyst HA-CAN 14 at two different pressures.
Based on the reaction scheme proposed by Van den Berg and on the results obtained in the present work, the pathway could be represented by the scheme in Figure 5.9.

5.3) **Chryso-zeolite catalysts**

The presence of Mg in the catalysts creates a basic site. It could influence the adsorption of the oxygenated species. As presented earlier, two adjacent sites, one acid and one basic, increase the adsorption and the dissociation of the alcohol or ether species. These sites could also stabilize the oxonium intermediates.

The magnesium could partially neutralize the acid site, lowering the acidity, and limiting the possibility of formation of aromatic compounds. As observed in this work, the chryso-zeolite catalysts with a low MLD gave less aromatics and paraffins, favoring the light olefins.

5.4) **Influence of metals**

Zn doped catalysts (zeolite or chryso-zeolite) showed a greater selectivity for aromatics compounds, at the expense of paraffins. The Zn had some aromatization capacities (in ref. 19). It acted as a hydrogen reservoir, limiting the H-transfer. The amount of aromatics formed
Figure 5.9: Reaction pathway for the conversion of methanol.
increased at the expense of light paraffins.

C$_1$-C$_4$ alcohols were decomposed to ketone, aldehyde or alkenes on a ZnO catalyst. Zinc favored the dehydrogenation of most of the alcohols (74-76).

Addition of manganese to the catalysts increased the production of light olefins. The role played by Mn is not well known. It should favor the dehydrogenation of light paraffins.

5.5) Conclusion

No systematic mechanism studies were done in the present work. However, the main aspects of the mechanistic key steps were investigated. The primary product of the reaction was investigated. From the results obtained, the trimethyl oxonium intermediate proposed by Van den Berg was the mechanism retained since it could explain the formation of propylene as the first olefin desorbed. A carbene intermediate, as proposed by Chang, should favor ethylene as primary product. These questions about the reaction mechanism and the primary product are still under investigation in our laboratory. Since many reactions occur simultaneously on the catalyst, the kinetic study of the methanol to gasoline process appears extremely complicated and needs the use of an ensemble of sophisticated techniques involving also the use of tracer molecules.
Conclusion

Methanol conversion into hydrocarbons is now a well established industrial process. Many groups are doing research on the conversion of oxygenated compounds, as well as on the synthesis and preparation of various zeolites as active catalysts. The amount of publications in those domains represents well their importance.

Chryso-zeolites are now part of the field. These catalysts were tested in the selective conversion of methanol into hydrocarbons. They exhibited interesting catalytic behavior in the MTG process when compared to pure zeolite ZSM-5.

Starting from a microstructural support, ZSM-5 zeolites were synthesized. Other zeolitic structures can be successfully prepared starting from asbestos (24). In each case, the first step was a magnesium leaching of the chrysotile fibers using various acids. The silicon is available for the synthesis of various alumino-silicates. Others Si containing materials could act as potential supports.

The activity of the composite catalysts varied according to their composition. The content of magnesium influenced the efficiency and the selectivity of the
catalysts. High yields in light olefins were obtained with chryso-zeolite containing a fair amount of Mg. It is advantageous to be able to control the selectivity of the solid catalysts. The chryso-zeolites ZSM-5 with a low MLD have to be used under mild condition (température, L.H.S.V.) in order to get a complete conversion to hydrocarbons.

The stability of the chryso-zeolites should be improved in order to get a catalyst resistant to steaming. Higher Si/Al or the introduction of metals (Zn$^{+2}$, Ba$^{+2}$) could lower the high rate of the catalyst aging. The metal should prevent the release of aluminum species from the framework during the steaming (78).

Incorporation of small amount of various metals well dispersed in the zeolite structure is also another interesting area to obtain selective and stable catalysts. The addition of zinc and/or manganese to the zeolite or chryso-zeolite played an important role. By controlling the addition of metal, it was possible to direct the selectivity toward valuable products like aromatics or olefinic compounds.

The MTG process developed by Mobil is an interesting new way to produce hydrocarbons. Starting from syngas, high octane gasoline or light olefins were prepared using selective catalysts.
In the present work, new zeolitic catalysts like chryso-zeolites or metal-zeolite were found to be very effective in the MTG process. Being able to control the products distribution is a real advantage in the MTG process. The catalysts prepared in the present work may need more investigation in order to determine the most appropriate catalyst properties for the process.

A disadvantage when working with methanol is the amount of water produced. For each gram of methanol converted, 56% will be recovered as water and discarded. A potential alternative which could make such a process more efficient is the use of a mixture of light alcohols (C₁ to C₄) prepared from syngas. A C₁–C₄ mixture similar to the one proposed by IFP (Institut Français du Pétrole) (79), could give high yield in valuable hydrocarbons (aromatics, olefins), keeping the durene content low. The methylation reaction is reduced due to the small amount of methanol present in the feed.

At this stage of the research, it will be interesting to continue to develop new zeolite catalysts (chryso-zeolite or metal zeolite) in order to find the most efficient one. All the industrialised countries rely on crude oils as their source of energy and chemical feed stocks. The price of the barrels depend, at the present time, more on the goodwill of exporting countries. When the price is low, it is advantageous for the users. At 15 $ per barrel, it has hit the bottom of the wave and will go up again. In order to avoid tight dependance on petroleum
suppliers, it is important for countries with large amounts of carbon-containing compounds (coal, biomass, natural gas) to have an alternative route to guarantee a constant supply of chemicals. Canada is one of those countries. In this context, high performance catalysts in the "Alcohols-To-Hydrocarbons" domain will have good prospects for industrial applications.
References


(19) C. D. Chang, Hydrocarbons from Methanol, Marcel Dekker Inc, N.Y., (1983), and references therein.


Appendix 1

BET Computer Program
The quality of this microfiche is heavily dependent upon the quality of the thesis submitted for microfilming.

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THÈSES CANADIENNES

AVIS
10 CLS
20 DIM V(6),LVL1(10),LVL2(10),LVL3(10),LVL4(10)
30 DIM P(10),P2(10),P3(10),P4(10),X(10),Y(10),Pd(40)
40 CLEAR
50 DATA 0,13.32,32.2,59.61,93.23,136.43
60 REM read in the standard volumes
70 FOR I = 1 TO 6
80 READ V(I)
90 NEXT I
100 INPUT "Sample name : ";SAMPLES
110 PRINT " 
120 LPRINT "Sample name : ";SAMPLES
130 LPRINT " 
140 REM input the experimental data
150 INPUT "No. of equilibrium in step 1 : ";NEP1
160 INPUT "The equilibrium temperature in step 1 : ";TC1
170 PRINT "Enter the levels and equilibrium pressures in step 1"
180 PRINT 
190 FOR I = 1 TO NEP1
200 INPUT LVL1(I),P1(I)
210 NEXT I
220 PRINT " 
230 INPUT "No. of equilibrium in step 2 : ";NEP2
240 INPUT "The equilibrium temperature in step 2 : ";TC2
250 PRINT "Enter the levels and equilibrium pressures in step 2"
260 PRINT 
270 FOR I = 1 TO NEP2
280 INPUT LVL2(I),P2(I)
290 NEXT I
300 PRINT " 
310 INPUT "No. of equilibrium in step 3 : ";NEP3
320 INPUT "The equilibrium temperature in step 3 : ";TC3
330 PRINT "Enter the levels and equilibrium pressures in step 3"
340 PRINT 
350 FOR I = 1 TO NEP3
360 INPUT LVL3(I),P3(I)
370 NEXT I
380 PRINT " 
390 INPUT "No. of equilibrium in step 4 : ";NEP4
400 INPUT "The equilibrium temperature in step 4 : ";TC4
410 PRINT "Enter the levels and equilibrium pressures in step 4"
420 PRINT 
430 FOR I = 1 TO NEP4
440 INPUT LVL4(I),P4(I)
450 NEXT I
460 PRINT " 
470 PRINT "The weight of sample : ";W
480 REM calculate the dead volume
490 SUM = 0
500 FOR I = 1 TO (NEP4-1)
510 V1 = V(LVL1(I))
520 V2 = V(LVL2(I+1))
530 V3 = ((V2 * P4(I+1)) - (V1 * P4(I)))/(P4(I) - P4(I+1))
540 SUM = SUM + V3
550 NEXT I
560 DEAD = SUM / (NEP4-1)
570 LPRINT "Dead volume : ";DEAD;"cc."
580 REM calculate the total volume of Helium
590 SUM = 0
600 FOR I = 1 TO NEP1
610 V1 = V(LVL1(I)) + DEAD
620 SUM = SUM + (V1 * P1(I)*273.15/((TC1+273.15)*760))
630 NEXT I
198
640 HE = SUM / NEP1
650 LPRINT LPRINT " Total volume of He : " ; HE ;")cc."
660 REM calculate the free space
670 SUM = 0
680 FOR I = 1 TO NEP2
690 V1 = V(LVI2(I)) + DEAD
700 V2 = HE - (V1*P2(I)*273.15/(((TC2+273.15)*760))
710 FREE = V2 / P2(I)
720 LPRINT : LPRINT " Free space ";I ;" ;FREE
730 SUM = SUM + FREE
740 NEXT I
750 AVE = SUM / NEP2
760 LPRINT LPRINT " Average free volumes : " ; AVE
770 REM calculate volume absorbing gas introduced
780 SUM = 0
790 FOR I = 1 TO NEP3
800 V1 = V(LVI3(I)) + DEAD
810 SUM = SUM + V1 * F3(I)*273.15/(((TC3+273.15)*760))
820 NEXT I
830 N2 = SUM / NEP3
840 LPRINT : LPRINT " Volume of N2 introduced "; N2 ;")cc."
850 REM calculate the added volumes of N2 at various pressures
860 LPRINT LPRINT " Vol. abs.", P, relative","P, equil.", T, equil.
870 LPRINT " " ; " " ; " " ; " 
880 PO = 10^2.88066183#
890 FOR I = 1 TO NEP4
900 V1 = V(LVI4(I)) + DEAD
910 V2 = V1 * P4(I)*273.15/(((TC4+273.15)*760))
920 V3 = P4(I) * AVE
930 VADD = N2 - V2 - V3
940 X(I) = P4(I) / PO
950 Y(I) = P4(I) / (VADD * (PO-P4(I)))
960 LPRINT : LPRINT Vadder, X(I), P4(I), TC4
970 NEXT I
980 REM Calculate the slope and intercept by least square
990 SX = 0
1000 SY = 0
1010 SXX = 0
1020 SX = 0
1030 STY = 0
1040 FOR I = 1 TO NEP4
1050 SX = SX + X(I)
1060 SY = SY + Y(I)
1070 SXX = SXX + X(I)*X(I)
1080 SXY = SXY + X(I)*Y(I)
1090 STY = STY + Y(I)*Y(I)
1100 NEXT I
1110 ITA = ((SXX * SX) - (SXY * SX)) / ((NEP4 * SXX) - (SX * SX))
1120 LPRINT : LPRINT " Intercept "; ITA
1130 SLP = ((NEP4 * SXY) - (SX * SY)) / ((NEP4 * SXX) - (SX * SX))
1140 LPRINT : LPRINT " Slope "; SLP
1150 VM = 1 / (SLP + ITA)
1160 C = (SLP / ITA) + 1
1170 REM Calculate the surface area
1180 SA = VM * (6.023B * 23) * 16.2 * (9.999999 - 21)/(22414 * W)
1190 REM Calculate the correlation coefficient (r)
1200 CXY = 0
1210 XYVAR = 0
1220 XYVAR = 0
1230 PX = 0
1240 XAVE = SX / NEP4
1250 YAVE = SY / NEP4
```plaintext
1260 FOR I = 1 TO NEP4
1270 CY = CY + (X(I) - XAVE) * (Y(I) - YAVE)
1280 XVAR = XVAR + (X(I) - XAVE)^2
1290 YVAR = YVAR + (Y(I) - YAVE)^2
1300 PX = PX + X(I) * Y(I)
1310 NEXT I
1320 R = ABS(CY) / SQR(YVAR * XVAR)
1330 LPRINT : LPRINT " Correlation coefficient  r : "; R
1340 REM Calculate standard deviation
1350 MEAN = PX / SY
1360 DEVI = ABS((SY - STY^2 / NEP4) / (NEP4 - 1))
1370 STDEV = SQR(DEVI)
1380 LPRINT : LPRINT " Standard deviation : "; STDEV
1390 REM Calculate the surface area error
1400 FOR J = 1 TO 10
1410 READ FD(J)
1420 NEXT J
1430 DATA 12.706, 4.303, 3.182, 2.776, 2.571, 2.447, 2.385, 2.365, 2.306, 2.262, 2.228
1440 DATA 2.201, 2.179, 2.16, 2.145, 2.131, 2.12, 2.11, 2.101, 2.093, 2.086, 2.089
1450 DATA 2.074, 2.069, 2.064, 2.06, 2.056, 2.052, 2.048, 2.045, 2.042
1460 CORR = ABS(1 - R*R)
1470 ERROR1 = FD(NEP4-2) * SQR(CORR) * STDEV
1480 LPRINT : LPRINT " Error on the intercept  : "; ERROR1
1490 XM1 = 1 / (SLP + ITC + ERROR1)
1500 XM2 = 1 / (SLP + ITC - ERROR1)
1510 XM12 = ABS(XM1 - XM2) / VM
1520 ERROR2 = XM1 * XM2
1530 LPRINT : LPRINT " Monolayer volume  : "; VM; " cc."
1540 LPRINT : LPRINT " Parameters C per BET  : "; C
1550 LPRINT
1560 LPRINT : LPRINT : LPRINT " SPEC. AREA (m^2/g. ads.)  : "; SA
1570 LPRINT : LPRINT " ERROR (+/-)  : "; ERROR2
1580 END
```
Appendix 2

Conversion of Methanol to Hydrocarbons

(computer program to evaluate the conversion and the selectivity)
CLS
100 DIM NOS(16), NAS(5), NOS(15)
110 DIM CO(16), CA(5), CG(15)
120 DIM RO(16), RA(5), RG(15)
130 DIM T(16), TO(14)
140 DATA DME, 793, MeOH, 1.05, 0.806, 0.6, 0.776
150 DATA Benzene, 748, C6-H16, 781, Toluene, 765, C6-H14, 0.822
160 DATA Ethylene, 820, ppm-Xylene, 744, o-Xylene, 736, C6-H14, 0.787
170 DATA C9-arene, 737, 4MeBen, 821, Duranes, 806, C10+, 0.807
180 DATA DME, 793, MeOH, 1.05, C9-arene, 793, Ex, 749, C9-arene, 795
190 DATA Methane, 1.01, Ethylene, 1.12, Ethane, 1.07, Propylene, 1.15
200 DATA Propane, 1.15, iso-Butane, 1.12, Butenes, 1.22
210 DATA 1,3-butadiene, 1.41, n-Butane, 1.09, t-2 Butene, 1.29
220 DATA c-2 Butene, 1.06, C5+, 1.15, Benzene, 1.25, DME, 1.00, DMF, 1.00
230 REM
232 REM
240 FOR I=1 TO 16
250 "READ NOS(I), CO(I)
260 NEXT I
270 FOR I=1 TO 5
280 "READ NAS(I), CA(I)
290 NEXT I
300 FOR I=1 TO 15
310 "READ NOS(I), CG(I)
320 NEXT I
330 REM
340 REM __________ Enter experimental data (area or area%) __________
350 REM __________ Calculation of moles of carbon __________
360 REM
370 INPUT "catalyst :"; C8
380 INPUT "run #: "; R1$'
390 INPUT "date performed : "; D$'
400 INPUT "n2 flow (cc/min) : "; F8'
410 INPUT "temp. cat. (C.) : "; T1$'
420 INPUT "temp. pre-heating zone (C.) : "; T2$'
430 INPUT "MeOH injected (g.) : "; P
440 INPUT "WHSV (h-1) : "; Y
450 INPUT " Wert (h-1) : "; L$
460 INPUT "N2/MeOH : "; R2$
470 INPUT "pressure (psi) : "; P$'
480 PRINT
482 REM
484 REM
486 REM
490 PRINT "organic phase"'
500 INPUT "weight of org. phase : "; W'
510 IF W<0 THEN GOTO 570
520 FOR I=1 TO 16
530 T(I)=O
540 RO(I)=O
550 NEXT I'
560 GOTO 760'
570 K=W/14.02
580 PRINT "enter the area%"'
590 S=C
600 FOR I=1 TO 16'
610 PRINT NOS(I)
620 INPUT RO(I)
630 T(I)= RO(I)*CO(I)
640 S=S+T(I)
650 NEXT I
660 PRINT
670 PRINT
680 FOR I=1 TO 16
690 PRINT NOS(I),RO(I)
700 NEXT I
710 INPUT "area% ok (y or n)";AS
720 IF AS = "n" THEN GOTO 580
730 PRINT
740 PRINT
750 REM
760 LPRINT "Catalyst ":"CS","Run ":";R1$,"Date ":";DS
765 _
770 LPRINT "N2 flow(cc/min):";FS,"Temp. cat.(C.):";T1$,"Temp. p-h :";T2$
780 LPRINT "MeOH inj. :";F;"g. ","N2/MeOH:";R2$,"P. (psi):";P1
790 LPRINT "WHSV (h-1) :";V,"LHSV (h-1) :";L
800 LPRINT
805 LPRINT
810 LPRINT "ORGANIC PHASE"
820 LPRINT "wt. org. phase :";W;"g."
830 LPRINT
840 LPRINT "Compound","area%","correction","mole of C."
850 FOR I=1 TO 16
860 T(I) = T(I)/S
870 T(I) = T(I)*X
880 LPRINT NOS(I),RO(I),CO(I),T(I)
890 RO(I)=T(I)
900 NEXT I
910 LPRINT
920 LPRINT
930 LPRINT
940 M1=RO(2)*32.04
950 M2=RO(1)/2*46
960 W=(W-M1-M2)/14.02
970 REM
980 REM
990 REM
1000 LPRINT "AQUEOUS PHASE"
1010 INPUT "wt. aq. phase (g.):";Y
1020 LPRINT "wt. aq. phase :";Y;"g."
1030 INPUT "volume aq. phase (ml.):";V
1040 LPRINT "volume aq. phase :";V;"ml."
1050 INPUT "conc. std. (C/ml):";U
1060 LPRINT "conc. std. :";U;"C/ml."
1070 INPUT "area std. :";Z
1080 LPRINT "area std. :";Z
1090 LPRINT
1100 FOR I=1 TO 5
1110 PRINT NAS(I);
1120 INPUT RA(I)
1130 T(I) = RA(I)*CA(I)
1140 NEXT I
1150 PRINT
1160 PRINT
1170 FOR I=1 TO 5
1180 PRINT NAS(I),RA(I)
1190 NEXT I
1200 INPUT "area ok (y or n)";AS
1210 IF AS = "n" THEN GOTO 100
1220 T(I)=((T(I)*U)/Z)*V
1230 LPRINT NAS(I),RA(I),CA(I),T(I)
1240 RA(I)=T(I)
1250 NEXT I
1260 N5=RA(2)*32.04
1270 M4 = RA(1)/2*46
1280 N6 = RA(3)+ RA(4)+ RA(5)
1290 N5 = N5*14.02
Y = (Y - M3 - M4 - M5) / 18.01
LPRINT
LPRINT
LPRINT **** ;Y "moles of MEOH converted"
LPRINT "org. phase : ";W
LPRINT "aq. phase : ";M9
Y = Y - M9
LPRINT "gas phase : ";Y; "C. atoms"
LPRINT
REM
LPRINT
REM
PRINT "Gas Phase"
PRINT "Enter average area %"
S = 0
FOR I = 1 TO 15
PRINT N$(I);
INPUT RG(I)
T(I) = RG(I) * CG(I)
S = S + T(I)
NEXT I
PRINT
FOR I = 1 TO 15
PRINT N$(I), RG(I)
NEXT I
PRINT "area % ok ( y or n )";
INPUT AS
IF AS = "n" THEN GOTO 1420
FOR I = 1 TO 15
T(I) = T(I) * 100 / S
NEXT I
PRINT
LPRINT "GAS PHASE (based on 2,2-DNB (internal std.))"
INPUT "entry volume of the sample flask (in ml.) "; V1
LPRINT "vol. sample flask "; V1; " ml."
INPUT "carbon number dnb injected "; S
LPRINT "C, atoms "; S
S = S / V1
INPUT "enter total count on totalizer "; T1
LPRINT "totalizer "; T1
INPUT "enter average % MFW "; V2
LPRINT "aver. % MFW "; V2
INPUT "enter average volume from the bubble meter (in ml.) "; V3
LPRINT "aver. bubble "; V3; " ml."
TI = 10 * T1 * V3 / ( V2 * 10 )
T1 = T1 + S * ( 100 - (2(15)) / T(15)
LPRINT
LPRINT T1; " C. atoms"
LPRINT
LPRINT "Compound","area %","correction","C. atom"
S = S = 0
FOR I = 1 TO 14
S = S + T(I)
NEXT I
FOR I = 1 TO 14
T(I) = T(I) / S
NEXT I
T(I) = T(I) * TI
LPRINT N$(I), RG(I), CG(I), T(I)
RG(I) = T(I)
NEXT I
**FORTRAN Program for Calculating Chemical Values**

```
1910 LPRINT NGS(15),RG(15)
1920 M5=RG(14)/2*46
1930 LPRINT:
1931 REM
1932 REM ---------------------------------------------------------------
1933 REM
1940 LPRINT "CONVERSION:
1950 LPRINT "wt. MECH : ";M1:" + ";M3:" = ";M1+M3
1960 LPRINT "wt. DME : ";M2:" + ";M4:" + ";M6:" = ";M2+M4+M6
2000 LPRINT
2010 LPRINT "% Mech conversion : ";((P-M1-M3)/P)*100; " %
2020 S=O
2030 FOR I=3 TO 16
2040 S=S+RG(I)
2050 NEXT I
2060 FOR I=3 TO 5
2070 S=S+RA(I)
2080 NEXT I
2090 FOR I=1 TO 13
2100 S=S+RG(I)
2110 NEXT I
2120 LPRINT "% conversion to HC- ";S/(P/32.04)*100; " %
2130 LPRINT
2160 LPRINT "RESUME"
2170 LPRINT
2180 LPRINT "Compounds", "C. atom", "C. atom"
2190 LPRINT NGS(2),RG(2)+100/S,RG(2)
2200 LPRINT NGS(4),RG(4)+100/S,RG(4)
2210 Z=RG(7)+RG(8)+RG(10)+RG(11)
2220 Z1=Z+RG(2)+RG(4)
2230 LPRINT "Butene",Z*100/S,C,"C2=" + C4=" ;Z1*100/S; " %
2250 Z2=RG(1)+RG(3)+RG(5)+RG(6)+RG(9)
2240 LPRINT "C1=C4(ethers)",Z2*100/S,C2,"C1 C4 para ";Z2*100/S
2250 Z3=RG(12)+RA(3)+RO(3)+RO(4)+RO(6)+RO(8)+RO(12)
2260 LPRINT "C5 C6(alip)",Z3*100/S,Z3,"C5 + alip ";Z3*100/S
2270 LPRINT NGS(9),RO(9)+100/S,RO(9),"Arom ";(S-Z1-Z2-Z3)*100/S
2280 Z=RA(4)+RO(5)+RO(7)+RO(9)+RO(11)+RO(13)
2290 LPRINT NGS(4),Z*100/S,Z
2300 Z=RA(5)+RO(13)
2310 LPRINT NGS(5),Z*100/S/Z
2320 LPRINT NGS(15),RO(15)+100/S,RO(15)
2330 LPRINT NGS(14),RO(14)+100/S,RO(14)
2340 LPRINT NGS(16),RO(16)+100/S,RO(16)
2350 LPRINT
2360 LPRINT "Total : ";S
2362 REM
2365 REM ---------------------------------------------------------------
2367 REM
2370 IF ST=1 THEN GOTO 2500
2375 REM
2380 LPRINT
2389 LPRINT "GAS PHASE (based on water)
2390 LPRINT Y," C. atom"
2410 LPRINT
2420 LPRINT "Compound","C. atom"
2430 FOR I=1 TO 14
2440 TG(I)=TG(I)*Y
2450 LPRINT NGS(I),TG(I)
2460 RG(I)=TG(I)
2470 NEXT I
2480 ST=1
2490 GOTO 1920
2500 STOP
```
Appendix 3

POLYPLOT Computer Program

( polynomial function )
10 CLEAR
20CLS
30 PRINT
40 PRINT
50 PRINT "polynomial least squares"
60 PRINT"
70 PRINT
80 INPUT "please enter the number of data pairs";N
90 INPUT "please enter the desired order of equation";D
100 PRINT "please enter the data x,y"
110 PRINT
120 DIM X(N),Y(N),NE(D+1,D+2),R(D+1),YY(N)
130 FOR I = 1 TO N
140 INPUT X(I),Y(I)
150 NEXT I
160 PRINT "please wait!!!!"
170 REM generating the normalizing equation
180 FOR I = 1 TO (D+1)
190 M1 = I - 1
200 SY = 0
210 FOR J = 1 TO (D+1),
220 M2 = I + J - 2
230 SX = 0
240 FOR K = 1 TO N
250 SX = SX + X(K)^M2
260 NEXT K
270 NE(I,J) = SX
280 NEXT J
290 FOR K = 1 TO N
300 SY = SY + Y(K)*X(K)^M1
310 NEXT K
320 NE(I,D+2) = SY
330 NEXT I
340 REM solving simultaneous equations by gaussian elimination
350 FOR I = 1 TO D
360 FOR J = (I+1) TO (D+1)
370 IF NE(J,I) <> 0 THEN 400
380 PRINT "no unique solution"
390 GOTO 940
400 IF ABS(NE(I,I)) > ABS(NE(J,I)) THEN 440
410 FOR K = I TO (D+2)
420 SWAP NE(I,K),NE(J,K)
430 NEXT K
440 NEXT J
450 NEXT I
460 Z = NE(I,I) / NE(J,I)
470 FOR K = I TO (D+2)
480 NE(J,K) = NE(I,K) - Z * NE(J,K)
490 NEXT K
500 NEXT J
510 NEXT I
520 R(D+1) = NE(D+1,D+2) / NE(D+1,D+1)
530 FOR I = 1 TO (D+1)
540 K = (D+1) - I
550 S = 0
560 FOR J = 1 TO (D+1-K)
570 M = K + J
580 S = S + NE(K,M) * R(M)
590 NEXT J
600 R(K) = (NE(K,D+2) - S) / NE(K,K)
610 NEXT I
620 REM printing the results and the input data
630 PRINT "coefficient of"
640 PRINT.
650 FOR I = 0 TO D
660 PRINT TAB(14) "x";I=":R(I+1)
670 NEXT I
680 PRINT
690 PRINT "no.","x","y","y(interpolation)"
700 PRINT
710 S = 0
720 FOR I = 1 TO N
730 S = S + Y(I)
740 YY(I) = R(I)
750 FOR K = 2 TO (D+1)
760 M = K - 1
770 YY(I) = YY(I) + R(K) * X(I)^M
780 NEXT K
790 PRINT I,X(I),Y(I),YY(I)
800 NEXT I
810 PRINT
820 AVE = S / N
830 PRINT "calculate the coefficient of determination"
840 S1 = 0
850 S2 = 0
860 FOR I = 1 TO N
870 S1 = S1 + (Y(I) - AVE)^2
880 S2 = S2 + (Y(I) - AVE)^2
890 NEXT I
900 PRINT
910 CD = S1 / S2
920 PRINT "coefficient of determination is : r = ";CD
930 PRINT
940 INPUT "Would you like to have the print out (Y/N) ";AS
950 IF AS = "Y" OR AS = "N" THEN 1180
960 LPRINT
970 LPRINT "POLYNOMIAL LEAST SQUARES"
980 LPRINT " "
990 LPRINT " "
1000 LPRINT " "
1010 LPRINT "N"
1020 LPRINT "D"
1030 LPRINT "R(I+1)
1040 LPRINT "A"
1050 LPRINT "B"
1060 FOR I = 0 TO D
1070 LPRINT TAB(15) "x";I=":R(I+1)
1080 NEXT I
1090 LPRINT
1100 LPRINT "NO.","x","y","y(interpolation)"
1110 LPRINT
1120 FOR I = 1 TO N
1130 LPRINT I,X(I),Y(I),YY(I)
1140 NEXT I
1150 LPRINT
1160 LPRINT "COEFFICIENT OR DETERMINATION IS : R(2) = ";CD
1170 PRINT
1180 INPUT "Would you like to plot your data (Y/N) ";CS
1190 IF CS = "Y" OR CS = "N" THEN 1860
1200 PRINT
1210 PRINT "enter the minimum and maximum of x values for 
1220 PRINT "which the equation should be plotted 
1230 INPUT "x(min) ";XL
1240 INPUT "x(max) ";XR
1250 PRINT
1260 PRINT "enter the minimum and maximum y values that 
1270 PRINT "should appear on the grid"
1280 INPUT "y(min) : "; YB
1290 INPUT "y(max) : "; YT
1300 GOSUB 1550
1310 XA = (564 - 84)/XD
1320 YA = (360 - 40)/YP
1330 REM print all data points on the grid
1340 FOR I = 1 TO N
1350 XP = 84 + (480*IX) * ((I) - XL)
1360 IF XP < 84 OR XP > 564 THEN 1400
1370 YP = 360 - (320*YD) * ((I) - YL)
1380 IF YP < 40 OR YP > 360 THEN 1400
1390 CIRCLE (XP,YP),4
1400 NEXT I
1410 REM draw equation
1420 FOR XG = 84 TO 564
1430 XT = XL + (XG-84)/484*XD
1440 YT = R(1)
1450 FOR K = 2 TO (D+1)
1460 M = K-1
1470 YT = YT + R(K) * XT^M
1480 NEXT K
1490 YG = 360 - (YT-YB)*YA
1500 IF YG < 40 OR YG > 360 THEN 1520
1510 PSET (XG,YG)
1520 NEXT XG
1530 LOCATE 1,1
1540 GOTO 1810
1550 REM draw grid with labels
1560 CLS
1570 SCREEN 3
1580 FOR Y1 = 40 TO 360 STEP 64
1590 LINE (74,Y1)-(574,Y1)
1600 NEXT Y1
1610 FOR X1 = 84 TO 564 STEP 96
1620 LINE (X1,24)-(X1,376)
1630 NEXT X1
1640 XD = XR - XL
1650 YD = YT - YB
1660 R = Z3
1670 FOR K = 0 TO 5
1680 LOCATE R,1
1690 S = XB + YD * K/5
1700 PRINT USING "###.###";S
1710 R = R-4
1720 NEXT K
1730 CC = 7
1740 FOR K = 0 TO 9;
1750 LOCATE 24,CC
1760 S = XL + XD * K/5
1770 PRINT USING "###.###";S;
1780 CC = CC + 12
1790 NEXT K
1800 RETURN
1810 INPUT " Would you like to rescale your graph (Y/N) : ";GPS
1820 IF GPS = "n" OR GPS = "N" THEN 1850
1830 CLS
1840 GOTO 1210
1850 CLS
1860 END
Appendix 4

General aspect

of the composition of a gaseous

and organic phase formed during a reaction
Typical gas phase
Typical organic phase

- C_5
- C_6
- Benzene
- Toluene
- Ethylbenzene
- p-xylene
- o-xylene
- n-C_9
- C_10
- Durene
Appendix 5

Experimental procedure
for the high pressure reactor
Catalytic testing

Alcohols were contained in a one liter Pyrex reservoir, the pumping of which was accomplished using a Milton Roy Model #396-31 reciprocating mini-pump. The nitrogen used as a carrier gas was controlled by a Tescom Corporation Series 44-1100 pressure regulator which maintained an inlet pressure 50 psi above the reaction pressure. The fine control of the flow rate was achieved via a micrometering valve and monitored using a gas transducer model # 8141 HP and a mass flow meter model # 8143 both by Matheson Gas Products Canada.

The alcohol and carrier gas were mixed in a heated zone prior to reaching the reaction vessel.

The reaction steel with a volume of 103 ml divided into a pre-heating zone with mesh, and a reaction zone with a fixed catalyst bed supported in a similar fashion. There was a stainless steel thermocouple well supported in the center of the reaction vessel where chromel-alumel thermocouple were inserted to monitor the temperature of the reaction zones.

The entire reaction vessel was surrounded by a heating jacket, which was operated by a non-indicating potentiometric, time proportioning controller, the final temperature was controlled by manual input to each zone.

The desired pressure in the reaction vessel was maintained using a Tescom series 26-1700 back pressure
regulator.

Gaseous and liquid products passed through a water colled condenser, then into a collecting flask immersed in an antifreeze solution which was maintained at -5°C where the aqueous and organic liquids were trapped; the gas continued on through a dynamic gas sampling bulb, a second transducer connected to the mass flow meter and totalizer, and was then ented to a fume hood.

The products formed were analysed by gas chromatography.
Appendix 6

Answers to questions raised by the evaluating comity
Dr. M. Fuller, McGill University.

1) Considering (1) the force fields in the zeolite cavities and windows and (2) the ratio of the length of the nitrogen molecule to the radius of curvature of the solid surfaces in the zeolite crystal, how narrow would the pores have to be to make the measurement of the surface area by the BET method inappropriate?

The BET method used in this work to evaluate the total surface area of the catalyst was not found to be inappropriate to measure the surface. Since the material used was microporous (pore diameters of the ZSM-5 structure close to 5.5 Å), it is possible to have some errors in the surface area measurement due to the possible interaction between the zeolite wall and the adsorbed species. Inside the pores, only 1 or 2 layers of N₂ can condensed on the solid surface. However, the BET is not limited by the thin stacking of adsorbed molecules but actually by the thick one. In fact, the BET technique is recommended for the use with a relative pressure lower than 0.35, in situations where interactions between adsorbed species are small. Operating the instrument at low partial pressure should therefore favor the occurrence of a monolayer on the catalyst giving an approximate but relatively accurate total surface area. The BET method is a technique which is widely accepted for the evaluation of the surface of zeolitic materials with pore diameter as small as 3 to 4 Å, with obviously the assumption that the interaction zeolite wall-adsorbate molecules are negligible.
2) Considering the force fields on the molecules and the restricted mean free paths in the zeolite cavities, what proportion of the molecules within the cavities have energy states that would be typical of a gas? Is your answer consistent with the use of an Eley-Rideal mechanism (pp. 166 & 176)?

The molecules diffusing inside the pores of a zeolite should have a state which is much closer to the condensed (liquid) state than the gaseous one. The average pore diameter is smaller than the mean free path of the diffusing molecules (reactants or products). Such a state is closer to a Langmuir-Hinselwood type mechanism (reaction between two adsorbed species). But the reacting and products species should "diffuse" through the pores of the zeolite. An adsorption - desorption sequence could be proposed to explain the migration inside the catalyst particles.

3) Rabo (I think) proposed that the exchange of a divalent cation, such as magnesium, for sodium in a zeolite would result in a pair of charges in a zeolite cage. The cation would be located near one of the negative charges of the silica-alumina framework, but would have an un-neutralized negative charge. Please comment on this hypothesis as related to the MTG reaction.

An exchanged divalent cation inside a zeolite can be delocalized and this can favor the formation of an un-neutralized negative charge adjacent to an aluminum. The presence of a negative charge (or absence of a proton) can
alter the adsorption and lower the conversion of the reactant. Nevertheless, in this case, the zeolite and chryso-zeolite where subject to an ion-exchange after the synthesis, lowering the content in sodium or magnesium cations and creating the acidic sites. In the chryso-zeolite catalysts, the magnesium was supposed to be located within the zeolite structure creating an interaction detected by solid state NMR and not as ion-exchange on the surface (see figures 4.25 and 4.29).

4) Silica-magnesia is like silica-alumina in being a reasonably good cracking catalyst, although it does not have a long useful life. One hypothesis for the difference in selectivity of the HP and HA series of catalyst would be that the acid sites associated with the magnesia are the cause of the difference. Please cite experimental evidence for and against the hypothesis.

Although acid-base properties on solid surface depend on the preparation method and pretreatment, it is controlled principally by the electronegativity of the metal ions of the solid. Tanabe (62) developed a theory to predict the acidity and/or basicity of solid catalysts. He presented some experimental and predicted results for metal oxides and mixed metal oxides. The $\text{Al}_2\text{O}_3 - \text{MgO}$ and $\text{SiO}_2 - \text{MgO}$ mixed oxides showed acidic characters which are different from that of $\text{SiO}_2 - \text{Al}_2\text{O}_3$. The MgO alone exhibits basic properties. In the chryso-zeolite ZSM-5, magnesium and silicon should be in
adjacent position based on the structure of the original material (asbestos). The simultaneous presence of Al, Si and Mg in the catalyst should change the acidity of the solid. This could be seen on the temperature programmed desorption of ammonia and of oxygenated species. Some differences occurred between the HP and HA catalyst, suggesting a difference on the solid surface and possibly a different acidity.

5) Berzelius thought that a catalyst did not take part directly in the chemical reaction. Would you say that neither the reactant nor products in the MTG process form bonds with the catalyst?

To have a catalytic conversion of methanol into hydrocarbons, chemical bonds should be formed between the reactants and the surface of the catalyst (chemisorption). The simultaneous presence of reactive species (reactants or intermediates) close to the surface (adsorbed or in the gas phase) leads to the formation of products by a surface reaction. Without catalyst, no reaction occurs under the same experimental conditions. Bonding should therefore occur on the zeolite yielding to the formation of hydrocarbons.

6) Water is a coproduct of the reaction, but it is hardly mentioned in the discussion of mechanism. How is it formed? What happens to it after it is formed?

Water, a coproduct in the reaction, is formed by dehydration of methanol to dimethyl ether and by the
conversion of the ether species to hydrocarbons. The water is released and diffuse out of the hydrophobic zeolite ZSM-5 particles. An excessive water partial pressure can alter the catalyst (steaming effect) by changing the coordination of the aluminum (from tetrahedral to octahedral), or can alter the reaction (competitive adsorption and transformation of the methanol - dimethyl ether equilibrium). Hydrophilic zeolite ZSM-5 with high Si/Al ratio (greater than 20) were used to reduce the effect of water on the catalyst.

7) On p. 109 we see that "When the amount of reactant (methanol) increased with respect to the amount of active sites on the catalyst, the selectivity...". Are you saying that the selectivity changed as there was an increase in the cumulative amount of methanol passing over the catalyst? If not, what does this phrase in the thesis mean?

The selectivity of the reaction changed when the WHSV (or LHSV) changed.

8) On p. 116 and figure 4.17, what happens to the mean residence time in the reactor when the pressure is increased at the same liquid hourly space velocity? How would you distinguish between the effect of residence time from the effect of pressure, per se?

In a plug-flow (tubular) reactor, the residence time is defined as the following ratio: \( \frac{V}{F} \) where \( V \) = volume of the reactor and \( F \) = flow-rate of reactant(s). Since the
reaction is a catalytic one, the volume \( V \) must be related to the catalyst volume and the residence time becomes the space time or contact time which is exactly the converse quantity of the \( \text{LHSV} \) (also \( \text{WHSV} \)). Therefore, when you fix the \( \text{WHSV} \) and vary the pressure using the carrier gas, the observed effect are only related to the pressure since in a plug-flow reactor, all the reactant molecules are experiencing — irrespectively to the pressure — the same space time or contact time which is the main factor which can affect the activity (and selectivity) in the catalytic reactor.