THE UNIVERSITY OF CALGARY

AN FTIR STUDY OF THE CONVERSION OF METHANOL TO HIGHER HYDROCARBONS OVER FLUORIDED ZEOLITE H-ZSM-5

by

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THE UNIVERSITY OF CALGARY FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled, "An FTIR Study of the Conversion of Methanol to Higher Hydrocarbons over Fluorided Zeolite H-ZSM-5" submitted by Eric Villeneuve in partial fulfillment of the requirement for the degree of Master of Science.

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ABSTRACT

The conversion of methanol to hydrocarbons in the gasoline boiling point range, as catalysed by the zeolite ZSM-5, has sparked the interest of many workers recently, but the mechanistic details of the reaction are not yet very clear. A study of the relative rates of this conversion under different conditions was carried out using FTIR spectroscopy, and the surface species that were formed on the catalyst were studied. The catalysts were fluorided during synthesis, a new approach to fluoridation, and results showed that the incorporation of fluorine in the catalyst was successful. This process also had a beneficial effect on the reactivity of the catalyst, particularly in shortening the induction period before hydrocarbon formation commences.

The initial step of the reaction involves the dehydration of methanol to form an equilibrium with dimethyl ether (DME). Methanol and DME were interchanged as starting materials. it was found that when DME is used as feed, the reaction proceeds much faster than when methanol is used. It is proposed that this difference in rate is due to the absence of water in the DME reaction. It was observed that re-using a catalyst right after a reaction was effective in increasing the rate of the reaction; this has been attributed to the presence of active surface species. It was found that the deliberate generation of an organic species on the surface (from n-dodecane) also gave a more reactive catalyst. It was postulated (from IR spectra of the catalyst surface) that the active component on the modified surface is a species with a protonated double bond.

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Chapter 1

INTRODUCTION

Since the energy crisis of the mid 70's, many alternative sources of energy have been developed, using renewable resources (sun, wind, etc.) and hydrocarbons sources other than petroleum. The MTG (methanol to gasoline) process is one of the latter; it involves the conversion of methanol to hydrocarbons in the gasoline boiling point range. Recently, a plant was opened in New Zealand which produces gasoline from methane¹; the first step of the reaction is to produce methanol (from methane), `and , subsequently convert that methanol to gasoline. The interesting aspect of this process is that methanol can be obtained from many different sources, including coal and natural gas.

The active catalyst in the MTG process is the zeolite ZSM-5 (Zeolite Socony-Mobil, 5). It presents many features that are advantageous to the industry: it is relatively inexpensive, it is thermally very stable, and it is very resistant to poisoning. In this first chapter, the structure and properties of zeolites will be examined; and what is known of the MTG process itself will be reviewed.

§1.1 Zeolites

The origin of the word zeolite is attributed to the Swedish scientist Cronsted², who used it in 1756 to describe the behavior of the mineral stilbite, which acts as if it were boiling when heated (zeo-lite: the stone that boils). Although they occur naturally, many of the industrially interesting zeolites are synthetic (the synthesis of

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zeolites will be reviewed in the next chapter). They are composed of interconnecting TO_4 tetrahedra, where T can be Si, Al, B, Ga, Fe, Cr, Ge, Ti, P, V, Zn, Be, ..., although classically, Si and Al are used. These TO_4 units are arranged in such a way as to form cavities, which in turn create channels of discrete dimensions. Therefore the size and shape of the molecules that can enter the zeolite (to gain access to its active sites) and also the intermediate and product that can be formed in the catalyst, is limited by the physical size of these pores; this property is called shape-selectivity^{3,4}.

Fig. 1.1 shows a typical way of representing zeolites sub-units and structures using straight lines. The intersection of 2 or more lines represents a T unit, and the O atoms lie close to the centre of each line (for simplicity, their actual location is not shown). In this figure, we can see how different building units can be assembled to form different zeolites (zeolites Y and A are very common zeolite) with different pore sizes and shapes. While this is a convenient way to visualize the formation of a structure, it does not necessarily mean that this is what happens in solution as the crystals form.

What makes zeolites such interesting catalysts are their strong acid sites. (In the following, the "classical" zeolite, that is with T being Si or Al will be discussed). Basic sites are also present on zeolites, but their use in industrial processes is very limited⁵. Both Brønsted and Lewis acid sites are present, but the importance of the Brønsted ones is greater. The Lewis sites are formed by trivalent Al in

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the framework.



Fig. 1.1. Illustration of the assembly of building blocks to form faujasite-type zeolite and zeolite A. D4R stands for Double 4 (member) Ring, as D6R represents Double 6 (member) Ring.

The proton donor sites can arise from two situations : when Al is present in the framework of the catalyst, if it is coordinated to four oxygen atoms, a negative charge will arise in the structure (mostly localized on the Al). To compensate for that negative charge, a cation has to be introduced in the system. If the cation is strongly polarizing, it can be hydrolysed to form an acidic site in the following manner:

$$La(H_2O)_{x}^{3+} \longrightarrow La(OH)(H_2O)_{x-1}^{2+} + H^{4}$$

Another way to produce a strong proton donor is by the formation of an OH group on a Si adjacent to an Al, producing a bridged hydroxyl, as shown below:



It is now possible to see why zeolites are sometimes referred to as "designer catalysts", as their properties can be modified to obtain "tailor-made" catalysts. The pore size can be changed by choosing which type of zeolite structure to use, and then that size can be "fine-tuned" by choosing a cation of a specific size (since the cation sits in the pores of the catalyst, it will partly obstruct the channels). The acidity of the catalyst can be controlled by using H^+ as cation (by itself or with another cation) or by modifying the Si/Al ratio (more Al means more acidic sites), or by choosing a cation that can be hydrolysed.

§1.1.1 ZSM-5

ZSM-5 was patented by Mobil Oil in 1972⁶. The building unit, shown in figure 1.2, is made of a series of double 5 rings (DSR). These units will combine to form sheets, which when brought together create a structure with straight channels running perpendicular to zigzagging channels (Fig. 1.3). ZSM-5 was one of the first high-silica zeolites, having a Si/Al ratio higher than previous zeolites. This particular property makes them more hydrophobic and organophilic. Silicalite, the aluminium free member of the ZSM-5⁷ family is the most hydrophobic member of the ZSM-5 family. ZSM-5 is without any doubt the best catalyst for the conversion of methanol to gasoline (to date).





Fig. 1.2 Building unit of ZSM-5.



Fig. 1.3 Channel structure of ZSM-5.

§1.1.2 Fluoridation

One way of modifying the reactivity of zeolites is to fluoridate them. The process consists of introducing fluorine into the framework of the catalyst, where it will take the place of an O or OH. The fluorine, being very electronegative, will polarize the lattice, thus increasing the acidity of the catalyst (both Lewis and Brønsted), by pulling the electrons towards it, and thereby weakening any OH bonds nearby, and making the Lewis sites stronger electron accepter. Fluorine is usually introduced after synthesis; the sample can either be exposed to vapours of a fluorine containing compound (such as F_2 , CH_2F_2 , CF_3COOH , CF_3OH , CF_3OCF_3 , CF_3CH_2OH , SF_6 , SO_2F_2 or SOF_2) or it can be impregnated with a solution containing such compounds as HF, BF_3 , HBF_4 , NH_4F , NH_4BF_4 or NH_4SiF_6 . A review on the subject has been written by Ghosh and Kydd⁸, and current work in the subject with particular reference to zeolites can be found in the literature^{9,10,11,12}.

§1.2 Conversion of Methanol to Hydrocarbons

The formation of hydrocarbons from methanol (MeOH) can be divided into three steps: 1. The formation of dimethyl ether (DME). 2. The formation of the first C-C bond. 3. Chain growth, which can be accompanied by aromatization.

2 MeOH $\stackrel{I}{\longleftarrow}$ DME + H₂O II First C-C bond III Higher hydrocarbons Aromatization

Table 1.1 shows a typical distribution of hydrocarbon products for a conversion of methanol over ZSM-5 at 370°C. As can be seen, most of the aromatics are methyl substituted. The table shows one of the advantages of the MTG reaction; a fairly narrow range of molecular weight is obtained, with C_{10} being at the upper limit.

Table 1.1 Typical distribution of hydrocarbons over ZSM-5 (370°C, 1 atm., 1 LHSV), from ref. 16. C represents aliphatic hydrocarbons, with the superscript ⁼ indicating olefins, and A stands for aromatics.

	Hydrocarbon distibution (wt%)
C ₁	1.0
C2	0.6
$c_2^{=}$	0.5
c ₃	16.2
c_3	1.0
C ₄	24.2
$c_4^=$	1.3
C_5^+ aliphatic	14.0
A ₆	1.7
A ₇	10.5
A ₈	18.0
A ₉	7.5
A ₁₀	3.2
A ⁺ ₁₁	0.1

§1.2.1 The Methanol - Dimethyl Ether Equilibrium

This step is acid catalysed, but the nature of the acid site is not quite clear. While studying the dehydration of methanol over alumina and silica-alumina, Parera and Figoli¹³ found that the reaction occurs over strong acid sites. But more recently, Ono and Mori¹⁴ have shown, through poisoning of the acid sites on the ZSM-5 surface, that formation of dimethyl ether occurs on weaker acid sites, as it is still produced when the production of hydrocarbon is stopped. Since the stronger acid sites are believed responsible for the production of higher hydrocarbons, and would be poisoned first, that leaves only the weaker acid sites intact on the surface to catalyse the methanol dehydration. Results obtained by Sodesawa¹⁵ point to the same conclusion; he studied ZSM-5 with different degrees of proton exchange, and found that in the case where no H is present, the ether is still formed, but no hydrocarbons, suggesting that strong Brønsted sites are not necessary for the dehydration of methanol.

The reaction can be envisioned in the following ways, whether the reaction occurs over Lewis sites (L) or Brønsted sites (B):



§1.2.2 Formation of the First C-C Bond

The second step of the overall reaction, the formation of the first C-C bond, is characterized by an induction period. Many mechanisms have been proposed for that step (see the review by Chang¹⁶). Only the two most probable mechanisms, the carbene (or carbenoids) and the

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oxonium/ylide mechanisms, will be described in detail here.

§1.2.2.1 The Carbene Mechanism

It was proposed that olefins are formed via an α -elimination mechanism followed by polymerization of the resulting carbene¹⁷:

$$\begin{array}{ll} \text{H-CH}_2 \text{-OH} & \longrightarrow \text{H}_2 \text{O} + : \text{CH}_2 & (1.3) \\ \text{n: CH}_2 & \longrightarrow & (\text{CH}_2)_n \text{ , n=2,3,4,5} & (1.4) \end{array}$$

In a zeolite matrix, the formation of the carbene can be facilitated by a cooperative action of acidic and basic sites¹⁸, as shown below.



Additionally, the presence of a strong electrostatic field can help the dissociation of the bonds. Theoretical studies showed that an electrostatic field of the order of 10^{10} V/m can actually dissociate the bonds in the methanol molecule or dimer¹⁹. Very recently, Beran²⁰ calculated the electrostatic field inside ZSM-5 to vary between 5×10^9 V/m and 10^{10} V/m. *Ab initio* calculations have also shown that methylene is stabilized by interaction with a zeolite surface²¹. Furthermore, Lee and Wu²² showed that similar reaction products can be obtained by using diazomethane (a source of carbene) on ZSM-5 instead of methanol. An alternative to the polymerization of carbene (reaction 1.4) is the "rake mechanism" (Fig. 1.4). This mechanism was proposed by Cormerais and co-workers²³ when they observed methyl ethyl ether in the reaction mixture. They proposed that the intermediates between the ethers and olefins are carbonium ions, although the possibility of having carbenes as such intermediates can not be ruled out.



Fig. 1.4 Rake mechanism.

The presence of free radicals in the gas phase is unlikely, as was demonstrated by the study of Hunter *et al.*²⁴, who showed that NO (a free radical scavenger) in the reaction mixture has no effect on the rate of the reaction. But such findings do not negate the presence of carbene, or carbene-like species, on the surface, as they would be more stable than in the gas phase, and could resist attack by the scavengers.

§1.2.2.2 The Oxonium/Ylide Mechanism.

This mechanism was first proposed by Van den Berg et al.²⁵ and

 $Olah^{26}$, and further work was originally done by Mole and Whiteside²⁷. It involves the formation of an oxonium ion, trimethyloxonium (TMO) (A), which will deprotonate to form an ylide (B). The formation of ethylene would then follow, either via a Steven rearrangement, or from the addition of another dimethyl ether or methanol molecule and subsequent decomposition:



An ylide is described as a molecule, having two adjacent atoms, one of which is coordinated to one more atom than "usual" (O in species B), while the other is coordinated to one less atom than "usual" (C in species B); with the appearance of the appropriate charges. Olah *et al.*²⁸ pointed out that instead of a trimethyloxonium ion, one can have a surface bonded dimethyl ether acting as an oxonium ion.



Hellring *et al.*²⁹ studied the reaction of TMO salts on ZSM-5 using NMR spectroscopy and proposed a different mechanism for the decomposition of the TMO ion. This mechanism involves a bridged methoxy group as an intermediate.



In this last case, one can argue that the mechanism could be classified in the carbene category.

§1.2.3 Formation of Higher Hydrocarbons.

Once the initial C-C bond is formed, the reaction then proceeds largely from the reaction between olefins (one of the products of the reaction) and methanol/dimethyl ether. Higher hydrocarbons would then be cracked to produce lower olefins and react further. This scheme has been used to explain the autocatalytic character of the methanol conversion. Many workers have shown that the rate of reaction is greatly enhanced when olefins (or "olefin precursors" like alcohols) are present in the reaction mixture^{30,31,32}.

Kolboe³³ proposed that olefins on the surface would be protonated by the catalyst, forming a carbonium ion. The surface would then become a basic site (as shown in the reaction below); combined with the carbonium ion acting as an acid site, carbenes could then be produced according to the concerted acid/base mechanism mentioned earlier.



There is evidence in the literature 34,35,36,37 that olefins form oligomers on the surface of zeolites, and that these oligomers have carbonium character.

§1.3 Scope of this Work

The first objective of this work was to be able to synthesise samples of ZSM-5, and especially the Al-free member of the family, silicalite. No result had been reported on the reactivity toward the MTG reaction of a very pure sample of silicalite (that is with a very low concentration of Al, since Al-free sources of silicates are hard to obtain).

The introduction of fluorine in the catalyst structure during synthesis (a new approach to fluoridation) was also investigated, and the reactivity of those fluorided samples was studied to see what effect the strong acid sites expected from fluoridation would have on the MTG reaction.

A comparison of the reactivity of the catalysts with different feeds (methanol or dimethyl ether) was also carried out, in an attempt to determine which of these is the primary active species in the MTG reaction. It was hoped that a comparison of their reactivity as starting materials and an investigation of the gas phase species produced as they react would yield light on the subject.

In another part of this work, the effect of "surface species" on

the MTG reaction was studied. The surface species were produced by the MTG reaction itself, by pretreating the surface with n-dodecane, and by partial coking. n-Dodecane was used to see if the alkenes produced by cracking of higher hydrocarbons over acidic catalysts would be sufficient to increase the rate of the MTG reaction over ZSM-5. The nature of the surface species was investigated using FT-IR spectroscopy, in an attempt to gain insight into their functional groups and in the nature of the intermediates involved in the process. Spectra were take before a reaction, to see the species present on the surface, and to see which species interact with the reactant feed at room temperature. The evolution of the surface species during the MTG reaction was also investigated by interrupting the reaction at different times.

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Chapter 2 Synthesis and Characterization of Catalysts

One can start to understand the importance of zeolites by considering the number of patents dealing with that subject (as early as 1973, Breck¹ estimated that number to be over 2000 in the U.S.). Most of these are concerned with their synthesis. Originally, the study of the synthesis of zeolites was motivated by the need to understand reactions occurring in the lithosphere on or near the surface (zeolites exist as natural minerals but the most interesting ones commercially are synthetic), but that interest has shifted to the production of a better catalyst.

In recent years, many good books have been written that deal with the synthesis of zeolites, one of the first being that by Barrer². Very recently, Jacobs and Martens³ published a very comprehensive book' dealing with the synthesis of high-silica zeolites. In this chapter, the different theories explaining the synthesis of zeolites will be discussed, along with the different methods used in this lab to characterize them.

§2.1 Synthesis of ZSM-5

Zeolites are generally synthesized from an aqueous system containing a silica source, an alumina source, an alkali-metal base, and an organic base (usually a tetraalkylammonium salt). In the case of ZSM-5, a tetrapropylammonium salt (TPA) is used. Some modifications can be made to the above list of ingredients, as for example, the presence of the organic base can be replaced by seed crystals of the zeolite to be synthesized. The mixture is then put in an autoclave and heated under autogenous pressure for a few days (although some syntheses have been carried out over a period of many months). With the advent of NMR spectroscopy (27 Al and 29 Si), new light has been shed on the mechanism of the formation of zeolites.

§2.1.1 The Chemistry of Aluminosilicate Solutions.

For the formation of ZSM-5 (as for any other zeolite), the silica and alumina sources have to be rearranged into a new structure (the zeolite structure). This can be done in two ways: Dissolution of the silica-alumina followed by recrystallization from the liquid phase; or the zeolite can crystallize from a gel.

In alkali solution, silica will dissolve (explaining the importance of the alkali-metal base) and form a solution containing monomeric species and polymeric anions. Figure 2.1 shows the distributions of silicate species in an aqueous alkali metal solution⁴. The Q_n^{i} notation is used to represent the species, where i is the number of siloxane bridges surrounding the silicon atom, and n simply indicates the number of silicon atoms in that state. So the Q^0 species is Si(OH), and Q_2^1 would be (OH)₃SiOSi(OH)₃.

20



Fig. 2.1. Distribution of silicate species in aqueous solution. Adapted from ref. 4.

This distribution can be modified with the aid of additives, such as tetraalkylammonium salts, and other silicate species can be formed. Using ²⁹Si NMR, FTIR and mass spectrometry, Boxhoorn *et al.*⁵ showed that in the reactant mixture for the synthesis of ZSM-5, a Q_{10}^3 (figure 2.2)
species exists and it is obvious that minor modifications of that structure can give the building unit of ZSM-5.



Fig. 2.2. Q_{10}^3 species and building unit of ZSM-5.

Aluminium for its part exists only as the monomer $Al(OH)_4^-$ (in alkali solution), but with an organic base in the system, it can be incorporated in some of the silicate species.

§2.1.2 The Role of Tetrapropylammonium Ions

Early on, it was found that the TPA ion exists as such inside the pores of the zeolites. Nagy *et al.*⁶ showed using ¹³C NMR that the TPA sits at the intersection of two channels, a result which was also confirmed by Price *et al.*⁷ using single crystal X-ray crystallography. This lead to the suggestion that TPA acts as a template to the zeolite.

As was mentioned above, in the presence of an organic additive, one can change the distribution of silicate species in solution. Derouane *et al.*⁸ showed that in the presence of TPA, and at the right pH, Al will interact with the organic base, and through it with silicates, thus forming the aluminosilicate species. The role of the TPA template was also emphasized in a study by Gabelica *et al.*⁹, where they compared TPA against TBA (tetrabutylammonium) salts; their result showed that in the presence of TBA, only ZSM-11, a different zeolite, is formed, as opposed to ZSM-5 in the case when TPA is used. ZSM-11 is very similar to ZSM-5 (same building unit), except that instead of having zigzagging channels running perpendicular to straight channels, it has straight channels running perpendicular to another set of straight channels.

§2.1.3 Effect of the Alkali-metal Base.

The pH of the solution has to be adjusted to an optimum level. An increase in the pH will increase the solubility of the silica source, so that the surface nucleation will be faster, and so will be the reaction at the crystal solution interface. But too high a pH will also dissolve the zeolite.

The type of alkali-metal cation will also affect the synthesis. Derouane and Gabelica¹⁰ showed that the time required for the initial hydrogel to nucleate will vary with the cation ionic radii, Na^+ giving the fastest rate. This is the reason that NaOH is widely used as a source of alkali base.

The synthesis of ZSM-5 can be visualized with the diagram shown

on Fig. 2.3.



Fig. 2.3. Schematic representation of the synthesis of ZSM-5.

Whether nucleation occurs in solution or in the gel depends on the type and concentrations of reactants. Derouane *et al.*¹¹ labelled the nucleation in solution as type A, and the nucleation in the gel as type B. They concluded that for type A nucleation, one needs a higher concentration of TPA, and usually a more polymerized source of silica, such as silica gel, should be used. For type B nucleation, less TPA should be used, the solution should have a lower pH, and the silica source should be close to monomeric (waterglass is very good for that purpose).

§2.1.4 Typical Synthesis of ZSM-5, as Performed in this Lab.

The synthesis used was of type A. In a beaker, 0.14 mole of silica gel (Fisher grade 63) and 0.01 mole of TPABr (Aldrich) were mixed in 40 ml of water. In another beaker, 0.0035 mole of alumina (Fisher certified) were stirred in 25 ml of a NaOH solution. After approximately 30 min., the contents of the 2 beakers were mixed together. In some cases, different quantities of NH_4F were introduced, and in all cases, the pH was adjusted to between 10 and 11, and the mixture was stirred for 2 hours at around 80°C (to eliminate carbonate from the solution). The mixture was then transferred to an autoclave, the temperature was raised to between 155 and 160°C and the solution stirred for 2 days. This gave a reaction mixture with a TPA/Si ratio of 0.07 and a Si/Al ratio of 20.

After synthesis, the samples were heated in air at 500° C overnight, to decompose the TPA occluded in the framework. H-exchange was carried out by refluxing 2 g of the catalyst in 25 ml of a 0.5 M solution of NH₄Cl for 2 hours; the reflux was then repeated 2 more times. In this way, any Na⁺ left in the pores from the synthesis would be replaced by NH₄⁺, which would be converted to H⁺ after calcination of the catalyst in oxygen.

A sample of silicalite (the Al-free member of the ZSM-5 family) was also prepared. To ensure that no Al contaminant was present in the Si source, silica gel was prepared by distilling silicon tetrachloride (Aldrich gold label) into distilled de-ionized water, and drying the obtained gel. No H-exchange was performed on that sample, since there is no Al present in the structure (in the absence of tetravalent Al, there is no negative charge, therefore no need for a cation).

§2.2 Characterization of ZSM-5

In order to identify and characterize the catalyst produced, the XRD pattern of the product and its surface area were measured. Also, pyridine adsorption on the surface was used to characterize the acidity. The fluorine content was determined with a fluoride electrode and also by neutron activation measurements carried out by Nuclear Activation Services Ltd (Ontario). The latter technique was also used to determine Si and Al concentrations. The crystal size was observed using SEM.

§2.2.1 XRD

XRD powder patterns of our samples were obtained through the kind cooperation of the Department of Geology and Geophysics of this University. The instrument used was a Norelco X-Ray Diffractometer with Ni-filtered Fe K α radiation. The obtained patterns were compared to those published in the literature¹² to confirm that our product was indeed ZSM-5.

§2.2.2 SEM

The scanning electron microscopy of our samples was also obtained through the Department of Geology and Geophysics of this University. The

instrument is a Cambridge Stereoscan 250 Scanning Electron Microscope. The powdered samples were attached to the SEM sample holder with a two sided adhesive tape, and the catalysts were coated with gold and carbon. The micrographs obtained were used to determine the crystal size in the different catalyst samples.

§2.2.3 Surface Area

A Micromeritics model 2200 high speed surface area analyzer was used to ensure that all samples had comparable surface area. The area was measured from the quantity of nitrogen gas adsorbed at liquid nitrogen temperature.

§2.2.4 Fluoride Electrode

The fluoride content of our sample was determined using a fluoride electrode (Orion combined fluoride electrode, model 96-09-00). The electrode was calibrated using solutions with different concentration of NaF. The samples of zeolite were digested in a 0.1N solution of NaOH overnight, then the solution was decanted and an equal amount of ionic buffer Tisab IV (prepared in this lab, it is a solution of HCl, TRIS(hydroxymethyl)aminomethane and sodium tartrate) was added to avoid interference from other ions in the solution, and to maintain a constant pH. The electrode was dipped in the solution and the observed potential was compared to the calibration curve to establish the concentration of F in the catalyst.

§2.2.5 Neutron Activation

The Si, Al and F content of our sample was determined by neutron activation. The catalyst samples were sent to Nuclear Activation Services Limited, in Hamilton Ont. for this analysis.

§2.2.6 Pyridine Adsorption

Pyridine adsorption was used to characterize the acid sites in the catalyst. The IR spectra of pyridine coordinately bonded to the surface is different than that of the pyridinium ion, therefore, it is possible to obtain the relative number of Brønsted and Lewis acid sites from the IR spectra of adsorbed pyridine. Table 2.1 gives us the position of the IR bands for pyridine adsorbed on solid acids¹³. As can be seen from that table, the bands at 1540 and 1447-1460 cm⁻¹ are the most useful to characterize the Brønsted and Lewis acid sites respectively.

Prior to pyridine adsorption, the catalysts were pretreated in the same way as for an MTG run (see chapter 3). Pyridine vapour was then brought in contact with the catalyst surface at 100°C for 30 min., then desorbed for 1 hour prior to taking a spectra, to avoid interference from too much physisorbed pyridine. Further desorption at higher temperature was also carried out to determine the strength of the acid sites (on stronger sites, the pyridine bands would be still observed after further desorption).

Table	2.1	Infrared	bands	\mathbf{of}	pyridine	adsorbed	on	solid	acid.	(From
ref. 3	13)									

Hydrogen bonded pyridine	Coordinately bonded pyridine	Pyridinium ion
	(Lewis Py)	(Brønsted Py)
1440~1447 1485~1600	1447~1460 1488~1503	1485~1500
1580~1600	~1580 1600~1633	~1620 ~1640

+ 1

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Chapter 3

Experimental Method for Studying the MTG Reaction

In the previous chapter, the synthesis and characterization of the catalyst samples were described. However, the most interesting property of these zeolites is their catalytic reactivity. In this chapter, the method used to study the conversion of methanol to hydrocarbons over these catalysts will be discussed. In addition, because of the importance of the FTIR spectrometer in this work, the principles behind its operation will be discussed.

§3.1 Catalyst Preparation

The H-form of the catalyst (that is where the cation present is H^+) was pressed using a load of 1-2.5 metric tons, into 20 or 30 mg self supporting wafers of 13 mm diameter. For a typical MeOH reaction, three 30 mg wafers and one 20 mg wafer were placed into the reaction cell. The thinnest one was necessary so that IR light could be transmitted through it, and the thicker ones were needed to have enough catalyst to get a reasonable reaction rate. The wafers were mounted in sample holders which attached to a stainless steel rod within the IR cell (see Fig. 3.1)

The IR cell was designed in such a way that the samples could be thermally treated, observed in the IR, and different gases could be admitted. Half of the cell was made of quartz glass (resistant to high temperature), and the other half was made of pyrex glass. with infrared transmitting BaF₂ windows mounted on it, and a connector to a vacuum line. BaF_2 windows were used because they transmit IR radiation to approximately 800 cm⁻¹ (lower than CaF_2) and they are resistant to water, a byproduct of the MTG reaction, much more than KBr windows are.



Fig. 3.1 Diagram of the IR cell.

In preparation for a reaction, the cell was connected to the vacuum line, and a tubular furnace was placed around the quartz end of the cell (with the catalyst in that position). The cell was evacuated to pressures of 10^{-5} mm Hg, and the temperature was brought from room temperature to 100°C at a rate of 2.5°C/min. To avoid any damage to the framework of the catalyst by too rapid desorption of water, the samples were kept at 100°C for 2 hours, then dehydration was continued by raising the temperature to 500°C again at a rate of 2.5°C/min. The catalysts were kept at that temperature overnight under vacuum, then 350 mm Hg of O_2 was admitted for *ca.* 8 hours to calcine any organic contaminants on the surface. After that period, the samples were then ready for

further testing (either pyridine adsorption or a catalytic conversion of methanol or dimethyl ether to higher hydrocarbons). Surfaces pretreated in this way were labelled "fresh". In other experiments, to investigate the effect of surface species, the samples were simply evacuated overnight at room temperature, after a methanol or DME reaction, without calcining the surface; such surfaces were designated "used".

The schematic diagram of the temperature controller is shown in Fig. 3.2. The heart of the system was an Apple II+ computer which was connected to a digital thermometer via an A/D converter (for reading the temperature), and to a solid state relay (to turn on and off the furnace) to the rest of the system. The program to operate the computer was written during the course of this work and is included in this work in the appendix.



Fig. 3.2. Schematic diagram of the temperature controller.

§3.2 FTIR Spectroscopy

Using IR spectroscopy for the study of surface species on a zeolite surface is not a trivial problem. The thin wafers of catalyst

did not transmit much light. Typically, in the best region, around 1500 $\rm cm^{-1}$, only 35% of the IR light is transmitted through, and near 3000 $\rm cm^{-1}$, transmission drops to less than 3%, therefore multiscanning is necessary. To be able to distinguish the surface species (which may be present in very low concentrations) from the spectrum of the surface itself, subtraction of the spectra has to be done, and for this, a high wavenumber accuracy and constant resolution is required. For these reasons, the choice of FTIR spectroscopy was obvious.

The heart of the FTIR instrument is the Michaelson interferometer (Fig. 3.3). At the centre of it is the beam-splitter, which has the property of reflecting approximately half the incident light, while at the same time letting the other half through. Part of the light will be reflected back from a fixed mirror, while the other part will be reflected back from the moving mirror. When the moving mirror is at the same distance from the beam-splitter as the fixed mirror, the waves coming back from both mirrors are in phase and add to each others. At this point the intensity of the output signal is a maximum: this position is called z.p.d. (zero path difference). In the case of monochromatic light, when the moving mirror is at a position z.p.d.+ $1/4\lambda$ (or z.p.d.-1/4 λ), λ being the wavelength, the two waves coming back from the mirrors are out of phase by 1/2 $\lambda,$ and therefore cancel each other and the output signal is zero. For a monochromatic light source, the output signal as a function of the moving mirror position would be a sine wave, and this output is called an interferogram. For a polychromatic light source, an interferogram that would look like

Fig. 3.4 would be obtained. When the interferogram is Fourier transformed, a spectrum is obtained.



Fig. 3.3 Michaelson interferometer.

§3.2.1 The Advantages of FTIR

The Felgett advantage states that the ratio of S/N between an interferometer spectrum and a grating instrument spectrum will be given by:

$$\frac{(S/N)_{I}}{(S/N)_{C}} = M^{1/2}$$

Where M is equal to $(\Delta \sigma)/\delta \sigma$ where $\Delta \sigma$ is the wavenumber range studied and $\delta \sigma$ is resolution in wavenumbers. Typically $\Delta \sigma$ will be equal to 3000 cm⁻¹, while $\delta \sigma$ will be 2 cm⁻¹. Thus M is quite large, and this provides a significant gain in signal to noise.



Position of moving mirror



Another advantage is the Jacquinot Advantage, which reflects the fact that FT instruments do not have slits. Therefore a large circular beam of light passes through the instrument, and the energy getting to the detector is much larger, so the signal to noise ratio is enhanced again.

The possibility of rapid multiscanning is another advantage allowing better S/N. The collection of one scan (that is the one back and forth movement of the moving mirror) takes approximately one second, therefore a great number of scans can easily be collected in a reasonable time. For the catalyst samples studied here, 400 scans were usually collected, which means a collection time of approximately 5 min.

§3.3 Calibration of the IR Cell

In order to better study the speed at which the reaction occurs was convenient different catalysts, it to convert over the IR absorbances into pressure of the reacting gases. Fig. 3.5 shows a typical IR spectrum (between 1400 and 800 cm^{-1}) of the gas phase of the reaction mixture (after 30 min. of reaction at 265°C). A calibration curve relating pressure to IR absorbance was developed by introducing different pressures of dimethyl ether (DME) or methanol (MeOH), into the cell. The intensity of characteristic bands (the 1175 cm^{-1} band (CH₂ rocking) for DME, and the 1030 $\rm cm^{-1}$ band (CO stretching) for MeOH) were recorded and plotted against the pressure as shown in Fig. 3.6 and 3.7. These calibration curves were used to convert the observed IR intensity



Fig. 3.5.Spectrum of the gas phase products from a methanol reaction over H-ZSM-5 $_{\rm f}$ after 30 min. The reaction temperature is 265°C.



Fig. 3.6. Calibration curve relating the pressure of dimethyl ether to the intensity of the IR band at 1175 cm⁻¹.



P_{MeOH} (mm Hg)

Fig. 3.7. Calibration curve relating the pressure of methanol to the intensity of the IR band at 1030 $\rm cm^{-1}.$

to pressures of the different gases during the catalytic experiments.

A blank reaction (no catalyst) was also performed to show that no part in the cell or sample holder was acting as a catalyst, and that the reaction was not proceeding through just a thermal effect. The results were satisfactory, as no reaction was observed up to a temperature of 500° C.

§3.4 MTG Reaction

Before reaction, spectra were taken of the empty cell (that is with the cell under vacuum, and no catalyst in the IR beam) for background subtraction from the gas phase spectra. Spectra were also taken of the catalyst surface before reaction, again for background subtraction, but for surface species spectra. These subtractions were necessary to avoid interference from the BaF_2 windows or from IR vibrations of the zeolite lattice. In this way, only bands due to species in the gas phase, or on the catalyst surface, would appear in the spectra.

Both methanol and dimethyl ether were used as starting materials for the MTG reaction. In the case of MeOH, a small (*ca.* 5 ml) sample of MeOH (Fisher spectranalyzed grade), which had been degassed through 3 freeze-pump-thaw cycles, was cooled by immersion in a water ice bath (to control the pressure of methanol). The cell was opened to the MeOH vapours for 45 seconds, which proved to produce a convenient and fairly reproducible initial pressure. For DME (Matheson), a lecture bottle of the gas was connected to the vacuum line, and the desired pressure admitted directly (as measured using a mercury manometer).

In some cases, a mixture of DME with water was used. The water vapour was introduced and its pressure estimated using a mercury manometer, then DME gas was introduced and the total pressure measured. The exact pressure of DME in the cell was determined by IR spectroscopy, and the pressure of water was calculated by difference from the total pressure. Since the total pressures are fairly low (*ca.* 20 mm Hg), any non-ideal behavior of the gas mixture (due to water hydrogen-bonded to DME for example) was taken to be negligible.

After introducing the desired reactant gas, the cell was then placed in the spectrometer in such a way that the BaF_2 windows were in the IR beam, and the quartz part of the cell was in a tubular furnace (the catalyst pellet holders being at that end of the cell). The same temperature controller as described in section 3.1 was used to adjust the furnace temperature; the furnace was preheated to the desired temperature before starting the reaction. The progress of the reaction was followed by taking spectra of the gas phase (typically 50 scans) at given intervals, and recording the variations in the intensity of the MeOH band at 1030 cm⁻¹ or the DME band at 1175 cm⁻¹. These intensities were converted to pressures as described above. At the end of the reaction (usually when the pressure of the starting material fell below 10% of its initial value), spectra were taken of the catalyst surface (400 scans) to characterize the surface species at that time.

Chapter 4

Results

§4.1 Catalyst Properties

Table 4.1 gives a list of the catalysts studied and results of analysis. All analyses were performed on the H-form of the catalyst, except for ZSM-5.

Catalyst	Surface Area m ² /g	Si/Al mole/mole	%F wt∕wt
ZSM-5 _a	333	ω	0
H-ZSM-5	314	7	0
H-ZSM-5 _c	302	*	.0034
H-ZSM-5 _d	296	9	. 0092
H-ZSM-5e	265	8	.011
H-ZSM-5	264	*	.080
		1	

Table 4.1 Characteristics of the catalysts studied.

* Results from Nuclear Activation Services were unavailable at time of publication.

The fluoride content was taken from the fluoride electrode analyses, rather than from neutron activation, as the latter method was not as sensitive to low amounts of F. The samples in the table are listed in order of the increasing amount of NH_4F present in the synthesis mixture; as can be seen, the amount of F in the final product increases with the amount introduced in the synthesis, although not linearly (in the synthesis mixture, the molar F/Si ratio was for c=5%, d=10%, e=20% and f=30% compared to 0.02\%, 0.03\%, 0.04\% and 0.3\% respectively in the final product).

Fig. 4.1 shows the XRD patterns of sample $ZSM-5_{f}$ (all the samples were identified using XRD); the peak positions are in agreement with those described in the literature¹. The only difference from one catalyst sample to another is in the total height of the peaks. This height is an indication of the degree of crystallinity of the sample and of particle size. No phase other than ZSM-5 was detected from the XRD patterns. The surface area of the samples decreases with fluoride content; this observation will be discussed in the next chapter.

A typical scanning electron micrograph of one sample is shown in Fig. 4.2. All the crystals within a sample, and between samples look quite similar, with a typical length of 10 to 15 μ m.

§4.1.1 IR Spectra of the Surface

 $H-ZSM-5_{f}$ was the most extensively studied sample using IR spectroscopy, although the other catalysts were also studied. Unless otherwise mentioned, the surface species observed on other catalysts were similar to the one observed on $H-ZSM-5_{f}$. Fig. 4.3 shows the spectrum of a clean fresh surface of $H-ZSM-5_{f}$. The region above 3000 cm^{-1} is not very clear because of light scattering due to particle size, which is also responsible for the sloping base line; but the only absorptions above that region are the CH stretching, which offers a



Fig. 4.1. XRD pattern of ZSM-5_f.

4:4

Fig. 4.2. SEM micrograph of $ZSM-5_b$. The magnification on the upper micrograph is $\times 700$, and is $\times 3400$ on the lower one.







limited amount of information, and the OH stretching (3600 to 3700 cm^{-1}), which is very noisy for all the catalysts studied because of the scattering mentioned above. Below 1300 cm⁻¹, the catalyst itself absorbs so much light that no information is available. For these reasons the region between 2000 and 1300 cm⁻¹ was most extensively studied. To clarify the data, the spectrum of the catalyst surface with surface species present was ratioed to the spectrum of the clean fresh surface, so that the only peaks observed are due to surface species, and the sloping base line disappears.

§4.1.2 Pyridine Adsorption

Pyridine adsorption/desorption experiments were carried out to study the surface acidity, as described in chapter 2. Fig. 4.4 shows the surface species after desorption at 200°C. Except for ZSM-5_a, all the peaks described in Chapter 2 are observed, indicating that both Lewis and Brønsted acid sites are present. In the case of ZSM-5_a, the absence of a band at 1545 cm⁻¹ indicates the absence of Brønsted acid sites on the surface. Only in the case of ZSM-5_f was it observed that the peak due to pyridine associated with a Brønsted site (1545 cm⁻¹) is stronger than for pyridine associated with a Lewis site (1450 cm⁻¹). This suggests that fluoridation is particularly effective in enhancing the ratio of Brønsted to Lewis sites.

§4.2 Catalytic Activity

As was mentioned in the previous chapter, the progress of the ' reaction was followed through monitoring the intensity of bands in the



IR spectra of the gas phase (methanol by the 1030 cm⁻¹ band and dimethyl ether by the 1190 cm⁻¹ band). From that data, three quantities were derived: the pressure of methanol (P_{MeOH}), the pressure of DME (P_{DME}), and the sum of the pressure of methanol and twice that of DME (P_{Σ}). Since 2 methanol molecules dehydrate to give one molecule of DME, P_{Σ} provides an indication of the number of C atoms in the methanol-DME equilibrium. Although the position of that equilibrium might change, P_{Σ} should remain constant until higher hydrocarbons start to form, so this value is a good indicator of the point when the reaction starts to produce higher hydrocarbons.

§4.2.1 Typical Reaction.

Figure 4.5 shows a typical plot of pressure vs time for a methanol reaction. The curve is divided in 4 parts, labelled A through D. At first, (part A) there is an increase in the pressure of the starting gas (methanol in this case); this initial increase is due to desorption of physisorbed gas on the surface as the catalyst reaches the reaction temperature (the data at point 0 is taken at room temperature, before the reaction, and time 0 is taken when the furnace is placed around the catalyst).

The next part (B) is characterized by a decrease in P_{MeQH} and an increase in both P_{DME} and P_{Σ} as the MeOH-DME equilibrium is reached. To understand why P_{Σ} increases at this point (when it would be expected to remain constant), it must be realized that for all the substances present, there exists an equilibrium between that species in the gas



Fig. 4.5. Evolution of the pressure of methanol and dimethyl ether during a methanol reaction over a fresh surface of H-ZSM-5 $_{\rm d}$ at 300°C.

phase and physisorbed on the surface of the catalyst, and that equilibrium will not be the same for every substance. In this case, methanol physisorbs more strongly than dimethyl ether, so that as the total number of "C" in the equilibrium shifts toward DME, the number of "C" in the gas phase will increase (as indicated by the increase in P_{Σ}), while the number of "C" physisorbed on the surface will decrease.

Part C is characterized by no apparent activity (in the gas phase only, for there is undoubtedly some activity on the surface of the catalyst). This part is not always distinctly seen on every sample, as when the reaction is faster, the equilibrium between MeOH and DME might not be reached; in such cases, P_{Σ} becomes very important in determining when the formation of higher hydrocarbons starts. The combination of parts A,B and C is referred to as the induction period. During part D, the formation of higher hydrocarbons occurs. The rate of that reaction increases with time, and has been labelled autocatalytic by some workers, although the use of that term is not widely accepted. The increase in rate is short lived, and soon after, the rate starts to decrease as the concentration of methanol and dimethyl ether decreases.

§4.2.2 Silicalite

Sample ZSM-5_a (silicalite) proved to be totally unreactive toward the conversion of methanol to higher hydrocarbons. Tests were performed up to a temperature of 400°C but no evidence of reaction was detected. Dehydration of methanol to dimethyl ether, the first step of the reaction, was not even observed.

§4.2.3 Effect of the Fluoride Content on Reactivity

Fig. 4.6 shows the progress of the reaction, plotted as P_{Σ} as a function of time, for all catalysts (except ZSM-5_a). The reactions were carried out at 300°C, and like all catalytic results presented here, were reproducible. To quantify the results, an approximation of the induction period was taken by measuring the time before the P_{Σ} curve falls to 90 % of its maximum value (this will therefore be a measure of part A,B,C and a very small fraction of part D). This value should be taken for comparative purposes, and has no absolute significance. To get some indication of the rate of the reaction after the induction period (i.e. the rate of formation of higher hydrocarbons), the slope of the curve in part D was taken at the point where P_{Σ} is equal to its initial value. Again this is for comparison purpose. All those results are shown in table 4.2.

Catalyst	Induction period min.	Slope of the Curve in part D -mm Hg/min.
H-ZSM-5 _b	86	0.42
H-ZSM-5 _c	63	0.64
H-ZSM-5 _d	104	0.53 -
H-ZSM-5 _e	68	0.51
H-ZSM-5 _f	8	0.65

Table 4.2 Result of catalytic testing of the catalysts at 300°C.



Fig. 4.6. Evolution of Σ during a methanol reaction over different samples of H-ZSM-5 at 300°C. b=H-ZSM-5, c=H-ZSM-5, etc.

The effect of fluoridation is seen primarily on the induction period, which varies from nearly 100 min. to 8 min. for the most fluorided sample. The variation in the slope of the curve in part D is so small that it is very close to experimental error, and therefore is not very meaningful, although the difference between 0.42 and 0.65 mm Hg/min. for the unfluorided and most fluorided sample may be significant. In general, the fluoridation has a beneficial effect on the reactivity of the catalyst, although reaction on sample d showed a longer induction period than that on sample b (the unfluorided sample); this result appears anomalous and will be discussed in the next chapter. The most fluorided sample, ZSM-5_f was the most reactive, having an induction period of only 8 minutes.

The similarities between the rates of formation of higher hydrocarbons (slopes of the curve in part D) could be explained by a rate dependence on gas diffusion. For the induction period, the wide varieties of induction times suggest that diffusion control plays only a minor role, and that the length of the induction period is surface controlled.

§4.2.4 Methanol vs Dimethyl Ether as Starting Material

The effect on the rates of reaction of using different feed was also studied. Dimethyl ether was used as starting material to compare its reactivity to that of methanol. As seen on Fig. 4.7, when DME is used as the feed, the reaction is much faster, and practically no induction period is observed: Interestingly also, small amounts of



Fig. 4.7. Comparison of the progress of the MTG reaction over a fresh surface of H-ZSM-5 at 265°C, for different feed (methanol=A, dimethyl ether=B).

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methanol are detected before the P_{Σ} curve starts to decrease, that is before higher hydrocarbons are formed (these quantities are so small that they do not show up very well on the graph, but as will be seen further, IR spectra of the gas phase show without a doubt the formation of methanol before higher hydrocarbons). To further test DME as reactant, a simulation of the methanol reaction was performed by using an equimolar amount of DME and water vapour as feed (in a methanol reaction, an equimolar quantity of water and DME is produced when methanol is dehydrated). The results are shown on Fig. 4.8, and it is very clear that the rate of the reaction is now much slower, and an induction period has appeared, which is of comparable length to that observed when methanol is used as feed.

IR spectra, between 1700 and 1300 cm⁻¹, of the surface species present just after DME or DME and water was admitted are shown on Fig. 4.9 and 4.10 respectively. The spectrum for DME alone is very simple, with only three peaks (1472, 1456 and 1427 cm⁻¹), due to adsorbed DME. In the case of DME and water, no major changes are observed from the spectrum of DME alone, except for a broad band at 1630 cm^{-1} due to water. It is therefore evident that DME is not interacting with water at room temperature on the surface of the catalyst, and in particular, no evidence for methoxy bands (which would appear at 1464 and 1410 cm⁻¹) is seen.

IR spectra of the gas phase in the alkene CH deformation region (Fig. 4.11 to 4.13) reveal that ethene (950 cm^{-1}), propene (912 cm^{-1})


Fig. 4.8. Evolution of methanol and dimethyl ether during an MTG reaction over a fresh surface of H-ZSM-5 at 265°C. The feed is an equimolar amount of DME and water.



Fig. 4.9. Spectrum of the surface species present on a fresh surface of H-ZSM-5 f after adsorption of dimethyl ether at room temperature.



Fig. 4.10. Spectrum of the surface species present on a fresh surface of $H-ZSM-5_{f}$ after adsorption of an equimolar mixture of dimethyl ether and water at room temperature.



Fig. 4.11. Spectra showing the evolution of the gas phase of an MTG reaction over a fresh surface of H-ZSM-5 $_{\rm f}$ at 265°C. The feed is methanol.



Fig. 4.12. Spectra showing the evolution of the gas phase of an MTG reaction over a fresh surface of H-ZSM-5 at 265°C. The feed is dimethyl ether. (Region between 1200 and 850 cm⁻¹).



Fig. 4.13. Spectra showing the evolution of the gas phase of an MTG reaction over a fresh surface of H-ZSM-5_f at 265°C. The feed is dimethyl ether. (Region between 955 and 875 cm⁻¹).

and isobutene (890 cm^{-1}) are the first hydrocarbons formed. In the case of the DME reaction, the spectra (Fig. 4.12) clearly show that methanol (1030 cm^{-1}) is formed before ethene or propene, as was mentioned earlier. In the methanol reaction, the quantities of ethene formed were larger than those of propene, and the situation was reversed for the DME reaction. (The extinction coefficient of the two relevant bands of ethene and propene were measured and found to be very similar).

§4.3 Study of the Surface-active Species

As was mentioned in the introduction chapter, other workers^{2,3,4} found that pretreating the catalyst surface with olefins increases the overall rate of reaction dramatically, mostly by decreasing the induction period. This decrease in the induction period was studied in three ways. An attempt was made to reuse a catalyst surface after a reaction (a used surface, as opposed to a fresh surface) in order to determine if any species left on the surface of the catalyst after a reaction could increase the rate of the reaction. A reaction was also performed where the surface had been pretreated with n-dodecane to study the effect on the reactivity of an alkane (instead of an alkene).

A study of the effect of heating the catalyst surface in the presence of reactant gases to induce more complete polymerization (i.e. partial coking) of the surface adsorbed species was also performed. IR spectra of the surface species in all cases were taken to try to identify what species are responsible for the change in reactivity.

§4.3.1 Fresh vs Used Surfaces

Fig. 4.14 shows P_{Σ} plotted against time for methanol reaction on both fresh and used surface (at 265°C). As can be seen, the induction period is much shorter for the reaction on the used surface (46 against 90 min. for the reaction over the fresh surface). But the slope for the disappearance of P_{Σ} is very similar for the reaction on either surfaces (0.29 mm Hg/min for the reaction over the used surface and 0.26 for that over the fresh surface).

Looking at these results, it becomes obvious that some species on the catalyst surface (produced during the conversion of methanol) is interacting in some way with the methanol to facilitate the production of higher hydrocarbons. Fig. 4.15 shows the spectrum of the surface species on a fresh surface (H-ZSM-5_f) after methanol has been admitted (in addition to having been ratioed to the fresh surface, the spectrum of the gas phase was also subtracted). This spectrum is similar to that obtained on other catalysts, except for the band at 1716 cm⁻¹. That band is assigned to methanol hydrogen-bonded to a F atom on the surface (H-F stretch). The lower percentage of F in the other catalysts explains why this peak was not observed in those samples. The bands at 1464 and 1410 cm⁻¹ can be assigned to surface methoxy group, in agreement with Beebe *et al.*⁵ and the band near 1450 cm⁻¹ is due to physisorbed methanol.

Fig. 4.16 shows the surface species on the used surface, before and after MeOH was introduced. The bands between 1500 and 1350 $\rm cm^{-1}$ are



Fig. 4.14. Evolution of Σ during a methanol reaction over a fresh surface (A) and used (B) surface of H-ZSM-5_f at 265°C.



Fig. 4.15. Spectrum of the surface species of a fresh sample of H-ZSM-5 $_{\rm f}$ after adsorption of methanol at room temperature.



Fig. 4.16. Spectra of the surface species on a used sample of H-ZSM-5 f before (A) and after (B) adsorption of methanol at room temperature.

due to CH scissoring (Sayed and Cooney⁶ assigned the bands at 1375 and $1467-1457 \text{ cm}^{-1}$ to (CH₂)₂C=CH₂, but since olefins are known to oligomerize on the surface, it is unlikely that that compound exists as such on the surface); but in the light of subsequent results, the bands at 1624 and 1512 $\rm cm^{-1}$ are the most interesting features of that spectrum. In order to see which surface species are affected by methanol adsorption, and which new bands appear (as the strong intensity of the bands on the used surface masks the new weaker bands), the two spectra shown in Fig. 4.16 were subtracted (before MeOH from after MeOH was admitted), and the resulting spectrum is shown in Fig. 4.17. Most of the peaks are similar to the ones obtained for methanol adsorbed on a fresh surface (Fig. 4.15, see the previous paragraph for their assignment), except for the two negative peaks at 1624 and 1512 cm^{-1} . The negative peaks indicate that the species represented by those bands are disappearing, or that MeOH is interacting with the surface species represented by those bands, even at room temperature (although no higher hydrocarbons are observed in the gas phase, as will be seen later). The nature of these species will be discussed in the following chapter.

The same comparison between the reactivity of used and fresh surfaces was done for a reaction in which dimethyl ether was the reactant; the progress of the reactions is shown on Fig. 4.18. The used surface was produced from a DME reaction, as opposed to a methanol reaction in the above case. In this case, the differences between reaction over the two surfaces were not as large as for the methanol reaction: the induction periods are 18 and 30 min. for reaction over the



Fig. 4.17. Difference between the spectra of the surface species on a used sample of H-ZSM-5 f after and before methanol adsorption at room temperature.



Fig. 4.18. Evolution of P_{Σ} during the reaction of dimethyl ether over a fresh (A) and used (B) surface of H-ZSM-5 at 265°C.

used and fresh surfaces respectively, and the slopes are 0.41 and 0.32 mm Hg/min. in the same order; the differences in the slopes is probably not significant.

Fig. 4.19 shows the surface species present on the used surface (before DME was introduced). The surface species observed are the same as those observed on a used surface generated from a methanol reaction (Fig. 4.16). Fig. 4.20 shows the surface species on the used catalyst after DME was introduced (with the spectrum of the surface before DME was introduced subtracted from it). Again the 3 peaks observed in Fig. 4.9 (DME fresh surface) are present, over а but quite interestingly, the negative peak at 1624 $\rm cm^{-1}$ is still present. indicating that DME, like methanol, interacts with the surface species represented by that band. Surprisingly, although the band at 1512 $\rm cm^{-1}$ is present on the surface before DME is introduced, DME, unlike methanol, does not interact with that surface species.

An interesting point to note is that the surface species on the used surface are the same, whether they were produced from a methanol or DME reaction (Fig. 4.16 and 4.19 respectively). This indicates that the final reaction products are similar, and independent of the starting material (methanol or DME).

The spectra of the gas phase species formed during the methanol reaction (Fig. 4.21) reveals that ethene, propene and isobutene are the primary hydrocarbons formed. In the case of the DME reaction, the



Fig. 4.19. Spectrum of the surface species on a used sample of H-ZSM-5 $_{\rm f}$. The species were generated by a reaction of dimethyl ether.



Fig. 4.20. Spectrum of the surface species present on a used sample of $H-ZSM-5_{f}$ after adsorption of dimethyl ether at room temperature. This spectrum was obtained by subtracting the spectrum of the surface before adsorption of DME from the spectrum of the surface after adsorption.



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Fig. 4.21. Spectra showing the evolution of the species in the gas phase during the reaction of methanol over a used sample of H-ZSM-5 $_{\rm f}$ at 265°C.



Fig. 4.22. Spectra showing the evolution of the species in the gas phase during the reaction of dimethyl ether over a used sample of H-ZSM-5_f at 265°C. (Region between 1200 and 850 cm⁻¹).



Fig. 4.23. Spectra showing the evolution of the species in the gas phase during the reaction of dimethyl ether over a used sample of H-ZSM-5_f at 265°C. (Region between 955 and 875 cm⁻¹).

spectra (Fig. 4.22 and 4.23) shows that as in the methanol reaction, ethene, propene and isobutene are the initial gas phase higher hydrocarbon products, and that methanol is formed before these. But in contrast to the reaction of DME over a fresh surface (Fig. 4.13), ethene is initially formed in larger quantities than propene.

§4.3.2 Pretreatment of the Surface with n-Dodecane

A liquid sample of n-dodecane (Aldrich gold label) was degassed by three freeze-pump-thaw cycles. The catalyst surface $(H-ZSM-5_b)$ was exposed to n-dodecane vapours at room temperature, then evacuated before the catalyst was used for a methanol reaction at 300°C. As shown on figure 4.24, n-dodecane on the surface increased the rate of the conversion of methanol; the induction period for the fresh surface was 85 min., compared to 58 min. for the pretreated surface (similar to the 46 min. induction period observed for the reaction over the used surface).

A reaction was performed where n-dodecane was used as reactant to see what surface species would be present after a certain period of time at the reaction temperature. Fig. 4.25 shows the spectrum of the surface species obtained after 90 min (the spectrum represents the subtraction of the spectrum before reaction from that obtained after reaction). The negative bands at 1468 (CH₂ scissoring), 1456 (CH₃ asymmetric deformation) and 1377 cm⁻¹ (CH₃ symmetric deformation) are due to disappearing n-dodecane, and the positive bands at 1624 and 1490 cm⁻¹ are due to decomposition products. The broad band observed at around



Fig. 4.24. Evolution of P_{Σ} for a reaction of methanol over H-ZSM-5 at 300°C. Reaction were performed over a fresh surface (A) and over a surface pretreated with n-dodecane (B).



Fig. 4.25. Spectrum of the surface species on a sample of H-ZSM-5 after thermal treatment at 300°C for 90 min. The spectrum of the surface species before thermal treatment was subtracted from the spectra of the surface after thermal treatment.

1624 cm⁻¹ probably arises from a species similar to the one that caused the sharper band at 1624 cm⁻¹ on used surfaces.

§4.3.3 Effect of Coke Deposits on the Reactivity

A sample of $ZSM-5_f$ was "coked" by raising the temperature to 500°C while the reaction gas mixture was still in the cell, and leaving it for different periods of time. The process was repeated on the same sample, to study progressive coking; the sample designated "coke1" was coked for 10 hours, "coke2" for an additional 11.5 hours, "coke3" for 10 more hours and "coke4" for a further 10.5 hours. The catalytic results are shown on Fig. 4.26. It can be seen that the rate of reaction on coke1 is quite similar to that of the used surface, but that the other coked samples have a reactivity somewhere between that of the fresh surface and the used surface. This reactivity is relatively similar for the last 3 coked samples. However, despite the severe conditions used for the study, the reactivity never dropped as low as for reaction over the fresh surface.

Fig. 4.27 shows a comparison of the CH stretching region of the catalyst before a reaction, with different pretreatment. Not surprisingly, the fresh surface is free of any CH band, and so are the coked surface coke2, coke3 and coke4; on the other hand, the spectra of both the used and coke1 surface indicate the presence of CH groups. The implications of these results will be discussed in the following chapter.



Fig. 4.26. Evolution of P_{Σ} for a methanol reaction over different surfaces of H-ZSM-5_f at 265°C. a=fresh, b=used, c=coke1, d=coke2, e=coke3, f=coke4.



Fig. 4.27. Spectra of different surfaces of H-ZSM-5_f. a=fresh, b=used, c=coke1, d=coke2, e=coke3, f=coke4.







Fig. 4.29. Spectra of the surface species present on the "coke2" (a). "coke3" (b) and "coke4" (c) surfaces of H-ZSM-5 $_{\rm f}$.

Fig. 4.28 and 4.29 show the spectra obtained for the coked surfaces between 1700 and 1300 cm⁻¹. In this region, the spectrum of the surface species on coke1 (Fig. 4.28) shows many similarities to that on the used surface (Fig. 4.17), although the band at 1624 cm^{-1} is weaker and broader. This is not surprising since both show very similar reactivity. The intensities of the peaks of the surface species on coke2, coke3, and coke4 (Fig. 4.29) are weaker than on the used surface (the 1512 cm^{-1} band is about 10% of the size observed on the used surface). The peak positions show many similarities with those on the used surface, but the relative intensities are very different. Of importance is the fact that the bands at 1624 and 1512 cm⁻¹ are still present.

§4.3.4 Surface Species as a Function of Time

To better identify the 1624 cm⁻¹ band, and to observe the evolution of the surface species on the catalyst, spectra of the surface species at different times during a methanol reaction were taken. Three separate reactions were performed at 265°C with methanol as starting material. The reactions were carried out for different times (1, 2, and 3 hours) for each reaction. The cell was then evacuated at the reaction temperature for 2 minutes (to avoid interference by gas phase species adsorbing on the surface with cooling), then the furnace was removed to stop the reaction as quickly as possible. Spectra were recorded and are shown on Fig. 4.30. The band at 1624 cm⁻¹ appears quite early in the reaction (as early as the first spectrum, i.e. 1 hour), before many CH vibrations (identified by the bands between 1530 and 1460 cm⁻¹) are



Fig. 4.30. Spectra of the surface species present on a fresh sample of H-ZSM-5 $_{\rm f}$ at different times during a methanol reaction at 265°C.

observed; in particular, the band at 1512 cm^{-1} is practically absent at this time. That same band is strongest after 2 hours, and decreases at 3 hours. At that time, a new band appears at 1635 cm^{-1} which can be assigned to aromatic ring breathing, as after that period of time, one can expect from previous work⁷, to see aromatic compounds starting to form. The band at 1490 cm⁻¹ is probably also due to aromatics.

§4.5 Concluding Remarks

From the above data, new insights into the MTG process can be gained. In the next chapter, an explanation of why DME appears to be better than methanol as a starting material will be given, and this mechanism will also explain why cofeeding water with DME decreases the rate so much. Some explanation for the increase in reactivity of the used surface as compared to the fresh surface will be included as well as reasons why coking did not slow down the reaction rate to a lower level than for the fresh surface.

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CHAPTER 5

DISCUSSION

§5.1 Catalysts Characteristics

From the XRD data (Fig. 4.1), it is clear that ZSM-5 was synthesised in this lab, and from the result of the fluoride analysis, that samples of ZSM-5 were fluorided during synthesis. The SEM results (Fig. 4.2) show some amorphous material, but it is hard to say if it is more than just the glue from the adhesive tape. If there are substantial amounts of amorphous material (unreacted silica gel) in a sample, the XRD pattern contains a broad peak with a maximum around 30°. Such a peak was observed in the preliminary samples, but the final six samples represent the best synthesis results, containing no evidence for this peak, and therefore were chosen for the catalytic experiments.

The surface area of the samples (table 4.1) decreased with the fluoride content. This has been observed previously on fluorided samples of silica gel¹, and it was postulated that this decrease is due to OH groups on the surface forming H-bond with F, and decreasing the space in the pores. Another possibility could be the formation of an AlF_3 phase, since AlF_3 has a lower surface area, but the XRD patterns show no evidence for such a phase.

§5.2 Catalytic Activity

Chang described the current state of what is known of the mechanism of the MTG process as the "mechanism sweepstakes"². While the

results obtained here cannot provide an absolute answer to that problem, the various mechanisms proposed will be considered when interpreting the results obtained here.

§5.2.1 Silicalite

The result obtained for silicalite (ZSM-5) showed that without any aluminium, ZSM-5 is totally inactive for the MTG reaction. As we saw in the introduction chapter, aluminium polarizes the OH bond to create a very strong Brønsted acidic site, the bridged hydroxyl, and is also the site for Lewis acidity. The absence of Al creates a catalyst without Lewis acid sites, and much weaker Brønsted sites. The pyridine adsorption results (Fig. 4.4) show the complete absence of a band at 1545 cm^{-1} (pyridinium ion) in silicalite, a clear indication of the absence of Brønsted acid sites. It then becomes clear that these sites are essential for the MTG reaction. The band observed near 1450 cm⁻¹ is probably due to physisorbed pyridine, rather than to pyridine coordinated to a Lewis site, since in the latter case, a band at 1490 cm^{-1} would also be observed (see table 2.1).

§5.2.2 Fluoridation and Catalytic Activity

As was mentioned in the introductory chapter, fluorine has a polarizing effect on the catalyst, increasing the strength of its acid sites; the more F present, the stronger this effect should be. This was observed in the MTG reaction, as reactivity of the catalyst studied generally increased with the percentage of fluorine present in the lattice (Fig. 4.6).

The relationship between fluorine content and reactivity (shown on Fig. 4.3 and table 4.2) does not appear to be a linear one. Sample c and e are very similar in reactivity, but their fluorine content is quite different; also sample d and e have similar fluorine content, but their reactivity is quite different. The explanation for these results probably lies in the method used to analyse the fluorine content: it gives a quantitative value, but not a qualitative description of the sites where F is located. One is left to wonder if some F atoms are not located outside the framework of the catalyst; it is possible to have aluminium oxide/hydroxide species present outside the framework, but still in the pores of the catalyst, and F attached to such species would not affect the catalyst in the same way as F attached to the framework of the catalyst. Such alumina present in the pores would not be observed in the IR spectra, as the AlO vibrations are similar to those of SiO, and amorphous species of that kind would not be detected on the XRD pattern if present in only trace amounts. However, from the results of the catalytic testing (Fig. 4.6), it is obvious that fluoridation has a positive effect on the reactivity of the catalyst, but such an explanation could explain the anomalous behavior of $H-ZSM-5_{b}$ which showed the longest induction period.

The increase in reactivity with fluoride content can not be expected to be a simple one; the increase has to stop at one point, where the reactivity starts to decrease. As the F concentration increases, the acidity of a particular site should increase; but the

number of such sites will decrease as F is thought to replace surface OH groups. Therefore there must be a point where the concentration of acid sites will be too low, and reactivity of the catalyst will decrease. Becker and co-workers³ observed such a decrease when studying the cumene cracking reaction over fluorided ZSM-5 (fluorided by impregnation). They also found that an increase in fluoridation resulted in dealumination of the catalyst, probably because of the more severe nature of the fluoridation process. A decrease in reactivity was not observed with the samples under study here, since the concentration of F was kept at a relatively low level. In addition, the method of fluoridation appears to be milder and does not cause any dealumination of the catalyst (as seen on table 4.1).

This result represents the first study of the influence of fluoridation on the MTG reaction, and it clearly shows that this type of modification of the surface acid sites affects the induction period significantly.

§5.2.3 Methanol vs Dimethyl Ether as Starting Material

Looking at the progress of the reaction when either methanol or dimethyl ether is used as feed (Fig. 4.7), it is obvious that using DME gives a much faster reaction. The effect is most obvious on the induction period; in the case of the DME reaction, there is practically no induction period. One could conclude that the induction period in the methanol reaction is due to the time required to build up a sufficient amount of DME, and therefore that DME is the active species in the
MeOH/DME equilibrium. But a closer look at the evolution of these two reactions (Fig. 4.7) reveals that the situation is more complex than this. The pressure of DME used initially (in the DME reaction), was very close to the pressure of DME (ca 13 mm Hg) in the methanol reaction when the MeOH/DME equilibrium is reached (after ca 40 min.). Yet in the methanol reaction, an induction period is still observed after the point where that equilibrium is reached, while in the DME reaction, practically no induction period is seen. So the induction period in the methanol reaction is not simply caused by the need to build up a certain pressure of DME. To understand what is causing the induction period, and see if it is possible to tell which of methanol or DME is the active component, one has to gain more knowledge about the surface species involved in the formation of the first C-C bond, that is the events that constitute the induction period. The results from the DME reaction were fruitful in providing new clues to that process.

The first important observation is that methanol is produced in the DME reaction before any higher hydrocarbons, as seen clearly from the IR spectra of the gas phase during the reaction (fig 4.12). The simple methanol-DME equilibrium involves water as a source of H atoms, but no water is present at the initial stage of this reaction, since a fresh surface (dehydrated at 500°C) was used. (Water will be produced in later stages of the reaction, as higher hydrocarbons are produced). In the absence of H_2O , the H needed to produce the methanol has to come from the acid sites on the surface, and the reaction can occur in the following two ways:





All the species shown in reaction 5.2 are stabilized by interaction with the catalyst surface (for simplification, the surface was not shown).

Species B is the trimethyl oxonium ion (TMO) that was discussed in Chapter 1. Engelen and co-workers⁴ showed using MINDO 3 calculations that the formation of the TMO is more energetically favored (+20 kJ/mole) than the formation of CH_2 (+320 kJ/mole) or CH_3^+ (+200 kJ/mole) species, both of which could be produced from the bridged methoxy A. But those calculations do not take into account any stabilizing effect from the surface, which could easily decrease those energies of formation.

There is spectroscopic evidence for the existence of the bridged methoxy group. Forester and co-workers⁵ using *in-situ* FTIR spectroscopy observed its presence when both methanol and DME were used as feed. Hellring and co-workers⁶ while studying the decomposition of TMO salts, observed using CP-MAS ¹³C NMR spectroscopy the presence of the bridged methoxy. So the bridged methoxy appears to be the intermediate in the formation of higher hydrocarbons, whether methanol is formed via reaction 5.1 or 5.2. If reaction 5.2 occurs, the TMO formed would then decompose to form the bridged methoxy, and whether that species is a primary or secondary product remains unknown.

Whether dimethyl ether or methanol is the active component in the formation of that bridged methoxy (that is the active component in the MTG reaction) remains uncertain. The bridged methoxy could be formed from methanol in the following way:



The next question is why is the reaction slower when methanol is used as starting material instead of DME, since either can form the bridged methoxy. The answer is water. If water is present, it might be expected to replace the bridged methoxy to produce the initial bridged hydroxy and another methanol molecule. To prove this, the obvious experiment to do was to cofeed water and dimethyl ether, in equimolar ratio so as to mimic the conditions in the methanol reaction. The progress of the DME/water reaction (shown on Fig. 4.8) is quite conclusive. A very long induction period is observed, similar in length. to that observed when methanol is used as feed.

The induction period in the case of methanol can then probably be explained by a lower concentration of bridged methoxy (due to the presence of water). Another possibility is that a different mechanism from that observed in the DME reaction is occurring. However, there is no evidence to show that such a mechanism is taking place, and the observation by Forester⁵ of the presence of bridged methoxy species when methanol is used as feed indicates that this species is probably an intermediate in the methanol reaction, as in the DME reaction.

Having accepted the bridged methoxy as an intermediate in the formation of higher hydrocarbons (as supported by the results shown in this work and previous work described above), the next step is then to understand how the first C-C bond is formed from that species. One proposal, by Ono and Mori⁷, is that the bridged methoxy group acts as a carbonium ion, forming higher hydrocarbons in the following way:

$$CH_{3}^{+} + CH_{3}OR \longrightarrow \left[CH_{3} \xrightarrow{H} CH_{2}OR \right]^{+} \longrightarrow CH_{3}CH_{2}OR + H^{+}$$
(5.4)

An alternative proposal by Hellring and co-workers⁶ is that the bridged methoxy is deprotonated to form a surface stabilized ylide, which as was shown in the introduction, is in resonance with a surface carbene (equation 5.5). For the deprotonation of the bridged methoxy group, both groups believe that the process occurs via a nucleophilic attack from the basic sites in the catalyst structure, rather than a typical acid/base reaction.



(5.5)



The source of "Me" in the above mechanism could be methanol, DME, or an adjacent bridged methoxy or surface ylide. Of these, methanol or DME are the most likely source, by virtue of their higher concentrations, so the formation of higher hydrocarbons would involve a $CH_2CH_3^+$ intermediate.

If the carbonium ion mechanism is occurring, methane would be expected to be produced in significant amounts, as a carbonium ion can easily abstract an hydrogen from methanol⁸, DME or hydrocarbons. According to Herzberg⁹, methane will give two strong peaks in the IR, at 3020 and 1306 cm⁻¹; careful examination of the IR spectra of the gas phase throughout the MTG experiment revealed the total absence of these peaks. Therefore, experimental evidence points toward the stabilized ylide mechanism as the most likely to be occurring.

The gas phase IR spectra of the reaction products (Fig. 4.11 and 4.13) shows that ethene, propene and isobutene are the primary gas phase products, in agreement with results obtained by other workers^{10,11}. The formation of these alkenes can be accounted for by any of the mechanisms mentioned previously. All these mechanisms involve a $C_2H_5^+$ species as an intermediate, and this species can then be deprotonated to give ethene, or it can react with another C_1 species (methanol, DME, or a surface intermediate) to produce the propene precursor, which in turn could also deprotonate to give propene or react with another C_1 species to produce the isobutene observed.

From the IR spectra of the gas phase product, it can be seen that in the case of the DME reaction (Fig. 4.13), propene is initially formed in larger quantity than ethene, in contrast to the methanol reaction (Fig. 4.11), where the situation is reversed. This can be explained by the lower concentration of water in the initial stages of the reaction when DME is used as feed (in the methanol reaction, an equimolar amount of water is produced with DME). Bolis and co-workers¹², and Gabelica and co-workers¹³ showed that ethene does not adsorb as strongly in the presence of water. Therefore, in the methanol reaction (where water is present in large quantities), ethene will desorb readily, rather than stay on the surface to produce propene. In the DME reaction (where there is very little water), the ethene will be adsorbed more strongly, and therefore a larger concentration of propene will initially be formed.

§5.3 Study of the Surface Active Species

The results described in the previous chapter were quite clear about the fact that the introduction of organic species to the catalyst surface, either by using a used surface, pretreating the catalyst with n-dodecane, or even coking the surface, leads to an increase in the rate of the reaction compared to a fresh surface. In the following section, the identity of the active species will be speculated from the IR results.

§5.3.1 Fresh vs Used Catalysts

The most interesting result was obtained by subtracting the IR spectrum of the used surface after methanol was admitted from that of

the surface before methanol was admitted (Fig. 4.17). In addition to the bands expected from the interaction of methanol with the surface, it can be seen that the bands at 1624 and 1512 cm⁻¹ are affected by the addition of methanol, and disappear (as shown by negative peaks). It is also clear that these two bands do not represent the same species, as they appear in different relative ratio for different experiments.

Bezuhanova and co-workers^{14,15} and Grady and Gorte¹⁶, while studying the adsorption of olefins on ZSM-5 have observed a band at 1520 cm⁻¹, which they assigned to a protonated olefin attached to the surface:



It is quite likely that the band observed at 1512 cm^{-1} is due to the same species. The difference in wavenumber could be due to small differences in the catalyst preparation (not complete H-exchange, more or less Al).

The 1624 cm⁻¹ has not been described by other workers. It was assigned to a double-bonded species, and being at higher wavenumber, its double bond character must be higher than the protonated double bond at 1512 cm^{-1} . As was mentioned in the introduction chapter, olefins are known to oligomerize on the surface. Therefore a species with a high double character would be expected to polymerize, so the presence of such a species should not be observed. Gabelica and co-workers¹³ showed that in the presence of water, the oligomerization of ethene is prevented. The catalyst surface in this experiment was "used" and

therefore water was present on the surface (from the MTG reaction). This water might also be expected to inhibit polymerization of other olefinic species, so that the presence of the double bond species on the surface could be detected.

The spectra of the evolution of the surface species during a methanol reaction (Fig. 4.30) shows that the band at 1624 cm⁻¹ is produced early in the reaction (as early as the first spectrum, 1 hour). After 2 hours, the 1512 cm⁻¹ band is present and strong, and after 3 hours, both the 1512 and 1624 cm⁻¹ bands have decreased, and new bands at 1635 and 1502 cm⁻¹ have appeared. This sequence of events suggests that the double bond species is formed first (ethene, propene and isobutene are observed in the gas phase, so the surface species observed is probably not larger than C_4). It then reacts, with time, with the surface to form a protonated double bond species (possibly of an oligomerized form of the initial olefins), showing up at 1512 cm⁻¹. Later in the reaction, aromatics are formed, and the bands at 1635 (ring breathing) and 1502 cm⁻¹ (another ring breathing mode) testify to that.

As was mentioned in the introduction, an increase in the reactivity of ZSM-5 catalyst has been observed when the surface was previously treated with olefins, or olefins precursors like $alcohol^{17,18,19}$. Kolboe²⁰, studying the MTG reaction when the catalyst has been pretreated with olefins, proposed that the olefin is protonated by the catalyst surface (although without spectroscopic evidence), and that this species is responsible for the increase in reactivity (by making it

easier to form carbene; refer to the introduction for more details). Spectroscopic evidence presented here, and in agreement with other workers 14,15,16 , shows the presence of a band at 1512 cm⁻¹ which was assigned to a protonated double-bond, the same species proposed by Kolboe.

The increase in reactivity of the used surface can therefore be explained in the following way. Methanol can add to the "double bond" present on the surface, and then produce a higher hydrocarbon. As the chain grows, it will be cracked by the catalyst (ZSM-5 is known to be a cracking catalyst), and more "double bond" species are formed on the surface, to which methanol can add. The reaction is therefore faster, because we do not require the formation of an initial C-C bond from two C_1 species (methanol or dimethyl ether), which is the step responsible for the induction period observed. The evidence shown here adds weight to the revised scheme for the MTG reaction that was proposed in 1988 by Prinz and Riekert²¹:



The "double bond" responsible for the increase in reactivity

would then appear to be the protonated double bond observed at 1512 cm^{-1} . The interaction observed between methanol and dimethyl ether with the band at 1624 cm⁻¹ could be explained in two ways: Methanol could simply displace the olefin from the surface, or the interaction between the surface and the olefin might be strong enough to render the olefin more reactive, and methanol could add to that double bond.

Surprisingly, dimethyl ether does not interact with the protonated double bond at room temperature, as can be seen by the absence of the decrease in intensity of the band at 1512 cm^{-1} (Fig. 4.20). Two possibilities are now opened: Either DME can interact with the protonated double bond only at higher temperature (which can not be observed in this study), or only methanol can interact with the protonated hydrocarbons, and therefore, methanol would be the active species for the chain growth. Unfortunately, without the ability to obtain FTIR spectra of the surface at high temperature during the reaction, it is not possible to distinguish between these possibilities.

§5.3.2 Modification of the Surface with n-Dodecane

Zeolites are known to be cracking catalysts, and ZSM-5 is no exception²². When n-dodecane was used as a reactant, the IR spectra of the final product (Fig. 4.25) shows indeed that the n-dodecane has reacted (the negative peaks indicates a disappearance of that species), and a broad band centered around 1625 cm⁻¹ is observed, which can be related to the 1624 cm⁻¹ band observed on the "used" surface.

IR spectra of the gas phase reveals the presence of olefins (bands are observed around 890 cm^{-1} , the region of C-H deformation of alkenes) as early as after 15 min. of thermal treatment. After 30 min. isobutene was observed, and propene was detected after 60 min. This observation confirms that n-dodecane is cracked on a ZSM-5 surface, and that olefins are produced in that reaction. The increase in reactivity is then due to the presence of olefins as discussed in the previous section. The induction period for the methanol reaction over the catalyst pretreated with n-dodecane was 58 min., compared to 46 min. for the reaction over the used surface. The difference, 12 min., could then be explained as the time required for the formation of the first alkene from n-dodecane, which was shown to be *ca.* 15 min.

Surprisingly, the band at 1512 cm^{-1} does not appear after thermal treatment of the surface treated with n-dodecane. A new band is observed at 1490 cm⁻¹ which could also represent a species similar to that observed at 1512 cm^{-1} . The absence of water will promote a higher degree of polymerization of the olefins, as Gabelica and co-workers¹³ have shown. The band at 1490 cm^{-1} may be a protonated double bond belonging to a more highly polymerized species, or the higher degree of polymerization might simply inhibit the formation of the protonated double bond. Under the MTG reaction conditions (on the catalyst treated with n-dodecane), water is produced in large quantities, so the surface species formed from n-dodecane can be expected to be different (because of less polymerization of olefins). Therefore under these conditions the active species which is identified with the band at 1512 cm⁻¹ could be

expected to appear soon after the cracking takes place (*ca* 15 min.), early enough to decrease the duration of the induction period, as is observed experimentally.

§5.3.3 Coking of the Catalyst Surface

The coking experiments were surprising in the fact that the reactivity of the modified catalyst did not decrease below that of the fresh surface (Fig. 4.26). The sample cokel was as reactive as the used surface, and looking at the IR spectra of its surface (Fig. 4.27), it can be seen that some C-H are still present, indicating that the extent of the coking was limited. In addition, the IR spectra of the surface species between 2000 and 1300 cm^{-1} (Fig. 4.28) was very similar to that of the surface species on the used catalyst (Fig. 4.16). The similarities between the surface species present on the catalyst surface explains why the rates of reaction were so similar between the two samples, since the same surface species are present on both surfaces.

The samples coke2, coke3 and coke4 did not show any C-H stretching in their IR spectra (Fig. 4.27), so it can be concluded that the C/H ratio of the coke formed on these samples was very high, and that the coking process was more advanced than for coke1. In addition, from the spectra between 1700 and 1300 cm⁻¹ (Fig. 4.28 and 4.29), it can be seen that for all these samples, the bands at 1624 and 1512 cm⁻¹ are still present. It can therefore be concluded that the reaction rates were faster on the coked surfaces than on the fresh catalyst, because

again species with double bond character were present. To explain why the rate was slower in the case of reaction over the surfaces coke2, coke3 and coke4 than for the used catalyst, two reasons could be used: The concentration of species with double bond character is less, as is observed by the intensity of the IR spectra (Fig. 4.29); or that the more extensive coking has physically blocked the pores of the catalyst, so that the reactant molecules cannot as easily access the active site. The exact reason is probably a combination of these two effects.

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Chapter 6

CONCLUSION

§6.1 Synthesis and Fluoridation

It was shown that it is possible to incorporate fluorine in the framework of ZSM-5 during synthesis. While a quantitative correlation between the fluorine content of the catalyst studied and its reactivity is not very good; it is clear that fluorine has a positive effect in the reactivity of the catalyst toward the conversion of methanol to higher `hydrocarbons. The induction period was the most affected by the extent of fluoridation, varying from 100 min. to 8 min. for the most fluorided sample.

Some anomalous behavior was observed with sample H-ZSM-5_d which showed an induction period longer than that for the unfluorided sample. It was postulated that this discrepancy could be due to fluorine located in different sites on that particular catalyst than on other samples. In order to better establish a correlation between fluoridation and reactivity, it would be essential to use an analytical method that would quantitatively determine the concentration of F in the different sites in the catalyst. MAS NMR (29 Si, 27 Al and 19 F) would be a very promising method for that purpose. One could see with this technique what is the portion of aluminium (if any) octahedrally coordinated, that is not incorporated (tetrahedrally) in the framework of the catalyst. Furthermore, one could also determine to which sites the fluorine attaches itself, and if it is in the framework, or with non-framework §6.2 Silicalite

No Brønsted nor Lewis acid sites were detected by pyridine adsorption/desorption experiments on the surface of ZSM-5_a (silicalite). Since the presence of these acid sites is due to the presence of Al in the framework of the catalyst, this experimental observation proves that the synthetic method used was successful in providing an Al-free source of silica, from which was obtained an Al-free sample of ZSM-5. That catalyst proved to be totally non-reactive toward the MTG reaction, not even dehydration of methanol occurred over that surface.

§6.3 Methanol vs Dimethyl Ether as Reactant

When dimethyl ether is used as starting material, the induction period is much shorter than if methanol is used. The reason for that increase in reactivity is thought to be due to the absence of water. It was concluded that the first C-C bond is formed via a surface bridged methoxy group, which will deprotonate to give a surface stabilized ylide:

Al.



This mechanism was preferred over a carbonium ion mechanism, since such a mechanism would involve the formation of methane as a byproducts, but no methane was detected in the IR spectra of the gas phase products.

It was postulated that water slows the reaction by interfering with the formation of the bridged methoxy, giving a molecule of methanol and a surface bridged hydroxyl, thus explaining the longer induction period observed when methanol is used as feed instead of dimethyl ether.

Both methanol and dimethyl ether can produce the bridged methoxy species, so that either one can be the active species in the formation the first C-C bond. The increase in induction period observed when

methanol is used as starting material is due to the water produced in the dehydration of methanol, a process that is very rapid over ZSM-5 catalyst.

§6.4 Modification of the Catalyst Surface

The reactivity of catalysts has previously been shown to increase with the introduction of olefins to the surface^{1,2,3}. In this study, the reactivity was increased by pretreating the catalyst with vapour of n-dodecane, partially coking the surface, or using the surface obtained `after an MTG reaction (a "used" surface).

In the last two cases, IR spectroscopy evidence showed that the increase in reactivity is due to the presence on the surface of a protonated double bond:



Kolboe⁴ proposed that such a species increases the reactivity by facilitating the formation of carbene from methanol (as mentioned in chapter 1, the formation of carbene is thought to occur via the cooperative action of acidic and basic centers, and the protonated double bond can act as an acidic centre). The decrease in the induction period observed is caused by the possibility for the reactant to produce higher hydrocarbons from reaction with a protonated double bond, instead of requiring the reaction of two C_1 species.

Since the protonated double bond is formed by the products of the

MTG reaction, as was shown from the spectra of the surface for the used and coked catalysts, the increase in reactivity observed after the induction period is due to the formation of higher hydrocarbons via reaction with newly formed protonated double bond. As higher hydrocarbons are formed, they will be cracked by the catalyst, and produce olefins that can be protonated, and as the concentration of the protonated double bond increase, so will the reaction rate. A revised mechanism was then proposed, in accordance with Prinz and Riekert⁵:



Methanol was observed to interact with the protonated double bond at room temperature, but DME does not. This suggest that methanol may be the active species in the formation of higher hydrocarbons. Certain proof of that might be obtained by the observation of DME interactions with the surface at higher temperature. Whether methanol or DME was used as feed, the gas phase products were similar, and so were the surface species on the catalyst at the end of the reaction. This suggests that at least for the latter part of the reaction (formation of higher hydrocarbons), the reaction proceeds via the same mechanism, regardless of the initial feed.

n-Dodecane is believed to increase the reactivity of the catalyst

in a similar manner as does pretreating the catalyst with olefins. This alkane was observed to react with H-ZSM-5 to form olefins, which could then be protonated.

§6.5 Recommendation for Further Work

In order to exploit better the FTIR technique, it is important to develop a method to look at the surface during the reaction, instead of interrupting the reaction, and looking at the species at room temperature. Such a technique could show if DME interacts with the `protonated double bond or not, therefore if it is an active species in the formation of higher hydrocarbons. It would also be useful in proving that protonated double bonds are formed when the surface is pretreated with n-dodecane.

The study of the reaction in flow conditions would also improve results by eliminating any diffusion control in the rate of the reaction. Since the rate of formation of higher hydrocarbons (labelled part D in chapter 4) did not show any significant changes for the different treatments, it was proposed that this step of the reaction may be under diffusion control. Using a flow system, one could then determine if fluoridation influences not only the induction period, but also the rate of the formation of higher hydrocarbons, or in other words if it influences the formation and acid strength of the protonated double bond.

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Appendix

The following is a copy of the listing of the program used to control the furnace temperature. The system is described in chapter 3.

:** 10 REM ***** 15 REM 20 REM * FURNACES CONTROLLING 30 * REM PROGRAM 35 REM * ******* 40 REM 45 REM * 50 REM PROGRAMMED BY * ERIC VILLENEUVE 60 REM * MAY 1987 70 REM 75 REM ***** 80 REM 90 REM 100 REM * LIST OF VARIABLES 110 REM * CLOCK VARIABLES 120 REM 130 REM 140 REM D\$=ADDRESS FOR THE CLOCK 150 REM T\$=TIME 160 REM T=TIME IN MINUTES (ABSOLUTE) 170 REM 180 REM * INTERFACE VARIABLES 190 REM 200 REM PL=POLARITY OF SIGNAL 210 REM AD(2)=ADDRESS OF A/D CONVERTER X=VALUE OF HI BYTE OF SIGNAL 220 REM 230 REM Y=VALUE OF LO BYTE OF SIGNAL 240 REM MV=CONVERTED SIGNAL 250 REM OU(2)=ADDRESS OF RELAY 260 REM 270 REM *PROGRAM VARIABLES 280 REM 290 REM TD(5,2)=DESIRED TEMP. 300 REM TI(5,2)=DWELL TIME 310 REM RA(5,2)=RATE OF HEATING 320 REM F AND AF=FURNACE WHICH IS BEING CONSIDERED 330 REM TP(2)=ACTUAL TEMP. 340 REM ST(2)=STATUS OF FURNACE (IN USE OR NOT) FU(2)=FURNACE ON OR OFF 350 REM 360 REM SI(2)=SITUATION (1=CONSTANT T., 2=HEATING OR COOLING) 370 REM LV(2)=LEVEL OF THE PROGRAM 380 REM RD(2)=IS FIRST T REACHED OR NOT

```
390 REM TO(2)=INITIAL TIME FOR ACTUAL LEVEL
400 REM OT(2)=ELAPSED TIME AT THE ACTUAL LEVEL
410 REM DT(2)=DESIRED TEMP., USED DURING HEATING OR COOLING
420 REM SP$=39 SPACES, USED TO CLEAR A LINE
430 REM A AND B$=WILDCARD FOR INPUT
440 REM J=COUNTER
498 REM
499
    REM ** DIMENSIONING THE VARIABLES
500
    DIM AD(2), OU(2), TD(5,2), TI(5,2), RA(5,2), TP(2),
     ST(2), FU(2), SI(2), LV(2), RD(2), TO(2), OT(2), DT(2)
505
    REM
506 REM * THE SYSTEM IS SET OUT FOR
507 REM * ONE A/D IN SLOT 1 AND
508 REM
          * ONE A/D IN SLOT 3
         ∗
509
    REM
510
    AD(1) = 49296: AD(2) = 49328
520 OU(1) = 49299:OU(2) = 49331: POKE OU(1), 0: POKE OU(2), 0
525 SP$ = "
530 HOME
535
    GOSUB 2500
548 REM
549 REM * SETTING UP DISPLAY
550
     HTAB (1): VTAB (3): PRINT "TEMP.";: HTAB (8): PRINT "DWELL T.";:
     HTAB (18): PRINT "RATE";: HTAB (26): PRINT "ELAPSED T.";
560
    HTAB (5): VTAB (5): PRINT "FURNACE 1";
570
    HTAB (15): VTAB (8): PRINT "OFF";
580
     HTAB (1): VTAB (12): PRINT "DES. TEMP.=";: HTAB (19): PRINT "ACT.
     TEMP. =";
590
     ===":
    HTAB (5): VTAB (14): PRINT "FURNACE 2";
600
    HTAB (15): VTAB (18): PRINT "OFF";
610
620
    HTAB (1): VTAB (21): PRINT "DES. TEMP.=";: HTAB (19): PRINT "ACT.
     TEMP. =";
630
    GOSUB 2500
640 GOTO 1500
698 REM
699 REM
         *MAIN MODULE
700 GOSUB 2500: HTAB (10): VTAB (1): PRINT T$;
710 A = PEEK (-16384)
720
    IF A < 127 THEN GOTO 900
725 POKE - 16368,0
730
    IF A < > 209 THEN GOTO 740
732
    HTAB (1): VTAB (23): PRINT SP$;: HTAB (1): PRINT "ARE YOU SURE TO
    QUIT (Y/N)?"; : J = 0
734
    A = PEEK ( - 16384): J = J + 1
735 IF J > 10000 THEN GOTO 780
736 IF A < 127 THEN GOTO 734
737
   POKE - 16368,0
738
    IF A < > 217 THEN J = 10001: GOTO 780
   POKE OU(1), 0: POKE OU(2), 0: END
739
740
    IF A = 208 THEN GOTO 1500
750 IF A < > 211 THEN PRINT CHR$ (7);: GOTO 900
```

760 HTAB (1): VTAB (23): PRINT SP\$;: HTAB (1): PRINT "WHICH FURNACE ?";:J = 0A = PEEK (-16384): J = J + 1770 780 IF J > 10000 THEN HTAB (1): PRINT "<P>ROGRAM <S>TOP A FURNACE <Q>UIT";: GOTO 900 790 IF A < 127 THEN GOTO 770 795 POKE - 16368,0 800 IF A = 178 THEN GOTO 860 IF A < > 177 THEN HTAB (1): PRINT CHR\$ (7);: PRINT "<P>ROGRAM 810 <S>TOP A FURNCE <Q>UIT";: GOTO 900 820 POKE OU(1), 0: HTAB (1): VTAB (7): FOR J = 1 TO 5: PRINT SP\$: NEXT J 830 HTAB (12): VTAB (12): PRINT " ";: HTAB (30): PRINT " "; 840 HTAB (15): VTAB (8): PRINT "OFF": ST(1) = 0: FU(1) = 0850 HTAB (1): VTAB (23): PRINT "<P>ROGRAM <S>TOP A FURNACE <Q>UIT":: GOTO 900 POKE OU(2), 0: HTAB (1): VTAB (16): FOR J = 1 TO 5: PRINT SP\$: NEXT 860 J 、870 HTAB (12): VTAB (21): PRINT " ";: HTAB (30): PRINT " ": 880 HTAB (15): VTAB (18): PRINT "OFF";:ST(2) = 0:FU(2) = 0HTAB (1): VTAB (23): PRINT "<P>ROGRAM <S>TOP A FURNACE <Q>UIT"; 890 900 IF ST(1) = 1 THEN F = 1: VF = 6: GOSUB 1000 IF ST(2) = 1 THEN F = 2: VF = 15: GOSUB 1000 910 920 **GOTO 700** 998 REM 999 REM * CONTROLLING THE FURNACES 1000 GOSUB 3000 1005 GOSUB 2500 1010 IF RD(F) = 1 THEN GOTO 1100 IF TP(F) < TD(1,F) - 5 AND FU(F) = 0 THEN POKE OU(F), 1: FU(F) = 11020 1030 IF TP(F) > TD(1,F) + 5 AND FU(F) = 1 THEN POKE OU(F), 0: FU(F) = 0IF TP(F) > TD(1,F) - 5 AND TP(F) < TD(1,F) + 5 THEN TO(F) =1040 T:RD(F) = 1:SI(F) = 1:LV(F) = 1:OT(F) = 01050 HTAB (12): VTAB (VF + 6): PRINT TD(1,F);: HTAB (30): PRINT TP(F);" ";: HTAB (37) 1060 IF FU(F) = 0 THEN PRINT "OFF":: GOTO 1070 1065 PRINT "ON "; 1070 RETURN IF SI(F) = 2 THEN GOTO 1300 1100 1110 IF OT(F) > T - TO(F) THEN TO(F) = TO(F) - (12 * 60)1120 OT(F) = T - TO(F)1130 IF TP(F) < TD(LV(F), F) AND FU(F) = 0 THEN POKE OU(F), 1: FU(F) = 11140 IF TP(F) > TD(LV(F), F) AND FU(F) = 1 THEN POKE OU(F), 0: FU(F) = 01150 HTAB (12): VTAB (VF + 6): PRINT TD(LV(F),F); "; HTAB (30): PRINT TP(F); " ";: HTAB (37) IF FU(F) = 0 THEN PRINT "OFF";: GOTO 1170 1160 1165 PRINT "ON ": HTAB (26): VTAB (VF + LV(F)): PRINT INT (OT(F) * 10) / 10; " "; 1170 1180 IF OT(F) > TI(LV(F),F) THEN LV(F) = LV(F) + 1:OT(F) = 0:SI(F) =2:TO(F) = TIF LV(F) = 6 AND F = 1 THEN GOTO 820 1190 1200 IF LV(F) = 6 AND F = 2 THEN GOTO 860 1210 RETURN

```
IF OT(F) > T - TO(F) THEN TO(F) = TO(F) - (12 * 60)
 1300
 1310
       OT(F) = T - TO(F): DT(F) = TD(LV(F) - 1, F) + OT(F) * RA(LV(F), F)
       IF TP(F) < DT(F) AND FU(F) = 0 THEN POKE OU(F), 1: FU(F) = 1
 1320
 1330
       IF TP(F) > DT(F) AND FU(F) = 1 THEN POKE OU(F), 0: FU(F) = 0
       HTAB (12): VTAB (VF + 6): PRINT INT (DT(F) * 10) / 10; " ";: HTAB
 1340
       (30): PRINT TP(F); ";: HTAB (37)
 1350
       IF FU(F) = 0 THEN PRINT "OFF";: GOTO 1360
 1355
       PRINT "ON ";
       HTAB (33): VTAB (VF + LV(F) - 1): PRINT INT (OT(F) * 10) / 10;"
 1360
       ":
 1365
       IF SGN (RA(LV(F), F)) < 0 THEN GOTO 1385
 1370
       IF DT(F) > TD(LV(F), F) THEN SI(F) = 1:TO(F) = T:OT(F) = 0
 1380
       RETURN
 1385
      IF DT(F) < TD(LV(F),F) THEN SI(F) = 1:TO(F) = T:OT(F) = 0
 1390 RETURN
 1498 REM
 1499
       REM * PROGRAMMING SUBROUTINE
 1500
       IF ST(1) = 1 AND ST(2) = 1 THEN PRINT CHR$ (7); GOTO 900
. 1510
      IF ST(1) = 1 OR ST(2) = 1 THEN GOTO 1590
      HTAB (1): VTAB (23): PRINT SP$;: HTAB (1): PRINT "WHICH FURNACE?";
 1520
      A = PEEK (-16384)
 1530
 1540
      IF A < 127 THEN GOTO 1530
 1545 POKE - 16368.0
       IF A < > 177 AND A < > 178 THEN PRINT CHR$ (7);: GOTO 1530
 1550
 1560
       AF = VAL (CHR$ (A - 128)):F = 0:LV(AF) = 1
       IF AF = 1 THEN AV = 6: HTAB (15): VTAB (8): PRINT "
 1570
                                                               ":: GOTO
       1600
       AV = 15: HTAB (15): VTAB (18): PRINT " ":: GOTO 1600
 1580
 1590
      IF ST(1) = 1 THEN F = 1: AF = 2: LV(AF) = 1: AV = 15: HTAB (15): VTAB
       (18): PRINT " ;: GOTO 1600
       F = 2:AF = 1:LV(AF) = 1:AV = 6: HTAB (15): VTAB (8): PRINT "
 1595
         HTAB (1): VTAB (23): PRINT SP$;: HTAB (1): PRINT "ENTER
 1600
       TEMP.#";LV(AF);"";: GOSUB 1900
       TD(LV(AF), AF) = VAL (B$)
 1610
       HTAB (1): VTAB (AV + LV(AF)): PRINT B$:
 1620
      IF F = 0 THEN GOTO 1650
 1630
 1640
       GOSUB 1000
 1650
       HTAB (1): VTAB (23): PRINT SP$;: HTAB (1): PRINT "ENTER DWELLING
       TIME (-1=INFINITY): ";: GOSUB 1900
       TI(LV(AF), AF) = VAL (B$)
 1660
 1670 HTAB (9): VTAB (AV + LV(AF)): PRINT B$;
       IF F = 0 THEN GOTO 1700
 1680
       GOSUB 1000
 1690
 1700
       IF LV(AF) = 1 THEN GOTO 1780
 1710
       HTAB (1): VTAB (23): PRINT SP$;: HTAB (1): PRINT "RATE OF HEATING
       BETWEEN "; TD(LV(AF) - 1, AF); " AND "; TD(LV(AF), AF); " ";
 1720
       GOSUB 1900
 1730
       RA(LV(AF), AF) = VAL (B$)
 1740
              SGN (TD(LV(AF), AF) - TD(LV(AF) - 1, AF)) <
         IF
                                                              >
                                                                     SGN
       (RA(LV(AF), AF)) THEN RA(LV(AF), AF) = -1 * RA(LV(AF), AF): B = "-"
       + B$
      HTAB (18): VTAB (AV + LV(AF) - 1): PRINT B$;
 1750
 1760
      IF F = 0 THEN GOTO 1780
 1770
       GOSUB 1000
```

```
1780 IF TI(LV(AF), AF) = -1 THEN TI(LV(AF), AF) = 10 * 24 * 60: ST(AF) =
      1:RD(AF) = 0:OT(AF) = 0:LV(AF) = 1:SI(AF) = 1:HTAB (1): VTAB
      (23): PRINT SP$;: HTAB (1): PRINT "<P>ROGRAM <S>TOP A FURNACE
      <Q>UIT";: GOTO 900
1790
      LV(AF) = LV(AF) + 1
1800
       IF LV(AF) = 6 THEN ST(AF) = 1:RD(AF) = 0:OT(AF) = 0:LV(AF) =
      1:SI(AF) = 1: HTAB (1): VTAB (23): PRINT SP$;: HTAB (1): PRINT
      "<P>ROGRAM <S>TOP A FURNACE <Q>UIT";: GOTO 900
1810
      GOTO 1600
1898
      REM
1899 REM * INPUT SUBROUTINE
1900
      J = 0:B = ""
1910 A = PEEK (-16384): J = J + 1
     IF J > 200 THEN GOTO 1990
1920
      IF A < 127 THEN GOTO 1910
1930
1935
      POKE - 16368,0
1940
      IF (A < 173 OR A > 174) AND (A < 176 OR A > 185) AND A < > 136
      AND A < > 141 THEN PRINT CHR$ (7); GOTO 1910
      IF A < > 141 THEN PRINT CHR$ (A);
1950
      IF A < > 136 THEN GOTO 1970
1960
     PRINT " "; CHR$ (A);
1962
1964
     IF LEN (B$) < = 1 THEN B$ = "": GOTO 1910
      B = LEFT$ (B$, LEN (B$) - 1): GOTO 1910
1966
1970
     IF A = 141 THEN RETURN
1980
     B$ = B$ + CHR$ (A - 128): GOTO 1910
     J = 0: IF F = 0 THEN GOTO 1930
1990
     CH = PEEK (36): CV = PEEK (37)
1995
2000
     GOSUB 1000
2005 HTAB (CH + 1): VTAB (CV + 1)
2010 GOTO 1930
2498
     REM
2499 REM * READING CLOCK
2500 D D = CHR (4): REM CNTL/D
     HTAB (39): VTAB (23): PRINT
2505
     PRINT D$; "PR#5"
2510
2520
     PRINT D$;"IN#5"
2530
     INPUT "%"; T$
2540 PRINT D$; "PR#0"
     PRINT D$;"IN#O"
2550
2560
      T = (VAL (MID $$ (T$, 12, 2)) * 3600 + VAL (MID $$ (T$, 15, 2)) * 60 +
      VAL ( MID$ (T$,18,2))) / 60
2570
     RETURN
2998 REM
2999 REM * READING FROM THE A/D
3000 PL = -1
3010 POKE AD(F),0
3020
     X = PEEK (AD(F))
3030 \cdot Y = PEEK (AD(F) + 1)
3040
     IF X > 63 THEN GOTO 3020
3050
     IF X > 31 THEN X = X - 32: PL = + 1
     IF X > 15 THEN X = X - 16: PRINT CHR (7); POKE OU(F), 0:ST(F) =
3060
      n
3070
     MV = (X * 256) + Y
3080 \text{ TP}(F) = PL * MV * .2
```

3090RETURN4000REM4010REM*ENDOFLISTING